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MEASUREMENT OF GAS ADSORPTION WITH JÄNTTI’S METHOD USING CONTINUOUSLY INCREASING PRESSURE

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Abstract

Jäntti *et al.* published a method to reduce the time necessary for adsorption measurements. They proposed to extrapolate the equilibrium in the stepwise isobaric measurement of adsorption isotherms by measuring at each step three points of the kinetic curve. For that purpose they approximated the kinetic curve by an exponential function which they derived empirically from there measurements. In the present paper we discuss the applicability of the method for adsorption measurements under continuously varying gas pressure.

Keywords: adsorption, continuous measurement, sorption, extrapolation

Introduction

In 1970 Jäntti *et al.* published an elegant timesaving method for the fast calculation of adsorption data from gravimetric measurements: after a change of the gas pressure the momentary adsorbed amount is measured at three equidistant times and from these values the adsorption equilibrium is calculated [1]. It was Jäntti’s aim to get an estimate of the adsorption equilibrium at an early stage of the measurement.

This procedure he used for samples satisfying simple molecular adsorption models, described by a first order differential equation:

$$\frac{\mathrm{d}m}{\mathrm{d}t}=-\frac{m}{\tau}+D \tag{1}$$

where m stands for the momentary adsorbed layer at time t, D represents the gas molecules hitting the surface, and τ is the characteristic time of the adsorption.

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In the present paper we consider another way to speed up measurements. We shall discuss an adsorption measurement where the gas pressure varies linearly with time so that plural measurements at different gas pressures are avoided and we shall consider whether in this way of measurement, Jäntti's method can lead to extra time-saving.

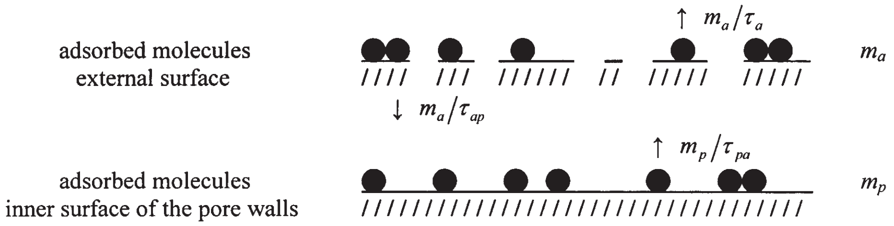

Fig. 1 Model leading to the differential equations for desorption. The arrows represent mass transport per second

In former papers we showed how Jäntti`s method can be used in the case of the adsorption of gases onto heterogeneous surfaces and onto porous materials [2–4]. We suggested to use a more complicated molecular model to enable accounting for the transport of the adsorbed molecules into the solid [5]. This model leads to a second order equation. We applied this model to adsorption at constant gas pressure and to desorption measurements [6]. In the present paper we shall apply it to adsorption at linearly increasing gas pressure. This could lead to faster measurements when adsorption data are wanted at different gas pressures.

Parameter evaluation

The explanation of the mathematics involved is easiest started from the treatment of desorption as in that case the differential equations are homogeneous. These equations read:

$$\frac{\mathrm{d}m_\mathrm{a}}{\mathrm{d}t}=-\frac{m_\mathrm{a}}{\tau_\mathrm{a}}+\frac{m_\mathrm{p}}{\tau_\mathrm{pa}}-\frac{m_\mathrm{a}}{\tau_\mathrm{ap}} \tag{2}$$

$$\frac{\mathrm{d}m_\mathrm{p}}{\mathrm{d}t}=-\frac{m_\mathrm{a}}{\tau_\mathrm{ap}}-\frac{m_\mathrm{p}}{\tau_\mathrm{pa}} \tag{3}$$

where m_a and m_p are the adsorbed amount of molecules at the outer surface and in the pores, respectively and τ_a, τ_ap and τ_pa are characteristic times for the transition of molecules from the surface to the gaseous phase and from surface to the pores and return. This molecular model is depicted in Fig. 1.

For the calculation of the values of the parameters of adsorptions characterised by Eq. (1), Jäntti used a function defined by

$$J(t)=\frac{m(t)^2-m(t+\Delta t)m(t-\Delta t)}{2m(t)-m(t+\Delta t)-m(t-\Delta t)} \tag{4}$$

We introduced the quantity J^* which, in the case that m is a simple exponential function, is identical with J.

$$J^*(t)=m-\frac{\left(\frac{\mathrm{d}m}{\mathrm{d}t}\right)^2}{\frac{\mathrm{d}^2m}{\mathrm{d}t^2}} \tag{5}$$

The symbols $m(t)$ and m are both used to refer to the measured adsorbed mass as a function of the time t. So $m(t)=m=m_a+m_p$.

In the case of adsorption at constant gas pressure an inhomogeneous term D is added to the first equation:

$$\frac{\mathrm{d}m_a}{\mathrm{d}t}=-\frac{m_a}{\tau_a}+\frac{m_p}{\tau_{pa}}-\frac{m_a}{\tau_{ap}}+D \tag{6}$$

where D represents the gas molecules hitting the surface.

In the present paper we shall introduce the linear variation of the gas pressure by using a time dependent inhomogeneous term so that Eq. (2) reads:

$$\frac{\mathrm{d}m_a}{\mathrm{d}t}=-\frac{m_a}{\tau_a}+\frac{m_p}{\tau_{pa}}-\frac{m_a}{\tau_{ap}}+Ct \tag{7}$$

Combined with the original homogeneous equation we get for the total amount m of gas bound to the solid:

$$\frac{\mathrm{d}^2m}{\mathrm{d}t}+\left(\frac{1}{\tau_a}+\frac{1}{\tau_{ap}}+\frac{1}{\tau_{pa}}\right)\frac{\mathrm{d}m}{\mathrm{d}t}+\frac{1}{\tau_a}\frac{1}{\tau_{pa}}m=C+\left(\frac{1}{\tau_{ap}}+\frac{1}{\tau_{pa}}\right)Ct \tag{8}$$

As in former papers we write the solution of the homogeneous equation involved as:

$$m=A\exp(x_1t)+B\exp(x_2t) \tag{9}$$

where x_1 and x_2 are the solutions of the characteristic equation and where A and B are constants to be chosen to satisfy the initial conditions. As particular solution we use:

$$m=M_0+M_1t \tag{10}$$

with

$$M_0=\tau_a\tau_{pa}\left[1-\left(1+\frac{\tau_a}{\tau_{ap}}+\frac{\tau_a}{\tau_{pa}}\right)\left(1+\frac{\tau_{pa}}{\tau_{ap}}\right)\right]C \tag{11}$$

and
$$M_1=\tau_a\left(1+\frac{\tau_{pa}}{\tau_{ap}}\right)C \tag{12}$$

For the complete solution we get:

$$m=A\exp(x_1t)+B\exp(x_2t)+M_0+M_1t \tag{13}$$

Using the initial conditions

$$m(0)=0;\ \left(\frac{\mathrm{d}m}{\mathrm{d}t}\right)_0=0 \tag{14}$$

we get:

$$A=\frac{x_2M_0-M_1}{x_1-x_2} \tag{15}$$

$$B=\frac{M_1-x_1M_0}{x_1-x_2} \tag{16}$$

As an expansion of the solution (13) we use for small values of t:

$$m=C\left(\frac{1}{2}t^2-\frac{1}{6}\frac{t^3}{\tau_a}\right) \tag{17}$$

Using Eq. (5) into Eq. (17) we get for the expansion of J^*:

$$J^*=C\left(-\frac{1}{2}t^2-\frac{1}{6}\frac{t^3}{\tau_a}\right) \tag{18}$$

Equation (17) can be used in practice to determine the values of the parameters C and τ_a using the measured values of m. This is shown in Fig. 2 which is not based on real measurements but on simulated 'measured' points, calculated with Eq. (13) and the parameter values mentioned in the subscript. Equation (17) demonstrates that the intersection of the straight line in Fig. 2 with the vertical axis gives us the value of the parameter C (in our example 10^{-2}), while its slope gives us the value of τ_a (in our example 100). Unlike the situation of adsorption under constant gas pressure comparable manipulations with the values of J^* do not result in extra information. This is due to the similarities of the Eqs (17) and (18). Besides it has to be mentioned that working with m is preferable to working with J^* as the calculation of the J^* values with Eq. (5) leads to an increase of the effect of the weighing errors involved in the measurement of m [5].

At large values of t, the measured values of m approach the particulate solution given by Eq. (10). In Fig. 3 it is shown how with the again simulated 'measured' points a straight line through these points gives us, using Eq. (10) the values of M_0 (in our example –1500) and M_1 (in our example 2.5) from its intersection with the vertical axis and its slope respectively. Once M_0 and M_1 are known, we can calculate the

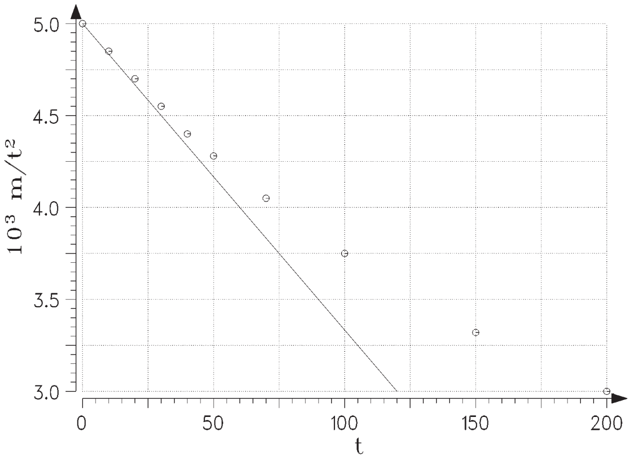

Fig. 2 m/t^2 is plotted *vs.* t, and according to Eqs (17) and (18) this gives the value of C, using the intersection with the vertical axis; time in s, mass in mg. The slope gives us the value of τ_a. For the calculation of the 'measured' points the following parameter values have been used: C=0.01, τ_a=100, τ_{ap}=400 and τ_{pa}=600

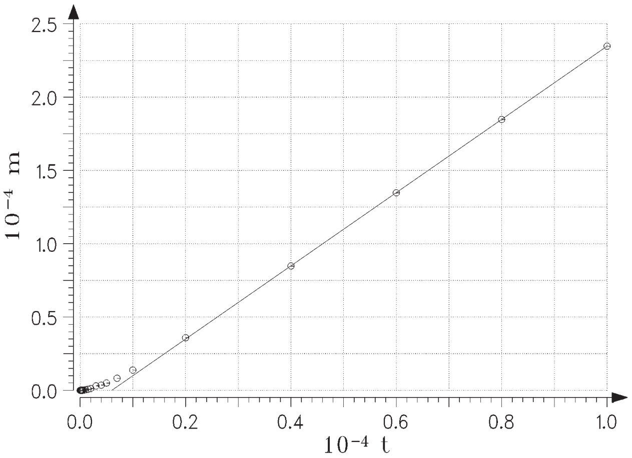

Fig. 3 The use of the particular solution (10) of m for the evaluation of the parameter values. For the calculation of the 'measured' points, parameter values have been chosen equal to those in Fig. 2; time in s, mass in mg

values of the parameters τ_{ap} (in our example 581) and τ_{pa} (in our example 389) with Eqs (11) and (12).

Using Eq. (13) into Eq. (5) we get an expression for J^* as a function of t at large values of t:

$$J^*=M_0+M_1t-\frac{1}{A}\left(\frac{M_1}{x_1}\right)^2\exp(-x_1t) \tag{19}$$

Here we used the facts that both, x_1 and x_2 are negative and that we have taken x_1 to be the solution which is nearest to zero.

In Fig. 4 ln($-J^*+m$) is plotted *vs. t*. According to Eq. (19) the slope of the straight line in this figure gives us the value of x_1 (in our example $12.4\cdot10^{-4}$). For estimating purposes at a relatively early stage of the adsorption measurements it can be of interest to know whether a model leading to a first order differential equation suffices or that a second order one is necessary. When the resulting values of τ_a and of $(-1/x_1)$ are equal, a treatment with a second order differential equation is not necessary. In our example this is not the case as we have chosen the values of τ_{ap} and τ_{pa} not to far from that of τ_a for the purpose of the demonstration. It should be mentioned that the use of the *J* function implies a substantial increase of the errors encountered when measuring *m*(*t*).

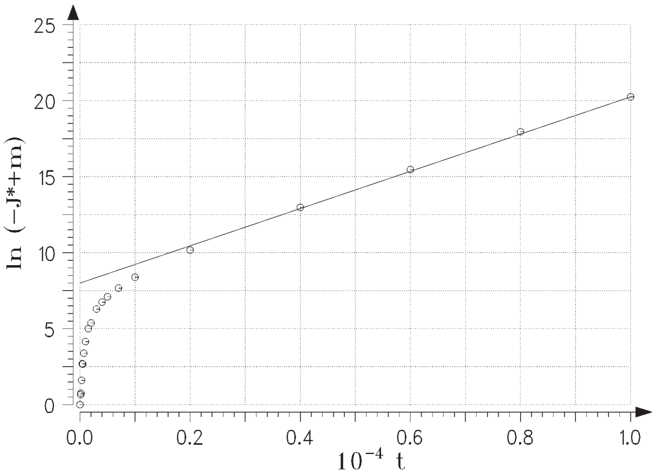

Fig. 4 The use of Jäntti's method for the evaluation of the parameter values. For the calculation of the 'measured' points, parameter values have been chosen equal to those in Fig. 2

Conclusions

The application of Jäntti's approach to the continuous measurement of adsorption isotherms at linearly increasing gas pressure leads to extra timesaving by accepting a larger error. This is justified bearing in mind that the continuos method is a fast but somewhat incorrect test in comparison to the conventional stepwise measurement. Jäntti's approach is originally developed to cope with linear adsorption effects. When adsorption measurements are performed with a continuously increasing gas pressure, the approach can also provide information about second order effects influencing the adsorption.

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