APPLICATION OF JÄNTTI'S METHOD TO VOLUMETRIC ADSORPTION MEASUREMENTS

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Abstract

Jäntti introduced a method to calculate the adsorption equilibrium by measuring the actual adsorbed amount three times after a change to the gas pressure. By this method the experimental time for adsorption measurement can be considerably shortened. The procedure was developed for use in adsorption measurements where the adsorbed masses are directly measured with a balance. In the present paper we will demonstrate that the method is particularly useful in volumetric (manometric) measurements.

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

Introduction

In 1970 Jäntti [1] introduced a method to shorten the time of the gravimetric measurement 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 [2, 3] we discussed more complicated adsorption mechanisms, which involved the introduction of more parameters [4]. 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.

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

If the time interval $\Delta t \rightarrow 0$ we can write J as J^* [5]:

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

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Equations (1) and (2) are particularly useful for small values of t as they deliver knowledge of the values of the sorption parameters in an early stage of the experiments. Such reduction of experiment time is especially important in the case of volumetric measurements, because they require small steps in the pressure and many time-consuming measurements, in order to avoid problems with the pressure–dependency of the parameters.

Volumetric/manometric method

The procedures for the application of the Jäntti method are different for the two kinds of measurements. For comparison we chose two examples of such measurements:

- In the gravimetric measurements, the gas pressure is varied stepwise from zero to a constant value p_c (Fig. 1).
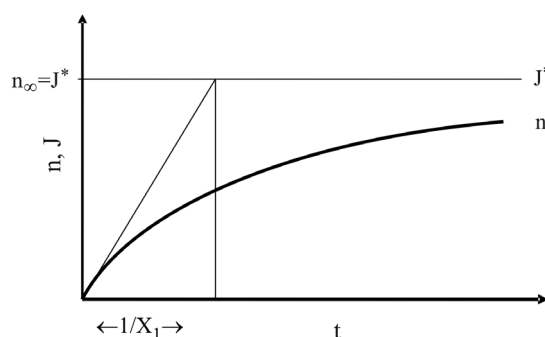

Fig. 1 Gravimetric measurement of the adsorbed amount n as a function of time t after a sudden admission of sorptive gas up to a constant pressure

- We shall consider a very simple execution of volumetric measurements. In these the gas pressure is varied also stepwise from zero to p_s but the value after each step is not kept constant; this is because after each step the vessel is closed immediately, resulting in the total number of gas molecules in the gaseous and adsorbed states remaining constant [6, 7] (Fig. 2).

The symbols used below are the same as those used in former papers, which all dealt with the gravimetric method [4, 5], namely:

n – number of adsorbed molecules,

n_m – total number of sites at the surface which are available for adsorption,

A – area of the surface relevant for adsorption,

X – number of gas molecules hitting a single site per unit time, occupied or not,

X_1 – refers to the possibility that an adsorbed molecule returns to the gaseous state, per unit of time,

X_c – value of X before the pressure step, so during the period of constant pressure p_c in gravimetric measurements,

X_s – value of X immediately after the pressure step in volumetric measurements.
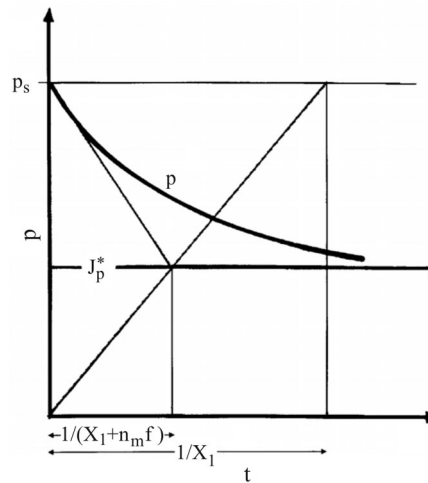
Fig. 2 Volumetric (manometric) measurement of the pressure p as a function of time t after a sudden increase of pressure of sorptive gas to p_s in the sample vessel and closure of the connecting valve. The gas pressure decreases as a result of adsorption. In this example the value of p_c has been chosen to be zero

We introduce the following quantities:

$$f = kTg/V \tag{3}$$

where V is the volume, T is the temperature and k is Boltzmann's constant; g is given by:

$$g = \frac{X}{p} = \frac{A}{4n_m}\sqrt{\frac{3}{mkT}} \tag{4}$$

where m is the mass of a molecule.

We shall restrict discussions to the adsorption of a single layer and use the same molecular model as Jäntti did.

The Eqs relevant for the gravimetric method ($p=p_c$) are:

$$dn/dt = X_c n_m - X_1 n \quad \text{with} \quad n_{t=0} = 0 \tag{5}$$

The solution of which reads:

$$n = (gp_c n_m/X_1(1-\exp(-X_1 t)) \tag{6}$$

J^* has the same dimension as n and is thus dimensionless. With Eq. (2) we get:

$$J^* = gp_c n_m/X_1 \tag{7}$$

For the volumetric method we use:

$$X = X_s - fn \tag{8}$$

and

$$dn/dt = Xn_m - X_1 n \quad \text{with} \quad n_{t=0} = 0 \tag{9}$$

From Eqs (3), (4) and (5) it follows:

$$\mathrm{d}p/\mathrm{d}t = p_s X_1 - (n_m f + X_1)p \quad \text{where } p_{t=0} = p_s \tag{10}$$

In case $p_c = 0$ the solution of Eq. (10) reads:

$$p = p_s(n_m f + X_1)^{-1}[X_1 + n_m f \exp(-(n_m f + X_1)t)] \tag{11}$$

For the volumetric method we (in analogy to Eq. (2)) define J_p^*:

$$J_p^* = p - (\mathrm{d}p/\mathrm{d}t)^2/(\mathrm{d}^2 p/\mathrm{d}t^2) \tag{12}$$

where J_p^* has the same dimension as p. We get

$$J_p^* = p_s X_1/(n_m f + X_1) \tag{13}$$

Because of the simple molecular model used, both the quantities J^* and J_p^* prove to be time independent as is shown by Eqs (7) and (13).

Parameter evaluation

For gravimetric measurements Fig. 1 shows both n and J^* as a function of t, according to Eqs (6) and (7). By drawing the tangent to the 'n vs. t' curve at $t=0$ we get the value of $gp_c n_m$ which, together with the value of n_∞ and Eq. (4) leads to the value of A.

In Fig. 2 both p and J_p^* are shown as a function of time for the volumetric measurements according to Eqs (11) and (13). By drawing the tangent at $t=0$ to the 'p vs. t' curve and using $J_p^* = n_\infty$ we can, using Eq. (11), deduce the values of X_1 and of $n_m f$, at a very early stage of the measurements. Combining the latter value with Eqs (3) and (4) leads to the value of A. This evaluation is elucidated in Fig. 2.

Conclusions

Jäntti's method when applied to volumetric measurements is equally useful as for gravimetric measurements. The little extra effort involved does not exceed the procedure shown in Fig. 2.

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