

EXTENSION OF THE APPLICABILITY OF JÄNTTI'S METHOD FOR FAST CALCULATION OF ADSORPTION DATA

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Abstract

The time for adsorption measurements can be substantially reduced by measuring several values at short time intervals at the beginning of the kinetic curve and extrapolation of the equilibrium value. The method used by Jäntti for simple adsorption processes has been extended for complicated processes using a second order differential equation. A simulated example is calculated.

Keywords: adsorption, extrapolation, gravimetric measurement, sorption

Introduction

In 1970 Jäntti published an elegant method for the fast calculation of adsorption data from gravimetric measurements: After a change of the gas pressure the actual adsorbed amount is measured at three equidistant times and from these values the adsorption equilibrium is calculated [1]. This procedure could be used for samples satisfying simple molecular adsorption models, described by a first order differential equation:

$$\frac{dm}{dt} = \frac{m_0}{\tau_0} - \frac{m}{\tau} \quad (1)$$

where m is the mass adsorbed at a solid surface as a function of time t , in which the surface is exposed to a gas at constant pressure. m_0 is a constant depending on the gas used and τ , τ_0 are characteristic times of the adsorption process (Fig. 1).

The method is not only attractive because it gives a quick estimate of the equilibrium value of the adsorbed mass, but also because the calculation involved does not require the use of curve fitting procedures [2]. In former papers [3–5] we showed how Jäntti's method can be used in the case of the adsorption of gases onto heterogeneous surfaces. We suggested that it could be applied for the treatment of adsorptions governed by more complicated differential equations. At the Polish-Ukrainian Sympo-

sium on Theoretical and Experimental Studies of Interfacial Phenomena, September 1–3, 1999 at Lublin, we suggested to apply Jäntti's method to measurements on samples satisfying more complicated adsorption models, governed by second order differential equations [6]:

$$\frac{dm_a}{dt} = \frac{m_{a0}}{\tau_{a0}} - \frac{m_a}{\tau_a} + \frac{m_p}{\tau_{pa}} \quad (2)$$

$$\frac{dm_p}{dt} = \frac{m_a}{\tau_{ap}} - \frac{m_p}{\tau_{pa}} \quad (3)$$

where symbols with index a relate to adsorption at the outer surface and with index p to adsorption at the surface of the pore walls (Fig. 2).

In the present paper we give the results of using Jäntti's method to computer simulated adsorption experiments, simulations starting from Eqs (2) and (3).

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

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

$m(t)$ is the adsorbed mass as a function of the time t . In the case of sorptions characterised by Eq. (1), $J(t)$ is independent of the values of both t and Δt .

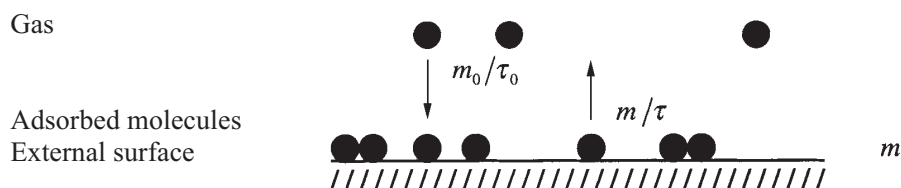


Fig. 1 Model leading to a first order differential equation. τ_i are characteristic times of the sorption processes

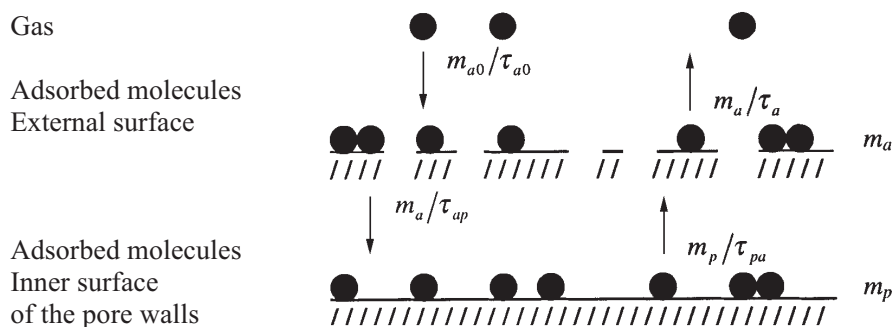


Fig. 2 Model leading to a second order differential equation

Determination of the parameter values

We shall explain the procedure to determine the values of the parameters with Figs 3 and 4. In Fig. 3 we started from the curve of the measured adsorbed mass in the case of adsorption characterised by Eq. (1). The ‘measured’ points $m(t)$ shown there are faked, they are calculated from the solution of Eq. (1) with values of the parameters as indicated in the subscript. With these points we shall explain the procedure of the determination of the parameter values as if these points were really measured. With the values of $m(t)$ we calculate values of $J(t)$ with Eq. (4). These should, according to Jäntti, result in a straight horizontal line, which as we see in Fig. 3, line BA , is indeed the case. The height OB of this line gives us the value of $m_i = m_0 / \tau_0 \tau$. In Fig. 3 we also see the tangent to the $m(t)$ curve in O . The intersection B of this tangent with the $J(t)$ line gives us the value of τ , being the distance between B and A .

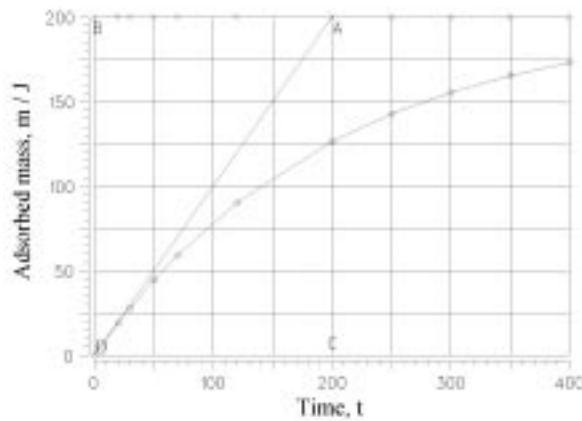


Fig. 3 Procedure for the calculation of the adsorption parameters from measured data when the model used is described by a first order differential equation. m_i =equilibrium mass adsorbed, for the calculation of the ‘measured’ points the following parameter values are used: $m_0/\tau_0=1$, $\tau=200$, $\Delta t=10$

In Fig. 4 the $m(t)$ points are also calculated, using the parameter values mentioned there. Again the $J(t)$ values are calculated with the Eq. (4). Unlike the situation seen in Fig. 3, $J(t)$ is now dependent of t , a dependency which we shall use for the determination of the values of the parameters m_{a0}/τ_{a0} , τ_a , τ_{ap} , τ_{pa} and the dependent parameters $m_{ai} = m_{a0}/\tau_{a0}\tau_a$ and $m_{pi} = m_{ai}\tau_{pa}/\tau_{ap}$.

The value of m_{ai} is read from Fig. 4 as

$$m_{ai} = J(0) = OB$$

Drawing the tangent OA in $t=0$ to the ‘measured’ points and intersecting this tangent with BA , which stands for a horizontal line through A , we can use:

$$\tau_a = BA$$

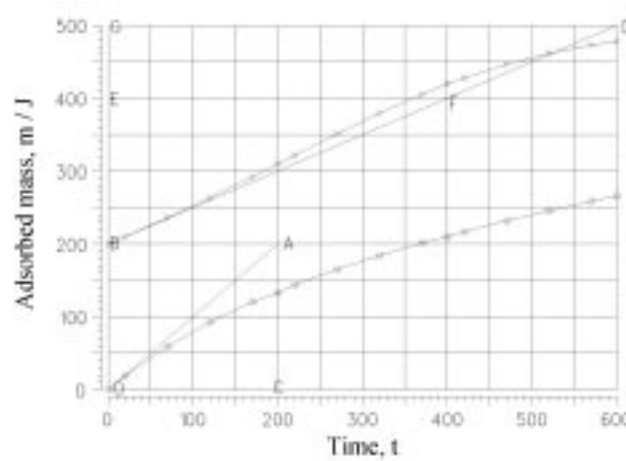


Fig. 4. Procedure for the calculation of the adsorption parameters from measured data when the model used is described by a second order differential equation. Parameter values used for calculating the ‘measured’ points: $m_{a0}/\tau_{a0}=1$, $\tau_a=200$, $\tau_{ap}=400$, $\tau_{pa}=600$, m_i , m_{ai} , m_{pi} are equilibrium data, $m=m_a+m_p$, $m_i=m_{ai}+m_{pi}$

We then draw a second horizontal line EF at height OE chosen such that:

$$OE=2OB=2m_{ai}$$

We draw the tangent BFD in $B(t=0)$ to $J(t)$, the point F of intersection gives us

$$EF=\tau_{ap}$$

It will take some extra time to perform the measurements to establish the horizontal asymptote GD , but once we got it, we can use:

$$OG=m_{ai}+m_{pi}$$

The intersection of this asymptote with the tangent BFD gives us

$$GD=\tau_{pa}$$

It has to be noted that the extra time for establishing the asymptote to $J(t)$ is much shorter than that for establishing the asymptote to $m(t)$.

Conclusions

Jäntti’s method allows a quick estimate of the adsorption parameters soon after the start of the determination of the adsorbed mass. Originally the method was applied to adsorptions satisfying a simple first order molecular model. We have shown that Jäntti’s method can also be useful, fast and easy to handle in the case of adsorptions satisfying a second order molecular model.

References

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