Criticism on Jäntti's Three Point Method on Curtailing Gas Adsorption Measurements

CAREL H. MASSEN AND JOHANNES A. POULIS
Faculty of Technical Physics, Technical University Eindhoven, Postbus 513, NL-5600 MB Eindhoven, The Netherlands

ERICH ROBENS
Institut für Anorganische Chemie und Analytische Chemie der Johannes Gutenberg-Universität, D-55099 Mainz, Germany

Abstract. Jäntti introduced a method to reduce the time required for the stepwise measurement of adsorption isotherms (Jäntti et al., Progress in Vacuum Microbalance Techniques, Vol. 1, Heyden, London, pp. 345–353, 1972). After a pressure change he measured the adsorbed mass three times and calculated its equilibrium value for the new pressure. In the present paper we discuss the applicability of this method in a broader scope (without starting from a single combination of gas and solid adsorbent) and also discuss the influence of measurement inaccuracies. It is shown that the method can serve as an early warning system, which decides whether an improvement of the adsorption model is necessary.

1. Introduction

Jäntti et al. (1972) introduced an elegant procedure for handling gravimetric gas adsorption measurements. In the present paper this procedure will be referred to as the Three Point Method (TPM). 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 (van der Wel, 1999). Experimental shortening of the measurement time can only be made by improvement of the heat transfer and by operation control (Rouquerol et al., 1999; Paulik, 1998).

With TPM the adsorbed mass is measured at times t_1, t_2 and t_3 (where $t_3 - t_2 = t_2 - t_1 = \Delta t$) yielding the values m_1, m_2 and m_3, respectively. For the evaluation involved Jäntti offered the choice between three molecular adsorption mechanisms represented by the following:

$$m(t) = m(\infty)\frac{t/\tau}{1 + t/\tau} \qquad (1a)$$

$$m(t) = m(\infty)(1 - e^{-t/\tau}) \qquad (1b)$$

$$m(t) = m(\infty)\tanh(t/\tau) \qquad (1c)$$

where a stepwise variation of the gas pressure is assumed at $t = 0$ and where $m(\infty)$ is the asymptotic equilibrium value of $m(t)$. For each of these equations Jäntti presented a relation to enable the application of TPM:

$$m_a = \frac{m_1 m_2 + m_2 m_3 - 2m_1 m_3}{2m_2 - m_1 - m_3} \qquad (2a)$$

$$m_b = \frac{m_2^2 - m_1 \cdot m_3}{2m_2 - m_1 - m_3} \qquad (2b)$$

$$m_c = \sqrt{m_2 m_a} \qquad (2c)$$

Apart from Eqs. (2a–c) TPM allows for a quick calculation of the parameter τ for infinitesimally small values of $\Delta t = t_3 - t_2 = t_2 - t_1$:

$$\tau = \frac{m_{a,b,c} - m_1}{m_2 - m_1}(t_2 - t_1)$$

where $m_{a,b,c}$ is either m_a, m_b or m_c.

Jäntti applied TPM to its own specific measurements and discussed its applicability for the case of a system of one adsorbate and a homogeneous sorbent. In the present paper we discuss the applicability of TPM based on Eq. (1b) for heterogeneous sorbents. Besides that we discuss two other aspects of TPM:

– The influence of weighing errors in the case of a uniform sorbent
– The consequence of the choice between Eqs. (1a–c).

2. Heterogeneous Sorbents

For a discussion on the influence of the heterogeneity of the sorbent on the TPM-results we present Fig. 1. This figure refers to the application of Eq. (1b) to a combination of two sorbents x and y with different values τ_x and τ_y of their characteristic adsorption times using the asymptotic values of the adsorbed masses $m_x(t)$ and $m_y(t)$ are $m_x(\infty)$ and $m_y(\infty)$, respectively. We assume the two adsorptions are independent and calculate the adsorbed mass $m(t)$ on the two sorbents as follows:

$$\frac{m(t)}{m(\infty)} = \frac{m_x(\infty)}{m(\infty)}\left(1 - e^{-t/\tau_x}\right) + \frac{m_y(\infty)}{m(\infty)}\left(1 - e^{-t/\tau_y}\right)$$
$$(3)$$

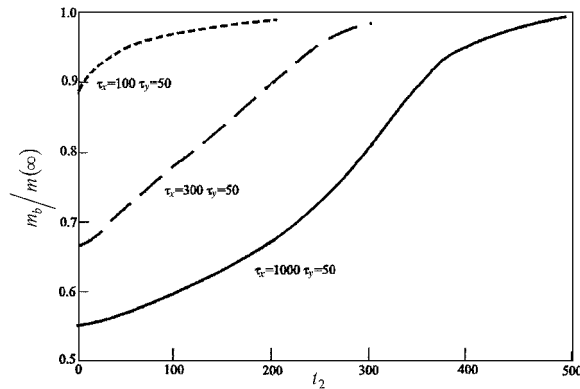where $m_x(\infty) + m_y(\infty) = m(\infty)$.

Figure 1. TPM-results obtained with Eqs. (4) and (2b) for a mixture of two sorbents x and y where $\frac{m_x(\infty)}{m(\infty)} = \frac{m_y(\infty)}{m(\infty)} = \frac{1}{2}$ and $\Delta t \ll t_2$.

For $t = t_1 = t_2 - \Delta t$, $t = t_2$ and $t = t_3 = t_2 + \Delta t$ we calculate the values m_1, m_2 and m_3 respectively using Eq. (3). We use these values m_1, m_2 and m_3 in Eq. (2b) to obtain a value of m_b, which is only dependent at t_2 if we take $\Delta t \ll t_2$ (see Fig. 1).

For a homogeneous sorbent (characterized here by $\tau_x = \tau_y$) Eq. (2b) should predict a value of m_b independent at t_2. This is expressed by a horizontal line at height $m_b/m(\infty) = 1$. For each of the curves the following conditions are chosen:

$$\frac{m_x(\infty)}{m(\infty)} = \frac{m_y(\infty)}{m(\infty)} = \frac{1}{2}, \quad \tau_y = 50 \quad \text{and} \quad \Delta t \ll t_2.$$

The three curves represent the results for different values of τ_x.

The discrepancies between each of the three curves and the horizontal line at height 1, particularly at small values of t_2, show that the application of TPM to a heterogeneous sorbent lacks the elegance of simplicity of Jäntti's original application.

From the combination of Eqs. (1b) and (2b) it follows that:

$$m_b = m_x(\infty) + m_y(\infty)$$
$$- \frac{m_x(\infty) \cdot m_y(\infty) \cdot (\tau_x - \tau_y)^2}{m_x(\infty)\tau_y^2 e^{t_2/\tau_y} + m_y(\infty)\tau_x^2 e^{t_2/\tau_x}} \quad (4)$$

for $\Delta t \ll t_2$.

Apart from the application to heterogeneous sorbents, Eq. (4) might well be of more use. Jäntti started with Eq. (1b) as the solution of a first order differential equation, based on a simple molecular adsorption model. When it is relevant to improve this model the next approximation will in many cases lead to a second order differential equation, the solution of which appears to have the form of Eq. (3). For such an approximation Eq. (4) can be applied.

Taking into account the aim of obtaining quick results with TPM, a line in Fig. 1 for small values of t_2 can be characterized by the intersection with the vertical axis and its slope at that intersection. With Eq. (4) we see that with quick measurements we obtain two relations between the four parameters $\frac{m_x(\infty)}{m(\infty)}$, $\frac{m_y(\infty)}{m(\infty)}$, τ_x and τ_y.

Though Fig. 1 shows that application of Jäntti demands careful consideration when more complicated adsorption mechanisms prevail, the use of TPM also in this case proffers remarkable advantages: Fig. 1 shows that already at small values of t_2, the variation of $\frac{m_b}{m(\infty)}$ with t_2 indicates the need for a more sophisticated model of adsorption. A consequence of this conclusion is that when $\frac{m_b}{m(\infty)}$ appears to be constant, it can

quickly be concluded that the TPM results can be used for the asymptotically adsorbed mass involving a substantial reduction of measurement time.

From the authors experience we give the following examples: The adsorption of Ar and Kr at 77 and 90 K on micro- and mesoporous glass took up to one hour (Robens et al., 1986). Afterwards Eq. (2b) proved to yield always a constant value of m_b (independent of t_2) which shows the reduction of the measurement time to a few minutes. Thus, the measurement of the complete isotherm could have been done within one hour. On the other hand, we found that a general extrapolation of the adsorption of water vapor on cement proved to be impossible (Robens et al. in press). Most probably a superimposed swelling process that depends on the relative pressure cannot be described by a second order differential equation. Also some degassing curves of organic polymers (Czabon et al., 1970) could not be described by one of the Eqs. (1a, b or c).

3.   The Influence of Non-Systematic Errors

As explained in the introduction TPM was developed to reduce the measurement time t_m. This reduction, however, is accompanied by an increase in inaccuracy, which is discussed here. We restrict ourselves to adsorptions allowing for the application of Eqs. (1b) and (2b) and we take $t_1 = 0$, so $t_2 = \frac{1}{2}t_m = \Delta t$ and $t_3 = t_m = 2\Delta t$.

With Eq. (1b) we calculated $m_1/m(\infty)$, $m_2/m(\infty)$ and $m_3/m(\infty)$, where m_1, m_2 and m_3 refer to $m(t_1)$, $m(t_2)$ and $m(t_3)$, respectively. Using this in Eq. (2b), we reach the obvious result $m_b = m(\infty)$. To introduce the weighing inaccuracy Δm_w of the balance, we replace m_3 by $m_3^* = m_3 + \Delta m_w$ and use m_1, m_2 and m_3^* in Eq. (2b), the result of which is m_b^*. For the error Δm_b of TPM we take the difference between m_b^* and m_b. It follows that when $\frac{t_m}{\tau} < \frac{1}{2}$ we can use the following estimate:

$$\frac{\Delta m_b}{\Delta m_w} = \frac{4\tau^2}{t_m^2} \tag{5}$$

We see that the error of TPM increases quadratically with decreasing measurement time. As yet we have found no exceptions to this rule in our experiments.

4.   Molecular Adsorption Mechanism

In the introduction we mention the fact that Jäntti considered three molecular adsorption mechanisms. Figure 2 shows how an incorrect choice of mechanism
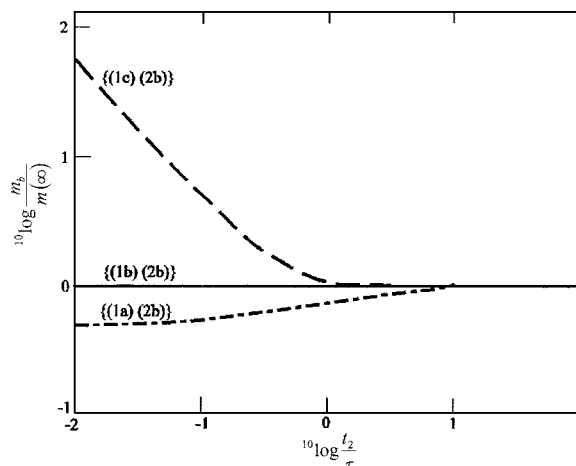

Figure 2.   Calculated adsorbed mass vs. measuring time if an incorrect choice of molecular adsorption mechanism and thus an incorrect combination of Eqs. (1a) or (1c) with (2b) is made.

influences the results calculated with TPM. To demonstrate this we started with the calculation of $m(t)$ with each of Eqs. (1a–c). We used the resulting values of $m(t)$ in Eq. (2b) where we took $\Delta t \ll t_2$. So we obtained three different curves for m_b (see Fig. 2). Due to the double-logarithmic scale we expect the correct choice (being the combination of Eqs. (1b) and (2b)) to result in a horizontal line at zero height. The discrepancies for small measuring times are apparent.

5.   Conclusions

1. TPM serves as an early warning system. The value of one additional parameter can be determined with Eq. (4) if one wants to improve the model of Eq. (1b).
2. Eq. (5) shows that the inaccuracy of TPM results increases with decreasing measurement time.
3. If we restrict ourselves to the adsorption models (Eqs. (1a–c)) offered by Jäntti, TPM allows one to choose between these models.

Acknowledgment

References

Czabon, H., G. Hild, E. Robens, G. Walter, and M.-L. Welling, "Microgravimetric Investigation of Degassing of Plastics in

Vacuum at Processing Temperature," *Industrial & Engineering Chemistry, Product Research & Development*, **9**(1), 27–30 (1970).

Jäntti, O., J. Junttila, and E. Yrjänheikki, "On Curtailing the Micro-Weighing Time by an Extrapolation Method," in *Progress in Vacuum Microbalance Techniques*, Vol. 1, T. Gast and E. Robens (Eds.), pp. 345–353, Heyden, London, 1972.

Paulik, F., *Special Trends in Thermal Analysis*, Wiley, Chichester, 1998.

Robens, E., U. Müller, and K.K. Unger, "Preliminary Experiments on Phase Transition of Adsorbed Gases on Porous Glass," *Thermochimica Acta*, **103**, 123–128 (1986).

Robens, E., B. Benzler, H. Reichert, and K.K. Unger, "Gravimetric, Volumetric and Calorimetric Studies of the Surface Structure of Portland Cement," *Journal of Thermal Analysis and Calorimetry*, in the print.

Rouquerol, F., J. Rouquerol, and K. Sing, *Adsorption by Powders and Porous Solids*, Academic Press, San Diego, 1999.

van der Wel, G.K., "Moisture in Organic Coatings—A Review," *Progress in Organic Coatings*, **37**(1/2), 1–14 (1999).