FAST GAS ADSORPTION MEASUREMENTS FOR COMPLICATED ADSORPTION MECHANISMS

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

[1]Institut für Anorganische und Analytische Chemie der Johannes Gutenberg-Universität
D-55099 Mainz, Germany
[2]Faculty of Technical Physics, Technical University Eindhoven, Postbus 513, NL-5600 MB
Eindhoven, The Netherlands

Abstract

Jäntti introduced a method to reduce the time required for the stepwise measurement of adsorption isotherms. After each pressure change he measured the adsorbed mass three times and calculated its equilibrium value at the new pressure. In the present paper, we discuss the applicability of this method in a broader scope without starting from a given combination of sorptive and adsorbent and the influence of measuring inaccuracies. The method is applied to detect whether the adsorption process is based on more than one adsorption mechanism or not.

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

Introduction

It is advisable to measure surface reactions very slowly, because often slow processes are included. In practice, however, we are often in a hurry. The measurement of sorption isotherms with nitrogen or noble gases may last hours and with water or solvent vapours days or weeks. In such cases we are forced to accept approximate results. It is, however, very dubious to extrapolate a kinetic curve by appearance.

Jäntti's three point method for a single adsorption mechanism

In 1969 Jäntti published a very simple method to calculate the adsorbed mass from gas adsorption measurements with a gravimetric procedure. He started from the equation:

$$m(t) = m(1 - e^{-t/\tau}) \tag{1}$$

where $m(t)$ is the momentary adsorption at time t, m is the adsorbed mass after waiting infinitely long, so it is the quantity the determination of which is that aim of the measurement. The time interval characteristic of the adsorption will be referred as τ.

Jäntti used three mass determinations at times $t_1 = t_2 - \Delta t$, t_2 and $t_3 = t_2 - \Delta t$ resulting in the momentary adsorption values of $m(t_1)$, $m(t_2)$ and $m(t_3)$, respectively. For the calculation of the adsorption m Jäntti used the equation

$$m_J(t_2)=\frac{m(t_2)^2-m(t_1)m(t_3)}{2m(t_2)-m(t_1)-m(t_3)} \tag{2}$$

When Eq. (1) holds it can be shown that $m_J(t_2)=m$. The advantage of Jäntti's method apart from the easiness is the fact that measurements can be completed in a time interval $t_m=t_3$ which can be taken small in comparison with t. So the method is not only a simple one, it is also a fast one [2].

Extension of the three-point method for complicated adsorption mechanisms

One of the disadvantages of Jäntti's method is the fact that it is especially developed for the case where there is only a single adsorption mechanism [3]. To discuss this disadvantage we use the approximation $m=m_J(t_2)$ in Eq. (1) and get:

$$\tau(t_2)=\frac{-t_2}{\ln(1-m(t_2)/m_J(t_2))} \tag{3}$$

The obvious advantage of using Eq. (3) is that in case of a single adsorption mechanism one gets extra information, namely the value of the characteristic time without an increase of the duration of the measurement.

If we neglect the criterion of short duration $t_m<<\tau$), the use of Eq. (3) gives extra information in the case of simultaneous occurrence of several adsorption mechanisms. We shall illustrate this advantage with two examples, Fig. 1 and Fig. 2. For these examples we did not take real measurements to get the momentary adsorptions but we calculated simulated momentary adsorptions with Eq. (1) using dummy adsorptions m_a and m_b and their dummy characteristic times τ_a and τ_b. In Fig. 1 we started from two equal dummy adsorptions $m_a=m_b$ but with different values of the characteristic times, namely $\tau_a=1$ h and
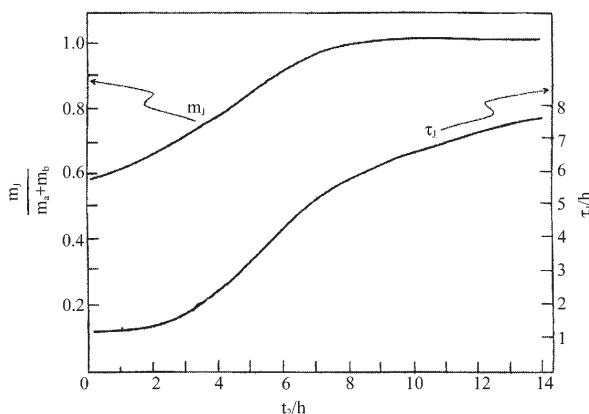

Fig. 1 Two equal dummy adsorptions $m_a=m_b$ but with different values of the characteristic times $\tau_a=1$ h and $\tau_b=12$ h, and superposition $m(t_2)=m_a(t_2)+m_b(t_2)$

τ_b=12 h. With Eq. (1) we calculated the two simulated momentary adsorbed masses $m_a(t)$ and $m_b(t)$ as a function of time and supposing these momentary adsorptions to occur simultaneously we used $m(t)=m_a(t)+m_b(t)$. The so obtained total simulated momentary adsorptions $m(t)$ we used in Eqs (2) and (3) resulting in the values $m_J(t)$ and $\tau(t)$.
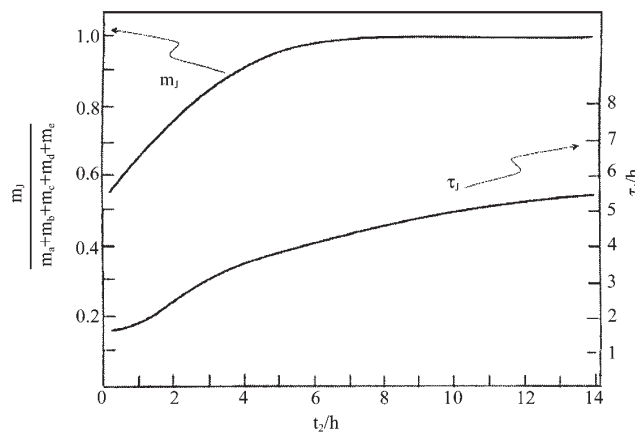

Fig. 2 Mixture of five equal dummy adsorptions $m_a=m_b=m_c=m_d=m_e$ with different characteristic times 1, 3, 5, 7 and 9 h

When we had had to do with only a single adsorption mechanism, Fig. 1 should have shown a horizontal line at height $(m_J(t))/(m_a+m_b)=1$. As such is not the case, Fig. 1 proves the existence of more than one adsorption mechanism. Actually, it is to be appreciated that Jäntti's method when extended to a longer measurement time indicates whether one has to do with a single adsorption mechanism or not.

If one allows an even longer duration of the measurement time, we see in Fig. 1 that the curve indeed approaches the expected value $m_J(\infty)/(m_a+m_b)=1$.

In Fig. 1 also the values of $\tau(t_2)$ resulting from the use of Eq. (3) are shown in dependency upon time t_2. Though the meaning of such a characteristic time of the mixture is not easily understood, the fact that its curve in Fig. 1 is so pronouncedly curved can also be used as an easy indication of the existence of more than one adsorption mechanism.

In Fig. 2 the same procedure is followed for a mixture of five equal dummy adsorptions $m_a=m_b=m_c=m_d=m_e$ with different characteristic times, namely 1, 3, 5, 7 and 9 h. Here also the signalling function of the τ curve is clear and we see that after a sufficiently long measurement time the total adsorption m approaches the expected value $m_J(\infty)=m_a=m_b=m_c=m_d=m_e$.

With an additional technique it is possible to improve the warning system, without being necessary to use more sophisticated tools than a pocket calculator. We shall explain this by considering the same two examples of dummy adsorptions we dealt with in Figs 1 and 2. Again, we calculate the simulated momentary adsorption as a function of time, by using Eq. (1), starting from two or five dummy adsorptions, re-

spectively. From the first three simulated momentary total adsorptions at times $t_s - \Delta t$, t_s and $t_s - \Delta t$ we make a first approximation of the total adsorption with Eqs (1) and (3), resulting in $m_{J1}(t_s)$ and $\tau_{J1}(t_s)$.

To evaluate the effect of this approximation we return to Eq. (1) and substitute m and τ by $m_{J1}(t_s)$ and $\tau_{J1}(t_s)$ respectively. The resulting momentary adsorptions we will refer to as $m_s(t)$ and we define

$$m_2(t) = m(t) - m_s(t) \tag{4}$$

We return to Eqs (2) and (3) and substitute $m(t)$ by $m_2(t)$. The result we refer to as $m_{J2}(t)$ and $\tau_{J2}(t)$ respectively.
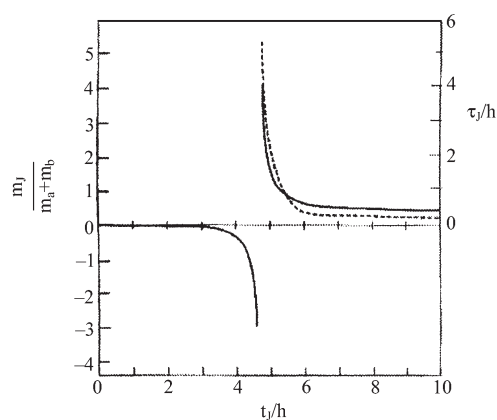

Fig. 3 $m_{J2}(t)$ and $\tau_{J2}(t)$ calculated by means of Eqs (2) and (3) as a function of time of two dummy adsorptions (Fig. 1) — m_{J2}, --- τ_{J2}
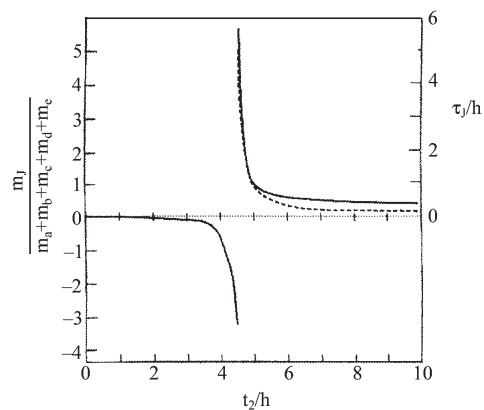

Fig. 4 $m_{J2}(t)$ and $\tau_{J2}(t)$ calculated by means of Eqs (2) and (3) as a function of time in the case of five dummy adsorptions (Fig. 2) — m_{J2}, --- τ_{J2}

In Fig. 3 $m_{J2}(t)$ is plotted as a function of t for the case of two dummy adsorptions. The same procedure is followed in Fig. 4 for the case of five dummy adsorptions.

We see in Figs 3 and 4 that the disappearance of the part of the curve for $\tau_{J2}(t)$ and the anomalous behaviour of the $m_{J2}(t)$ curve indeed give strong indications for the fact that the adsorption mechanism is complicated. The curves of Figs 3 and 4 show the existence of vertical asymptotes, the position of which we shall characterise by t_{as}. Combining the occurrence of the asymptotes with zero points of the denominator of Eq. (2) the following relation is easily derived:

$$\frac{m_{J1}(t_s)}{\tau_{J1}^2(t_s)}e^{-\frac{t_s}{\tau_{J1}(t_s)}} = \frac{m_a}{\tau_a^2}e^{-\frac{t_{as}}{\tau_a}} + \frac{m_b}{\tau_b^2}e^{-\frac{t_{as}}{\tau_b}} \tag{5}$$

Equation (4) can be useful as an extra equation to evaluate the values of the parameters m_a, m_b, τ_a and τ_b.

References

1 O Jäntti, J. Junttila and Yrjänheikki, In: Progress in Vacuum Microbalance Techniques, T. Gast and E. Robens (eds.), Vol. 1, Heyden, London 1972, p. 345.
2 J. A. Poulis, C. H. Massen, E. Robens and K. K. Unger, In: Characterisation of Porous Solids V, K. K. Unger, G. Kreysa and J. P. Baselt (eds), Elsevier, Amsterdam 2000, p. 151.
3 E. Robens, C. H. Massen and J. A. Poulis, IX. POROTEC-Workshop über die Charakterisierung von feinteiligen und porösen Festkörpen, 11–12, 11, 1998, Bad Soden.