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APPLICATION OF JÄNTTI'S METHOD FOR THE EXPLANATION OF ADSORPTION ONTO ROUGH SURFACES

J. A. Poulis[1*]*, E. Robens*[2]*, C. H. Massen*[1] *and M. Barczak*[3]

[1]Faculty of Technical Physics, Technical University Eindhoven, Postbus 513, 5600 MB Eindhoven, The Netherlands
[2]Institut für Anorganische Chemie und Analytische Chemie der Johannes Gutenberg-Universität, Duesbergweg 10-14
55099 Mainz, Germany
[3]Faculty of Chemistry, University of Maria Curie-Skłodowska, Maria Curie-Skłodowska Sq. 3, 20-031 Lublin, Poland

Jäntti introduced a method to calculate the final value of the adsorbed mass already in a very early stage of adsorption measurements. His method was restricted to gravimetric measurements and to adsorptions, which satisfy the simplest molecular model. One of the advantages of his method was that when more complicated molecular models were necessary, the curve resulting from Jäntti`s calculations showed discrepancies from the curve predicted for the simple situation. We used such deviations to evaluate the parameters of the models necessary for the explanation of the measurements. One of the examples we discussed concerned the influence of the occurrence of two parallel and simultaneous adsorptions.

In the present paper we discuss the application of these results to adsorption onto a surface where roughness could be expected to play a part. If we consider a rough surface as the sum of two extra surfaces we can apply Jäntti's method by using our former results of parallel adsorption. We characterise roughness by two parameters which we evaluated with Jäntti's method. We emphasise that the existence of roughness is not demonstrated by Jäntti's method, but that the method is useful for the evaluation of parameters introduced by other arguments or from other sources.

Keywords: *adsorption, dynamic, fast measurement, roughness, surface*

Introduction

In 1970 Jäntti [1–3] introduced a method to shorten the measurement time of adsorption isotherms by calculation of the adsorption equilibrium from the beginning of the kinetic curve. As a basis he applied a simple adsorption model. In earlier papers [4–15] we discussed more complicated adsorption mechanisms, which involved the introduction of more parameters and the four Jäntti approaches for their evaluation in an early stage of the measurements. The basis of the Jäntti procedure is the measurement of the actual adsorbed amounts n_1, n_2 and n_3 at three equidistant times immediately after a change of the gas pressure p.

$$J=\frac{n_2^2-n_1n_3}{2n_2-n_1-n_3} \tag{1}$$

If the time interval $\Delta t \to 0$, we use the symbol J^*:

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

To deal with the influence of roughness of the surface on which the adsorption takes place, we simplify the situation by supposing the surface to consist of two different parts A and B so that we have to deal with two parallel adsorptions.

Parallel adsorptions

To describe these parallel adsorptions we use the following differential equations:

$$\frac{\mathrm{d}n_\mathrm{a}}{\mathrm{d}t}=n_\mathrm{ma}X-n_\mathrm{a}X_{1\mathrm{a}} \tag{3}$$

$$\frac{\mathrm{d}n_\mathrm{b}}{\mathrm{d}t}=n_\mathrm{mb}X-n_\mathrm{b}X_{1\mathrm{b}} \tag{4}$$

where n_a stands for the number of gas molecules adsorbed on A sites, n_b for the number of gas molecules adsorbed on B sites, n_ma for the maximum number of n_a, so for the total number of A sites, n_mb for the maximum number of n_b, so for the total number of B sites, X for the number of gas molecules hitting each site per unit of time, X will be proportional to the gas pressure, X_a for the probability that a molecule, adsorbed at an A site escapes per unit of time into the gas and X_b for the probability that a molecule adsorbed at a B site escapes per unit of time into the gas.

As initial conditions we shall use the fact that

for t=0 $\qquad n_\mathrm{a}=n_\mathrm{b}=0 \qquad$ (5)

and consider the consequences of a step in the gas pressure at t=0 bringing X from 0 to its constant value X.

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* Author for correspondence: hannespoulis@hotmail.com

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Akadémiai Kiadó, Budapest, Hungary
Springer, Dordrecht, The Netherlands

From the measurements of $n(t)$ we can, by using the four Jäntti approaches (determination of $(\mathrm{d}n/\mathrm{d}t)_0$, J_0, $(\mathrm{d}J/\mathrm{d}t)_0$, and the asymptotical value $n_{\mathrm{as}}=J_{\mathrm{as}}$), construct only four equations, whilst our model has five parameters, X, X_{a}, X_{b}, n_{ma} and n_{mb}, which we consider to be the unknowns. If our aim had been to determine the values of all five parameters, it would have been necessary to create an extra equation, for instance by carrying out experiments at another gas pressure with another value of X.

Fortunately it will be possible with our four equations to solve for $n_{\mathrm{a}}/n_{\mathrm{b}}$ together with X_{a} and X_{b}, parameters, which are of major importance for the description of roughness. As a solution of Eqs (3) and (4), for small values of t, we get using expansions in t:

$$\frac{n(t)}{X}=G_0t-\frac{1}{2}G_1t^2+\frac{1}{6}G_2t^3+\ldots \tag{6}$$

where

$$G_{\mathrm{i}}=n_{\mathrm{ma}}X_{\mathrm{1a}}^{\mathrm{i}}+n_{\mathrm{mb}}X_{\mathrm{1b}}^{\mathrm{i}} \tag{7}$$

Using Eqs (2) and (6) we get:

$$\frac{J}{X}=\frac{G_0^2}{G_1}+G_0\left(\frac{G_2G_0}{G_1^2}-1\right)t \tag{8}$$

From Eqs (3) and (4) we learn that for the asymptotical solutions we may use:

$$\frac{n_{\mathrm{as}}}{X}=\frac{J_{\mathrm{as}}}{X}=G_{-1} \tag{9}$$

As an introduction to the calculation of values of the parameters, using the Jäntti approaches, we calculate the values of the quantities G_{i} using the relations:

$$XG_{-1}=J_{\mathrm{as}} \tag{10}$$

$$XG_0=\left(\frac{\mathrm{d}n}{\mathrm{d}t}\right)_{\mathrm{t=0}} \tag{11}$$

$$XG_1=\frac{(\mathrm{d}n/\mathrm{d}t)_{\mathrm{t=0}}^2}{J_{\mathrm{t=0}}} \tag{12}$$

$$XG_2=\left[\frac{(\mathrm{d}n/\mathrm{d}t)_{\mathrm{t=0}}^2}{J_{\mathrm{t=0}}^2}\right]\left(\frac{\mathrm{d}n}{\mathrm{d}t}+\frac{\mathrm{d}J}{\mathrm{d}t}\right)_{\mathrm{t=0}} \tag{13}$$

These equations enable us to calculate the values of the quantities $G_{\mathrm{i}}X$. It is helpful to introduce the quantity P from the following equation:

$$P=X_{\mathrm{x}}X_{\mathrm{b}}=\frac{G_0G_2-G_1^2}{G_{-1}G_1-G_0^2} \tag{14}$$

This equation gives us the numerical value of P, when those of XG_{i} are known from Eqs (10)–(13) and enables us to eliminate the unknown X_{b} by using:

$$X_{\mathrm{b}}=\frac{P}{X_{\mathrm{a}}} \tag{15}$$

We can also eliminate the unknown n_{b} by using Eq. (7) for i=0:

$$n_{\mathrm{mb}}=G_0-n_{\mathrm{ma}}=\frac{(\mathrm{d}n/\mathrm{d}t)_{\mathrm{t=0}}}{X}-n_{\mathrm{ma}} \tag{16}$$

Using substitutions from Eqs (15) and (16) into Eqs (10), (12) and (13) we get:

$$J_{\mathrm{as}}=\frac{Xn_{\mathrm{ma}}}{X_{\mathrm{s}}}+\frac{(\mathrm{d}n/\mathrm{d}t)_{\mathrm{t=0}}X_{\mathrm{a}}}{P}-\frac{n_{\mathrm{ma}}XX_{\mathrm{a}}}{P} \tag{17}$$

$$\frac{(\mathrm{d}n/\mathrm{d}t)^2}{J_0}=n_{\mathrm{ma}}XX_{\mathrm{a}}+\frac{P(\mathrm{d}n/\mathrm{d}t)}{X_{\mathrm{a}}}-\frac{Xn_{\mathrm{ma}}P}{X_{\mathrm{a}}} \tag{18}$$

$$\frac{(\mathrm{d}n/\mathrm{d}t)_{\mathrm{t=0}}^2}{J_{\mathrm{t=0}}^2}\left(\frac{\mathrm{d}n}{\mathrm{d}t}+\frac{\mathrm{d}J}{\mathrm{d}t}\right)=n_{\mathrm{ma}}XX_{\mathrm{a}}+ +\frac{P^2(\mathrm{d}n/\mathrm{d}t)_{\mathrm{t=0}}}{X_{\mathrm{a}}}-\frac{n_{\mathrm{ma}}XP^2}{X_{\mathrm{a}}^2} \tag{19}$$

Equations (17)–(19) can be seen as three equations with the unknowns Xn_{ma}, and X_{a}, because the values of all other quantities in the equation can be determined with the Jäntti approaches. To solve these equations we plot $n_{\mathrm{ma}}X$ *vs.* X_{a} using the Eqs (17)–(19) and get three curves, whose points of intersection will coincide. With Eq. (16) we can then evaluate Xn_{mb} and so of $n_{\mathrm{ma}}/n_{\mathrm{mb}}$. With Eq. (15) we get the value of X_{b}.

Experimental example

To illustrate the approach discussed in the above we used measurements of H_2O vapour adsorbed on a partly covered Al_2O_3 surface. The resulting data were kindly put at our disposition by POROTEC, Hofheim, Germany. The measured adsorptions are shown in Fig. 1, together with the calculated values of $J(t)$. From this figure we read:

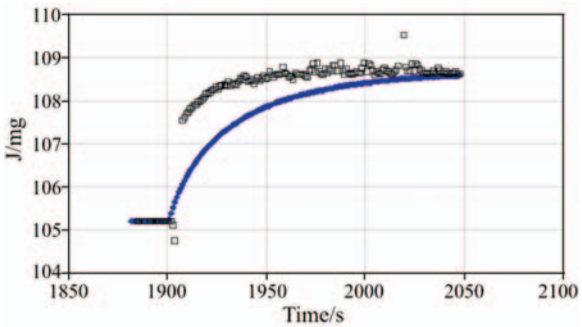

Fig. 1 The measured ◆ – $n(t)$ curve with the □ – $J(t)$ curve calculated with Eq. (1) with t_2–t_1=t_3–t_2=5; ordinate: J [mg], abscissa: time t [s]

$$n_{as}=J_{as}=0.68$$

$$(dn/dt)_{t=0}=0.025$$

$$J_0=0.375$$

$$(dJ/dt)_{t=0}=0.0133$$

with Eqs (10)–(13) we calculate:

$$XG_{-1}=0.68$$

$$XG_0=0.025$$

$$XG_1=0.00167$$

$$XG_2=0.00017$$

The X_a *vs*. (Xn_a) plot in Fig. 2 leads to:

$$X_a=0.024$$

$$Xn_{ma}=0.0142$$

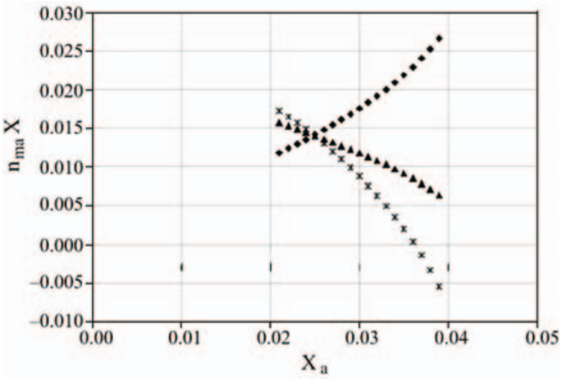

Fig. 2 The evaluation of Xn_a and X_a as the point of intersection of the three curves; ordinate: $n_{ma}X$, abscissa: X_a; ◆ – $(dn/dt)=0.025$, $G_0=0.025$, $i=-1$; ■ – $J_0=0.375$, $G_{-1}=0.68$, $i=1$; ▲ – $(dJ/dt)_0=0.0133$, $G_1=0.001667$, $i=1$; × – $n_{as}=0.68$, $G_2=0.0001702$, $i=2$

with Eq. (14) we get:

$$P=0.00291$$

$$X_b=P/X_a=0.12$$

$$Xn_{mb}=XG_0–Xn_{ma}=0.011$$

and so we get:

$$X_a=0.024,\ X_b=0.12 \text{ and } n_{ma}/n_{mb}=1.3.$$

Table 1 Results of parameter X_a and $n_{ma}X$ calculation from measurements of parts of a water vapour adsorption isotherm on Al_2O_3. The five columns refer to five different combations of values used in rows 1 to 4 and the resulting data in rows 5 and 6

		1	2	3	4	5
1	$(dn/d_t)_0$	0.025	0.035	0.025	0.025	0.025
2	J_0	0.375	0.375	0.450	0.375	0.375
3	$(dJ/dt)_0$	0.013	0.013	0.013	0.020	0.013
4	J_{as}	0.68	0.68	0.68	0.68	0.750
5	X_a	0.024	0.029	0.028	0.028	0.022
6	$n_{ma}X$	0.014	0.015	0.017	0.018	0.013

Conclusions

As explained above the aim of this paper is not to present a procedure to verify the validity of a model. The aim is to show that, given the measured data shortly after the beginning of the adsorption measurements and given the model, we can, with Jäntti's method calculate or at least estimate the values of parameters used in the model.

In this, it is of great interest to pay attention to the accuracy of these values. Therefore we have in our example checked up on the influence of variations of the four data from the Jäntti's expedients. The results are presented in Table 1. The first set of rows correspond to the values determined from the measured $n(t)$ and $J(t)$ curves. The last two rows show the resulting values of the parameters X_a and $n_{ma}X$. The first column refers to the best fit of the above measured values. In the other columns one of the measured values was varied from the best fit in order to test the effect of incorrect measurements. These calculations should be regarded as a demonstration of the possibilities and limitations of the procedure presented in this paper.

Nomenclature

A	area A
B	area B
G_i	auxiliary parameters
J	Jäntti's approach of the adsorbed amount
J^*	Jäntti's approach of the adsorbed amount for measuring intervals $\Delta t \to 0$
n_a	number of gas molecules adsorbed on A sites
n_b	number of gas molecules adsorbed on B sites
n_i	adsorbed amount
$n_{as}=J_{as}$	extrapolated value of the adsorbed amount in equilibrium using Jäntti's approach
n_{ma}	maximum number of adsorbed gas molecules n_a=the total number of A adsorption sites
n_{mb}	maximum number of adsorbed gas molecules n_b=the total number of B adsorption sites
p	adsorptive gas pressure
P_i	auxiliary parameters
t	time
X	number of gas molecules hitting each site per unit of time
X_a	possibility that a molecule, adsorbed at an A site escapes per unit of time into the gas
X_b	possibility that a molecule, adsorbed at a B site escapes per unit of time into the gas

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