

THE JÄNTTI APPROACH USING A TWO-LAYER MODEL

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Abstract

Jäntti introduced a method to calculate the adsorption equilibrium by the measurement of the actual adsorbed amount at three times after a change of the gas pressure. He applied that method for gas/solid systems in which simple adsorption processes occur and for an infinite number of adsorption sites. In the present paper we discuss the case that the number of sites is decreasing with increasing coverage.

Keywords: adsorption, fast measurement, gravimetry, kinetics, sorption

Introduction

In 1970 Jäntti [1] introduced a new function for the evaluation of the values of the parameters from measured adsorption isotherms. Jäntti applied this function in the case a simple model can be applied. We applied the method to adsorptions following more complicated molecular models, i.e. parallel adsorptions and adsorptions in connection with porosity effects [2–4]. In the present paper we shall discuss the use of Jäntti's method when the adsorption is so large that one could speak of the prelude of

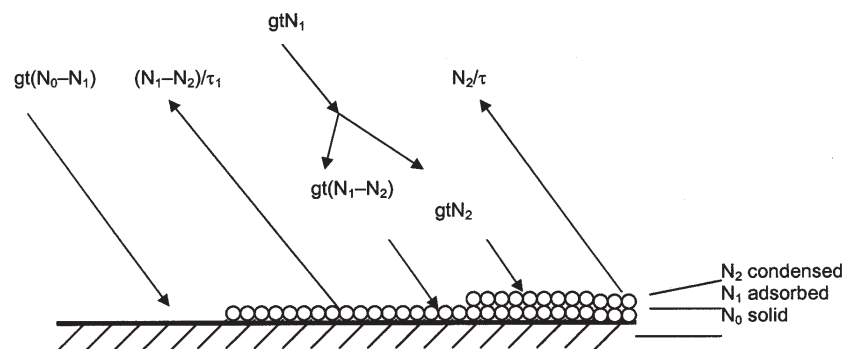


Fig. 1 Different types of molecule transport to the surface considered. The quantities denoted with capitals are dimensionless

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a condensation. For this purpose we introduced a two-layer model describing such a transition (Fig. 1).

For the measured values m_1 , m_2 and m_3 of the mass adsorbed after equal time intervals Jäntti used:

$$j = \frac{m_2^2 - m_1 m_2}{2m_2 - m_1 - m_3} \quad (\text{A1})$$

It will be useful to use a dimensionless presentation of this equation in which the corresponding numbers of adsorbed molecules are referred to as N_1 , N_2 and N_3 , respectively. Equation (A2) then expresses a quantity J , where the use of a capital indicates that the quantity is dimensionless.

$$J = \frac{N_2^2 - N_1 N_2}{2N_2 - N_1 - N_3} \quad (\text{A2})$$

For many purposes we use instead of (A1) and (A2) [3]

$$j^* = m - \frac{(dm/dt)^2}{d^2 m/dt^2} \quad (\text{B1})$$

$$J^* = N - \frac{(dN/dt)^2}{d^2 N/dt^2} \quad (\text{B2})$$

where m stands for the adsorbed mass as a function of the time t , N for the number of adsorbed molecules and j , J , j^* and J^* are calculated with Eqs (A1)–(B2). Capitals are used throughout in this paper for dimensionless quantities.

The two-layer model

The number of sites available for adsorption is referred to as N_0 . Of these N_0 sites we suppose that N_1 are occupied. On top of these N_1 adsorbed molecules we suppose that there is a second adsorbed layer of N_2 molecules (N_2 being smaller than N_1). The interaction between the two layers will resemble that of the liquid state. N is the total number of adsorbed molecules,

$$N = N_1 + N_2 \quad (1)$$

The number of gas molecules hitting the sample per unit of time we shall refer to as gt . This expression implies that we consider a gas pressure which increases linearly with time. In case a gas molecule hits a molecule adsorbed in the second layer, we suppose it to migrate and so to contribute to the number of molecules in the second layer (we do not consider the existence of a third layer). $1/\tau_1$ and $1/\tau_2$ determine the probability that an uncovered molecule of the first layer or a molecule of the second layer escape per unit of time into the gas, respectively.

Equations (2) and (3) represent the different transport mechanisms considered:

$$\frac{dN_1}{dt} = gt(N_0 - N_1) - \frac{N_1 - N_2}{\tau_1} \quad (2)$$

$$\frac{dN_2}{dt} = gtN_1 - \frac{N_2}{\tau_2} \quad (3)$$

For convenience we suppose that the binding between molecules of the first and second layer equals the binding of the molecules in the liquid state. The constant τ_2 may then be supposed to be independent on the nature of the adsorbent and so we will use it when starting a dimensionless treatment. Thereto we introduce the quantities T , T_1 and G by:

$$T = t/\tau_2 \quad (4)$$

$$T_1 = \tau_1/\tau_2 \quad (5)$$

$$G = g\tau_2^2 \quad (6)$$

We will, for the sake of convenience, use the quantities X and Y and Z :

$$X = GT \quad (7)$$

$$Y = 1 + (T_1 - 1)GT \quad (8)$$

$$Z = 1 + GT \quad (9)$$

The Eqs (2) and (3) read in a dimensionless form:

$$\frac{dN_1}{dT} = GT(N_0 - N_1) - \frac{N_1 - N_2}{T_1} \quad (10)$$

$$\frac{dN_2}{dT} = GTN_1 - N_2 \quad (11)$$

We shall consider also processes caused by a very slow increase of the gas pressure, which we shall refer to as Quasi Static processes, so in Eqs (10) and (11) we use the value 0 for the LHS. From the resulting linear equations we can solve N_1 and N_2 leading to Eqs (12)–(13). Such QS conditions could in hypothetical measurements be provided for by only increasing the gas pressure at constant rate only during short intervals separated by long intervals during which the increase of the gas pressure is cut of as well as the clock registering the time to be plotted in the m and J vs. t curves.

$$N_{QS} = N_{1QS} + N_{2QS} = \frac{N_0 T_1 XZ}{Y} \quad (12)$$

$$J_{QS}^* = \frac{N_0 T_1}{Y} \frac{XZ - (Z + XY)^2}{4 - 2T_1} \quad (13)$$

In Fig. 2 we plotted some numerical results determined by solving Eqs (10)–(13). The pronounced dependency of those curves on the parameters gives

rise to our hope that measured curves of N and J vs. t can contribute to the determination of the values of the parameters. For such an evaluation it is of importance to remark that when t reaches the value at which $N_1=N_2=N_0$, the equilibrium of the gaseous and the liquid state is reached and further raise of the gas pressure will lead to condensation, we shall refer to this time as t_c .

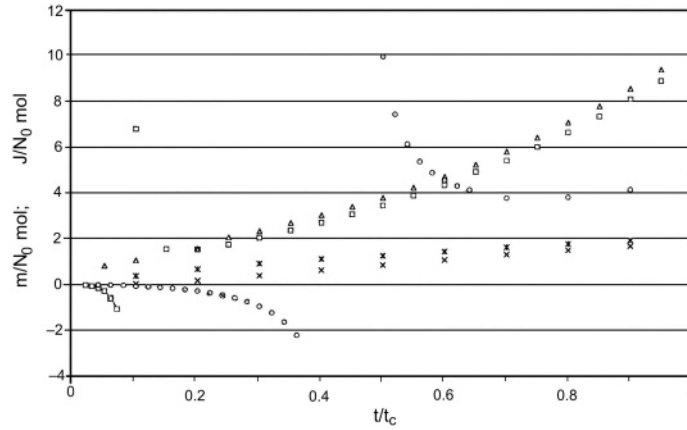


Fig. 2 Computer simulation of m and J as a function of time. Along the x -axis is plotted: $t/t_c=g\tau_2t=GT$

Plotted vertically		g	G	τ_1	t_2
$m/(N_0m_{\text{mol}}) 10^{-3}$	—*—	10^{-7}	10^{-3}	500	100
$m_{\text{QS}}/(N_0m_{\text{mol}})$	—x—	10^{-1}	10^{-1}	5	1
$j_{\text{QS}}/(N_0m_{\text{mol}})$	—Δ—	10^{-7}	10^{-3}	500	100
$j/(N_0m_{\text{mol}})$	—o—	10^{-1}	10^{-1}	5	1
$j/(N_0m_{\text{mol}})$	—□—	10^{-4}	10^{-2}	50	10

For the evaluation of the values of the parameters from measured data m_{meas} and j_{meas} we will use the following relations between these quantities and the quantities used in the above. These relations are given by the Eq. (14), where m_{mol} stands for the mass of a single gas molecule, the value of which we will consider to be known.

$$m_{\text{meas}} = m = m_{\text{mol}}N \quad (14)$$

$$j_{\text{meas}} = j = m_{\text{mol}}J \quad (15)$$

$$\frac{dm}{dt} = \frac{m_{\text{mol}}}{\tau_2} \frac{dN}{dT} \quad (16)$$

There exist many possibilities to evaluate the values of the parameters. We will discuss a few of them, all related to the point at the beginning and the point at the end

of the measured adsorption isotherms. At the starting point of such measured (m) and calculated (j) curves at $t=0$ we can use:

$$T=0 \quad X=0 \quad Y=1 \quad Z=1 \quad (17)$$

Using Eqs (12) and (15) we get:

$$\left(\frac{dm}{dt}\right)_{t=0} = \frac{m_{\text{mol}}}{\tau_2} GN_0 T_1 \quad (18)$$

Using Eqs (13) and (15) we get:

$$j_{t=0} = m_{\text{mol}} N_0 \frac{T_1}{2T_1 - 4} \quad (19)$$

At the end point of the measured curves at $t=t_c$ we can use:

$$T_c = 1/G \quad X_c = 1 \quad Y_c = T_1 \quad Z_c = 2 \quad (20)$$

Using Eqs (12) and (20) we get:

$$t_c = \frac{\tau_2}{G} \quad (21)$$

$$m_c = 2m_{\text{mol}} N_0 \quad (22)$$

$$j_c = m_{\text{mol}} N_0 \frac{T_1^2 + 8T_1 - 4}{2T_1 - 4} \quad (23)$$

Combining Eqs (19) and (23) we get:

$$\frac{j_c}{j_{t=0}} = T_1 + 8 - \frac{4}{T_1} \quad (25)$$

Equation (24) seems particularly useful for the determination of the value of T_1 . As mentioned in the above, the value of m_0 will usually be known, while the value of g is dependent of the rate of increase of the pressure of the gas.

The results of a computer simulation of our model is shown in Fig. 2. This figure shows the progress of the adsorption for different rates of the increase of the gas pressure. This rate is represented by the parameter G . To simplify comparison the plot along the horizontal axis has been chosen such that the condensation points coincide in horizontal projection. To avoid confusion one of the curves of the adsorbed mass has been left out. The mass curves shown are numerical solutions of the differential Eqs (10) and (11) and the j curves are calculated with the original Jäntti equation (A). We see that for values of G as small as 0.001 we can say we deal with a quasi static process so that the Eqs (12) and (13) can be used and so also the parameter evaluation of Eqs (15)–(24). For the curves with larger values of G the calculations were stopped when N_2 proved to be larger than N_1 , as in that situation our model can not be used. When the product of T and G becomes larger than 1, a static situation will no longer

be possible and the adsorbed (condensed) mass will continue to grow also when the gas-pressure is kept constant.

Discussion

The treatment presented above can also be applied to adsorption measurements where the gas pressure is raised stepwise and this pressure is kept constant long enough after each step to ensure equilibrium. When the steps are equal, Jäntti's original definition (A1) can be used to calculate j using the equilibrium values of the adsorbed mass.

References

- 1 O. Jäntti, J. Junttila and E. Yrjänheikki, Suomen Kemistilehti, A 43 (1970) 214.
- 2 C. H. Massen, J. A. Poulis and E. Robens, Adsorption, 6 (2000) 229.
- 3 E. Robens, C. H. Massen, J. A. Poulis and P. Staszczuk, Adsorption Sci. Tech., 17 (1999) 801.
- 4 J. A. Poulis, C. H. Massen, E. Robens and K. K. Unger, A fast two-point method for gas adsorption measurements. In K. K. Unger, G. Kreysa, J. P. Baselt (Eds): Characterisation of Porous Solids V. Studies in Surface Science and Catalysis, Elsevier, Amsterdam 2000, pp. 151–154.