*Journal of Thermal Analysis and Calorimetry, Vol. 86 (2006) 1, 43–45*

# EVALUATION OF THE APPLICABILITY OF JÄNTTI'S METHOD TO VOLUMETRIC SORPTION MEASUREMENTS

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

[1]Faculty of Applied Physics, Technische Universiteit Eindhoven, P.O. Box 513, 5600 MB Eindhoven, The Netherlands
[2]Institut für Anorganische Chemie und Analytische Chemie der Johannes Gutenberg-Universität, Duesbergweg 10-14
55099 Mainz, Germany

Jäntti published in 1970 a method to obtain values of the sorption parameters at an early stage of gravimetric sorption measurements. In the present paper we apply that method to volumetric sorption measurements to discuss its applicability. A method is presented to cope with inaccuracies when using Jäntti's method. This will be of special importance for volumetric measurements where accuracy plays a major part. In the paper a second order regression method is used. We use a computer simulation as well as experimental data on desorption of nitrogen from a silica aerogel at 77 K.

***Keywords:*** *adsorption, fast measurement, kinetics, sorption, volumetry*

## Introduction

According to Langmuir's theory [1, 2] the equilibrium of a gas with a solid surface at constant temperature and pressure is based on a dynamic process: gas molecules are adsorbed at the surface and simultaneously adsorbed molecules leave the surface. Sorption isotherms are usually measured by stepwise variations of the pressure of the gas. In this way a series of sorption curves is measured. The asymptotic gas pressure after each pressure step is used to calculate the gas volume adsorbed; these data are then plotted *vs.* gas pressure to obtain the sorption isotherm. Such measurements can be very time consuming [3, 4]. In 1970 Jäntti published a method to get results quickly for sorption equilibrium data measured by gravimetric methods [5. 6]. He was able to determine the parameters of the model used to describe the sorption kinetics very soon after the dosing step.

We studied the possible applications in a wider scope, applying Jäntti's method to different sorption models used for the explanation of measured data [7–9]. Besides we discussed the possibility of application of Jäntti's method to volumetric measurements [10]. In the present paper we will discuss such applications with a computer simulation and with an application to experimental volumetric desorption measurements of nitrogen on silica aerogel at 77 K [11].

### *Evaluation of Jäntti's method*

In the gravimetric method the adsorbed or desorbed mass is measured after each pressure-step, as a function of time, with a microbalance, which determines the accuracy of the measurements. In the volumetric method the change in the sorbed amount is calculated from the variation of the gas pressure as a function of time after each pressure-step. The accuracy of such measurements is therefore determined by the accuracy of the manometer.

In volumetric desorption measurements the gas pressure is lowered stepwise. Before each step, one has to wait until equilibrium is reached between the gas and the adsorbate. The step causing desorption consists of the fast removal of a part of the gas in a very short time implying a pressure drop. When the vessel is closed again after this removal, an approach towards a new equilibrium between gas and adsorbate will continuously take place. During this period the gas pressure can be measured as a function of time. The equilibrium value of such a dynamic isotherm delivers one point in the resulting final isotherm. This isotherm shows then the mass desorbed at equilibrium as a function of the pressure of the gas.

A disadvantage in this procedure is that many dynamic isotherms have to be measured to get one resulting isotherm, and that for each dynamic isotherm a long time interval is necessary to reach equilibrium. This is an incentive for the evaluation of the application of Jäntti's procedure.

When discussing Jäntti's method we shall start from the following time dependency of the pressure:

$$p_{ex}(t)=A+B(1-e^{-Xt}) \qquad (1)$$

For the Jäntti procedure we define the quantities $J$ and $J^*$ as

---

[*] Author for correspondence: c.h.massen@tue.nl

*1388–6150/$20.00*

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

$$J_{ex} = \frac{p_{ex2}^2 - p_{ex1}p_{ex3}}{2p_{ex2} - p_{ex1} - p_{ex3}} \text{ with } t_2-t_1=t_3-t_2 \qquad (2)$$

$$J_{ex}^* = p_{ex} - \frac{(p'_{ex})^2}{p''_{ex}} \qquad (3)$$

when Eq. (1) is satisfied we get

$$J_{ex}=A+B \qquad (4)$$

$$J_{ex}^* = A + B \qquad (5)$$

We used as an experimental example a dynamic isotherm from earlier volumetric measurements of Reichenauer *et al*. [11] concerning the desorption of nitrogen on silica aerogel at 77 K. In Fig. 1 this isotherm is shown. We see that the curve has a stepwise character due to discrete readings of the manometer. This results in very large errors for the value of $J_{ex}$. The situation is even worse than shown in Fig. 1 because one-third of the $J_{ex}$ values lie outside the limits of this figure. This stimulated us to investigate whether smoothing of the $p_{ex}$ curve could lead to better results.

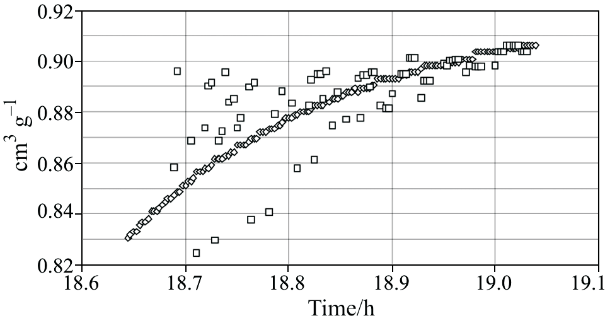

**Fig. 1** Measured desorption curve ◇ – $p_{ex}$ with calculated values of □ – $J$ as a function of time; $t_2$–$t_1$=0.02

### *Second order polynomial smoothing, computer simulation*

One possibility of dealing with the problems caused by the discontinuities in $p_{ex}$ is to smoothen this curve of $p_{ex}$ [11]. For simplicity we have chosen second order polynomial regression. As an example of sorption measured volumetrically we started with using the function given by the simple exponential relation of Eq. (1):

$$p_{ex}=3-2(1-e^{-2t}) \qquad (6)$$

As regression curve we chose:

$$p_r=a+bt+ct^2 \qquad (7)$$

To evaluate $a$, $b$ and $c$ we chose $t_1$=0.1, $t_2$=0.2 and $t_3$=0.3 and at these values of $t$ we took the values of $p_r$ to be equal to those of $p_{ex}$. This resulted in three equations with the solution: $a$=2.9881, $b$=–3.7753, $c$=2.6902. The curves of $p$ and of $p_{ex}$ are plotted in Fig. 2. In this figure the curve

$$J_r^* = a - \frac{b^2}{2c} - bt - ct^2 = 2.5168 + 3.775246t - 2.69015t^2 \qquad (8)$$

is also plotted. We see that the parabola of the regression gives the regular value of $A + B = J_{ex}^* = 1.0$ in the middle of the time interval where the regression values were equalised to the experimental values, so at $t$=0.2.

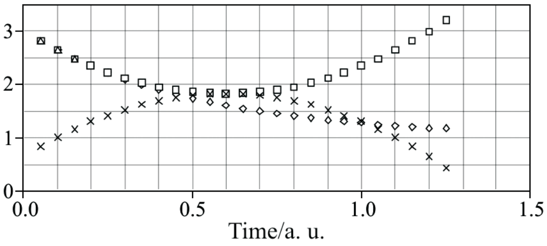

**Fig. 2** Second order regression of an idealised experimental adsorption curve as a function of time. ◇ – $p_{ex}$, □ – $p_r$, △ – $p_{ex}$=$p_r$ and ××× – $J_r$

### *Second order polynomial smoothing, practical example*

We return to Fig. 1, the curve here represents real measurements [11]. To get the values of $a$, $b$ and $c$ of the regression curve we used a standard second order regression procedure. It proved to be necessary to use a substantial number of measured points for the regression. In Fig. 3 we see two combinations of $p_r$ and $J_r^*$ as a function of $t$. These combinations differ as they belong to different time intervals. We recognise in each combination the two parabolas as in Fig. 2. Likewise, in order to get the final value of $A$+$B$, we shall use the value of $J_r^*$ at the central value of $t$. For the first combination we use $t$=18.728 and we get:

$$A+B=0.9209 \qquad (9)$$

For the second interval of time we use $t$=18.934 and we get:

$$A+B=0.921 \qquad (10)$$

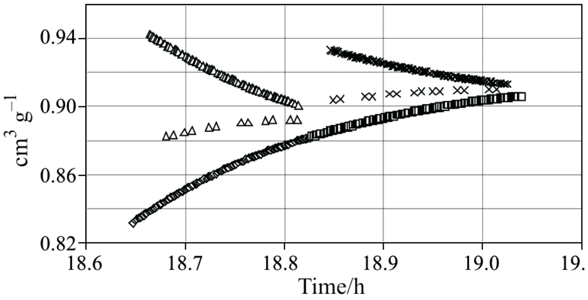

**Fig. 3** Regression curve belonging to the measured curve in Fig. 1; ◆,□ – $p_r$, △,× – $J_{pr}$, $t_2$–$t_1$=0.012

To get the value of $A$ we use the value of $t$ at the time of the step in the pressure of the gas, so at $t$=18.646 it leads to $A$=0.8315 and so to $B$=0.0897.

*Dependency on the regression chosen*

The importance of the fitting of these two values of $A$+$B$ should not be overestimated, as there remains another serious question to be solved i.e., 'Is the resulting value of $A$+$B$ independent of the way the regression has been carried out?'

To deal with this question we tried another regression equation:

$$p_r=a^*+b^*(1/t)+c^*(1/t)^2 \tag{11}$$

The resulting regression curve is shown in Fig. 4 together with the regression curve from Fig. 3 and it results in:

$$A+B=0.9252 \tag{12}$$

The discrepancy between the two results for the value of $A$+$B$ gives us an impression of the uncertainty we can ascribe to the choice of the regression curve.

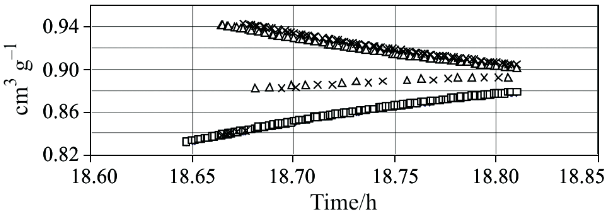

**Fig. 4** Comparison of two different regression treatments; ◇,□ – $p_r$, △,× – $J_{pr}$, $t_2$–$t_1$=0.012

## Conclusions

When a direct application of Jäntti's method results in large inaccuracies, it can be helpful to use smoothing of the measured adsorption curve. This implies that one has to choose time intervals for constructing regression curves of the measured data. In this paper second order regression curves were used. Using Eq. (8) for the values of $J^*(t)$ in each of the time intervals lead with Eq. (8) to acceptable values of $J_r^*(t)$ for the centres of the intervals. The width of the intervals should be a matter of trying out. The importance of this choice is comparable to that of the choice of the value of $t_2$–$t_1$, necessary when using Eq. (2) straightforwardly.

Though here applied to volumetric measurements, the regression method could be also applied to gravimetric measurements.

The advantage of the fact that some results of the calculations are available during the measurements and even soon after the beginning, is a speciality of Jäntti's method, this advantage is not reduced by the use of a regression method.

## Acknowledgements

The measured data were kindly put to our disposal by Dr. Gudrun Reichenauer. We appreciate her help and earnest discussions.

## References

1 J. Langmuir, J. Am. Chem. Soc., 38 (1916) 2221.
2 J. Langmuir, J. Am. Chem. Soc., 40 (1918) 1361.
3 J. Ośik, Adsorption, PWN, Warszawa 1982.
4 Z. Sedlácek, Kinetics of adsorption I. Collection Czechoslov. Chem. Commun., 34 (1969) 3985.
5 O. Jäntti, J. Junttila and E. Yrjänheikki, Suomen Kemistilehti, A 43 (1970) 214.
6 O. Jäntti, J. Junttila and E. Yrjänheikki, in Progress in Vacuum Microbalance Techniques, T. Gast and E. Robens, Eds, Heyden, London 1972, pp. 345–353.
7 J. A. Poulis, C. H. Massen, E. Robens and G. Reichenauer, in Characterization of Porous Solids VI., B.M. F. Rodríguez-Reinoso, J. Rouquerol and K. Unger, Eds, Elsevier, Amsterdam 2002.
8 J. A. Poulis, G. Reichenauer, C. H. Massen and E. Robens, Z. Phys. Chem., 216 (2002) 1123.
9 J. A. Poulis, C. H. Massen, E. Robens and G. Reichenauer, Z. Phys. Chem., 218 (2004) 245.
10 J. A. Poulis, E. Robens, C. H. Massen and G. Reichenauer, J. Therm. Anal. Cal., 76 (2004) 579.
11 G. Reichenauer and G. W. Scherer, J. Non-Cryst. Solids, 285 (2001) 167.

DOI: 10.1007/s10973-006-7592-4