GENERAL APPLICATION OF JÄNTTI'S METHOD FOR THE FAST CALCULATION OF SORPTION EQUILIBRIUM

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Abstract

On the basis of a molecular model for adsorption kinetics Jäntti introduced a method to calculate equilibriums shortly after a change of the pressure of the sorptive gas. In the present paper we show that this method is useful in many more situations than those intended originally.

Keywords: adsorption equilibrium, adsorption kinetics, gas adsorption, mathematical model, theory

Introduction

Jäntti *et al.* introduced a method to calculate the adsorption equilibrium by the measurement of the actual adsorbed amount at three times shortly after a change of the gas pressure [1, 2]. The method was designed for use in the case of an adsorption satisfying the equation

$$m(t) = m_i(1-e^{xt}) \qquad (1)$$

where $m(t)$ is the adsorbed amount observed as a function of time after a stepwise change of the gas pressure, m_i is the asymptotic equilibrium value, and x is a characteristic constant for the gas/solid system under consideration. This equation is based for gas/solid systems in which simple adsorption processes occur and for an infinite number of adsorption sites.

Jäntti suggested using three points of a kinetic adsorption curve. He showed that this results in a fast determination of the equilibrium value m_i. To get such a quick estimate of the values of the parameters from measured values of m, he introduced the equation:

$$J(t) = \frac{m(t_2)^2 - m(t_1)m(t_3)}{2m(t_2) - m(t_1) - m(t_3)} \qquad (2)$$

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where the adsorbed mass is measured at times t_1, t_2 and t_3 (while $t_3-t_2=t_2-t_1=\Delta t$) yielding the values m_1, m_2 and m_3, respectively. In the case the adsorption is characterized by Eq. (1) and $J(t)$ is independent of the values of both t and Δt it follows:

$$J(t) = m_i \tag{3}$$

In more complicated situations where the independence of J with regard to Δt is not certain it is useful to use the limit J^* of J for Δt approaching zero:

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

Jäntti used that method in particular to shorten measurements of adsorption isotherms of nitrogen on activated carbon. Activated carbon, however, has a rather complicated porous structure. We, therefore, critised [3] and extended the method [4–6]. Just slow adsorption processes of technical importance take place in complicated systems. To obtain a clearer insight we analyze the method by means of computer simulation using a basic multilayer model of adsorption.

Multilayer adsorption

The starting point that the adsorption should be restricted to a certain number of layers is only rectified by the simplicity of the calculations it brings along. In the equations we shall use there are two eye catching troubles which could result from the restriction:

- Firstly the calculations might lead to the not acceptable result that a higher layer should contain more molecules than the layer underneath.
- Another possible anomaly is a result in which one of the numbers of the adsorbed molecules per layer exceeds the number of sites available for adsorption on the solid surface.

Both anomalies are easily surpassed by adjusting the computation program. This however includes a variation of the molecular transport model used. In the figures shown in this paper no such adjustments had to be carried out.

In the following we discuss the adsorption of a finite number of – partly covered – layers and we start with the case of two layers where treatment is simple and results in an easy insight. We also will show the applicability of Jäntti's model in the case of four layers which will be nearer to reality.

The number of sites available for adsorption at the solid we refer to as n_0. The numbers of molecules in the first and second layer are n_1 and n_2, respectively. The total number n of the adsorbed molecules satisfy:

$$n = n_1 + n_2 \tag{5}$$

To avoid to be forced to consider a third layer, we make the following assumption: When a gas molecule hits a molecule already present in the second layer it will

not start to form a third layer, but find a not occupied site in the second layer. This leads to the following equations:

$$\frac{\mathrm{d}n_1}{\mathrm{d}t} = X(n_0 - n_1) - X_1(n_1 - n_2) \tag{6}$$

$$\frac{\mathrm{d}n_2}{\mathrm{d}t} = Xn_1 - X_2 n_2 \tag{7}$$

where X is the constant determining the possibility of molecules to leave the gaseous state to be adsorbed and X_1 and X_2 determine the desorption from the first and second layer, respectively.

Analysis of computer-simulated adsorption data

Let the data resulting from an adsorption curve we suppose to result from an adsorption following the two layers model, be presented as an n vs. t curve. Let there also be at our disposal a J vs. t curve, which has been calculated from the n vs. t curve using Eq. (2). The original aim of Jäntti's method was, assuming Eq. (1) to be satisfied, to get a quick (at small values of t) estimate of the asymptotical value n_{as} of n. Also in the more complicated molecular situation we discuss in this paper, we get very early information of this asymptotical value as is clearly shown by Figs 1 and 2. From Eqs (6) and (7) we see that this asymptotical value n_{as} satisfies:

$$n_{as} = n_0 \frac{1 + X/X_2}{1 + X_1/X - X_1/X_2} \tag{8}$$

At $t=0$ we can, using Eqs (6) and (7) and the initial conditions that at $t=0$ both n_1 and n_2 are zero, derive:

$$n = Xn_0 t \tag{9}$$

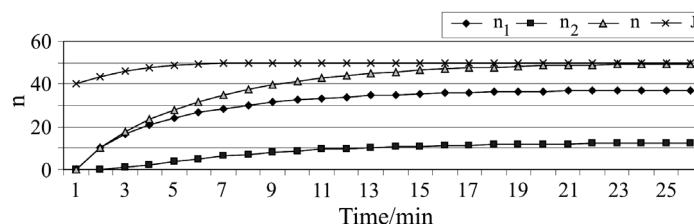Near $t=0$ we get, using Eqs (7) and (8) into Eq. (4):

Fig. 1 Computer simulation of the response of a two-layer adsorption model to a step in the gas pressure. Ordinate: number n_i or calculated number J of adsorbed molecules, abscissa: time t. The parameter values used are: $n_0=100$, $X=0.1$, $X_1=0.25$, $X_2=0.3$. With Eqs (6) and (7) we get for the asymptotical values: $n_{1as}=37.5$, $n_{2as}=12.5$, $n_{as}=50$
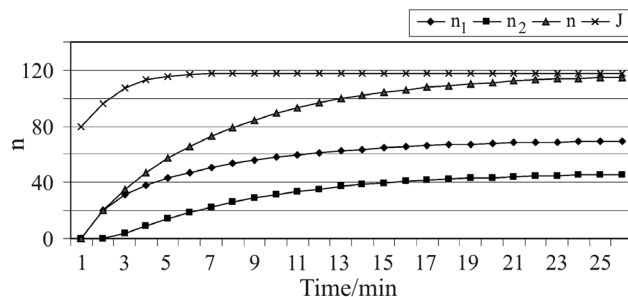
Fig. 2 Computer simulation of the response of a two-layer adsorption model to a step in the gas pressure. The parameter values used are: $n_0 = 100$, $X = 0.2$, $X_1 = 0.25$, $X_2 = 0.3$. With Eqs (6) and (7) we get for the asymptotical values: $n_{1as} = 70.6$, $n_{2as} = 47.1$, $n_{as} = 117.2$

$$J^* = \frac{X}{X_1} n_0 + \left(2\frac{X}{X_1} - \frac{XX_2}{X_1^2} \right) X n_0 t \tag{10}$$

From Eq. (10) it follows:

$$J^*_{t=0} = \frac{X}{X_1} n_0 \tag{11}$$

and

$$\left(\frac{dJ^*}{dt} \right)_{t=0} = \left(2\frac{X}{X_1} - \frac{XX_2}{X_1^2} \right) X n_0 \tag{12}$$

When the measured values of n and the ith Eq. (2) calculated values of J are plotted as functions of t we can from these curves derive the values of the parameters n_0, X, X_1 and X_2 with Eqs (9) – (12).

Examples of the use of these tools for the evaluation of the parameters are shown in Figs 1 and 2. Instead of measured data, use has been made of computer simulations by numerically solving Eqs (6) and (7). The number n_i or calculated number J of adsorbed molecules is plotted on the ordinate as a function time t (min, abscissa). The values of J are calculated with Eq. (2). In these figures different combinations of the parameter values are used. Care has been taken throughout that the parameter Δt, for use in Eq. (2), was small enough to guarantee the equality of J and J^*.

The resulting Figs 1 and 2 show in the first place that the early evaluation of the asymptotical value n_{as} is very well and quickly possible also in the case of the more complicated molecular model used. Besides, the evaluation of the values of the parameters X, X_1 and X_2 with Eqs (8), (9), (11) and (12) proofs to be a very simple matter.

When discussing the Figs 1 and 2 it has to be taken in mind that the parameter X can be taken to be proportional to the gas pressure so Figs 1 and 2 show the reaction of the adsorption on two different steps of the gas pressure, both from vacuum. To

link the parameters with temperature is not so easy as X, X_1 and X_2 will be in different ways depend on temperature. The use of two layers allows us in principle to distinguish between gas molecules adsorbed on solid material (first layer) and those adsorbed on other adsorbed gas molecules which are already present at the solid surface (second layer).

When the occupation of the second layer becomes too large, the results of the calculations should be considered with reserve as in reality a third layer might appear.

To demonstrate that also in the case of four layers the quick evaluation of the asymptotical value n_{as} of n is possible Fig. 3 is added. When four layers are considered, we have to broaden the scope of Eqs (6) and (7) to:

$$\frac{dn_1}{dt} = X(n_0 - n_1) - X_1(n_1 - n_2) + Yn_2 \tag{13}$$

$$\frac{dn_2}{dt} = X(n_1 - n_2) - X_1(n_2 - n_3) + Y(n_3 - n_2) \tag{14}$$

$$\frac{dn_3}{dt} = X(n_2 - n_3) - X_1(n_3 - n_4) + Y(n_4 - n_3) \tag{15}$$

$$\frac{dn_4}{dt} = Xn_3 - X_1 n_4 + Yn_4 \tag{16}$$

In these equations the parameter Y has been introduced for later use in this paper, for the moment we shall consider this parameter to have the value 0. To reduce the number of parameters we restrict our treatment to situations where:

$$X_4 = X_3 = X_2 = X_1 \tag{17}$$

In that case we may use, instead of Eqs (8)–(12) for large values of t:

$$n_{as} = n_0 \left(\frac{X}{X_1} + \frac{X^2}{X_1^2} + \frac{X^3}{X_1^3} + \frac{X^4}{X_1^4} \right) \tag{18}$$
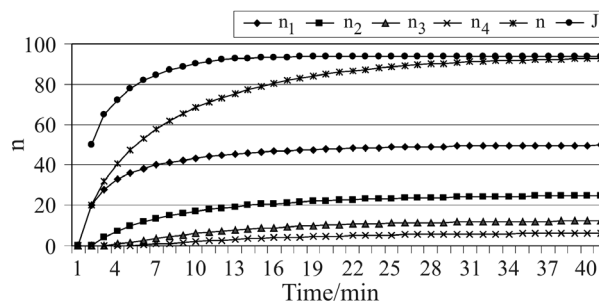

Fig. 3 Computer simulation of the response of a four-layer adsorption model to a step in the gas pressure. The parameter values used are: $n_0 = 100$, $X = 0.2$, $X_1 = X_2 = X_3 = X_4 = 0.4$. With Eqs (6) and (7) we get for the asymptotical values: $n_{1as} = 50$, $n_{2as} = 25$, $n_{3as} = 12.5$, $n_{4as} = 6.3$, $n_{as} = 91.3$

$$J_{as} = n_{as} \tag{19}$$

At $t=0$:

$$n_{t=0} = n_0 Xt \tag{20}$$

$$J^*_{t=0} = n_0 \frac{X}{X_1} \tag{21}$$

$$\left(\frac{\mathrm{d}J^*}{\mathrm{d}t} \right)_{t=0} = n_0 \frac{X^2}{X_1} \tag{22}$$

When using an infinite number of layers we get instead of Eq. (18)

$$n_{as} = n_0 \frac{X}{X_1 - X} \tag{23}$$

In Fig. 3 curves are shown the points of which were calculated in the same way as those in Figs 1 and 2, but now for the case of four layers. Again we see that at small values of t the value of n_{as} can be evaluated.

Several successive pressure steps

In the above we discussed experiments with a pressure step at $t=0$ starting from the gas pressure being zero. In practice it will often be useful to save time of measurement by enlarging the gas pressure by several steps in succession. That in such experiments Jäntti's method can still be useful is shown in Figs 4 and 5.
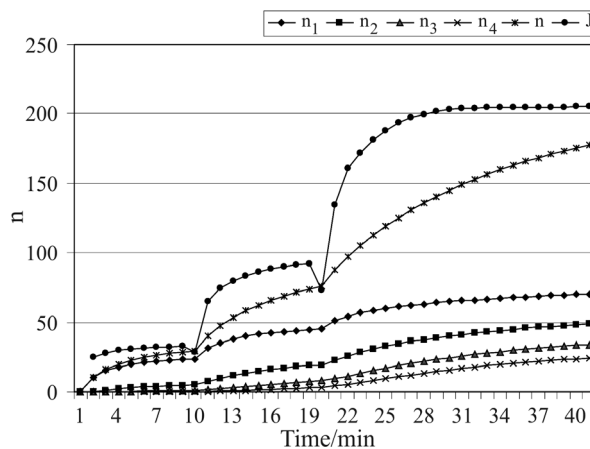

Fig. 4 Computer simulation describing with a four-layer model, the response to three succeeding steps of the gas pressure. The time intervals are taken long enough to reach a reasonable approach to an asymptotical situation. $X_1=X_2=X_3=X_4=0.4$, the successive values of X are 0.1, 0.2 and 0.3. From Eqs (13)–(17) it follows that the three successive values of n_{as} are 34, 94 and 205
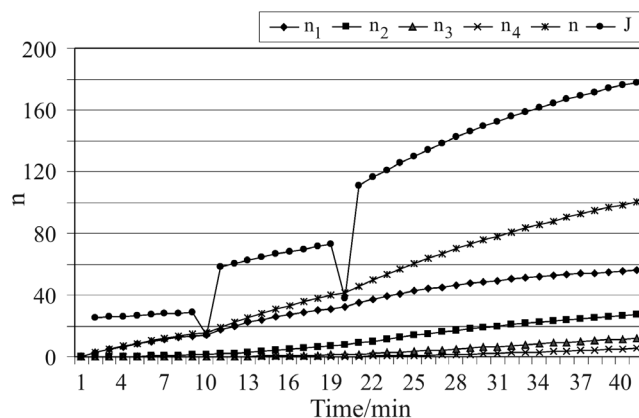
Fig. 5 As in Fig. 4 but with smaller time intervals between the pressure steps $X_1=X_2=X_3=X_4=0.1$, for successive values of $X=0.025$, 0.05, 0.075 was used. From Eqs (13)–(17) it follows that the three successive values of n_{as} are 33, 94 and 205

In these computer simulated figures the steps in the gas pressure is simulated by steps in the value of the parameter X. It is clearly demonstrated in Figs 4 and 5 that the J vs. t curve leads much faster to asymptotical adsorption values than the n vs. k curve. The striking dips of the J vs. t curve can be easily understood by taking in mind that a step in the value of X causes no discontinuity in the n vs. t curve, but a step in the derivative, while the second derivative will peak to infinity. From Eq. (4) it follows that this causes the value of J to become equal to that of n at the moment that the step occurs. After such a dip the J vs. t curve shows a stepwise increase.

To estimate the height of this step we start with adding Eqs (13)–(16), which leads to

$$dn/dt = Xn_0 - X_1n_1 \tag{24}$$

We shall restrict ourselves to the situation that before each step the asymptotical adsorption is reached, what is the case in the example dealt with in Fig. 4. Using Eq. (25) for the stepwise increase of X from X_{before} to X_{after} we get, considering that $(dn/dt)_{before}=0$ and that $n_{1before}=n_{2\ before}$,

$$\left(\frac{dn}{dt}\right)_{after} = n_0(X_{after} - X_{before}) \tag{25}$$

Starting from Eq. (24) we also get:

$$\left(\frac{d^2n}{dt^2}\right)_{after} = \left(\frac{d^2n}{dt^2}\right)_{before} + X_1\left(\frac{dn}{dt}\right)_{before} \tag{26}$$

Remembering that before the pressure step the adsorption had reached a situation near the asymptotical one, it follows from Eq. (4):

$$J_{\text{after}} - n_{\text{step}} = n_0 \frac{X_{\text{after}} - X_{\text{before}}}{X_1 - X_{\text{before}}} \qquad (27)$$

where n_{step} refers to the value of n at the time of the step, which coincides with the lower of the two J values at that time.

The usefulness of Eq. (27) is easily demonstrated by using the data from Fig. 4. In the case of Fig. 5 the asymptotic condition is clearly not fulfilled, but it still gives an estimate which might, in some experimental situations, be useful.

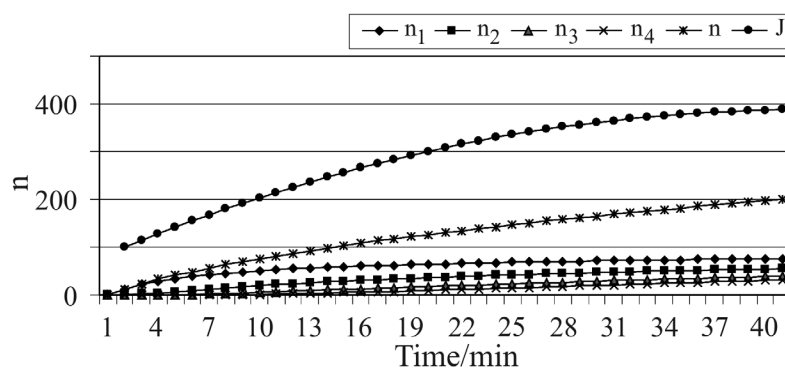## Exchange of adsorbed molecules between the layers

Fig. 6 The influence of transport between the layers at $X=X_1=X_2=X_3=X_4=0.12$, $Y=0$
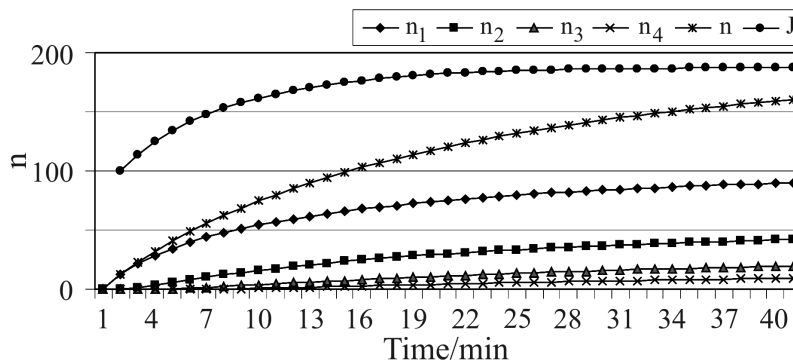

Fig. 7 The influence of transport between the layers at $X=X_1=X_2=X_3=X_4=0.12$, $Y=0.12$

Transport of adsorbed molecules between the layers can be taken into account by using the Y parameter introduced in the Eqs (13)–(16) (Figs 6–9). This allows us to incorporate the fact that each molecule in some layer has a tendency to go to the layer
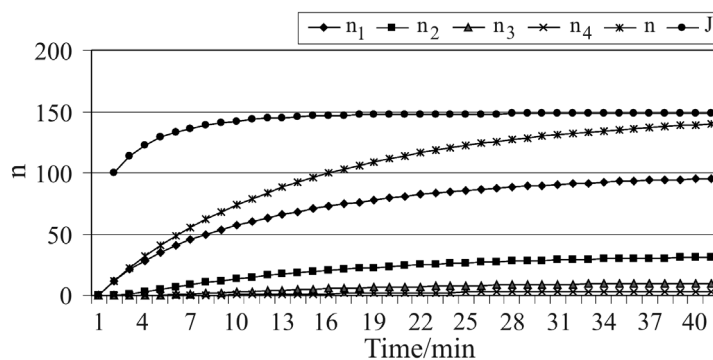
Fig. 8 The influence of transport between the layers at $X=X_1=X_2=X_3=X_4=0.12$, $Y=0.24$
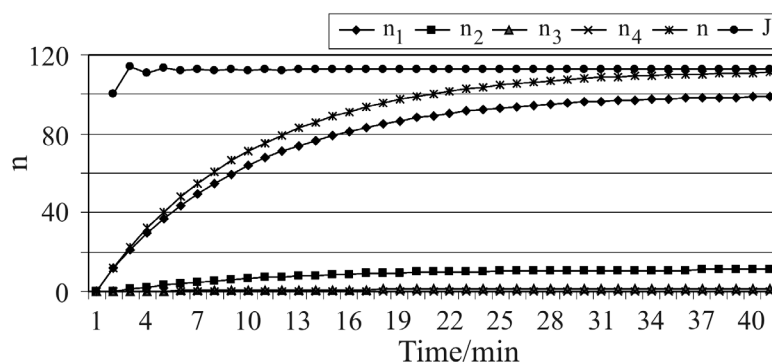

Fig. 9 The influence of transport between the layers at $X=X_1=X_2=X_3=X_4=0.12$, $Y=0.96$

underneath. In computer simulations, care has to be taken that the values of n_1, n_2, n_3 and n_4 do not exceed that of n_0.

We see especially in Fig. 9 that both the *n vs. t* curve and the *J vs. t* curve tend to the behaviour determined by Eq. (1) as the first layer is strongly dominant when the transport between the layers is large.

Table 1 Parameters used

Symbol	Parameter	Unit
J	Jäntti function	m
J^*	Jäntti function for t 0	m
$m(t)$	adsorbed amount as a function of time	m
m, m_i	adsorbed mass in equilibrium	m
n_0	number of adsorption sites at the solid surface	1
n_i	number of adsorption sites in layer i	1

n_{as}	asymptotical value of n	l
t	time	min
x	characteristic constant	min^{-1}
X	adsorption probability for layer (constant)	l
X_1, X_2	desorption probability from first, second layer (constant)	l
Y	desorption probability from subsequent layers (constant)	l

Conclusions

When measuring the adsorption following a stepwise variation of the gas pressure, the Jäntti approach results in a speeding up of the knowledge of the asymptotical adsorption during the experiment. Depending on the molecular model used, the J approach can also be helpful for the evaluation of other parameters. It seems doubtful whether the Jäntti approach can be of great help for the choice between the molecular models to explain experimental results.

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