

# On a simple model for the rate of surface coverage due to gas adsorption onto active porous samples exposed to rapidly varying gas phase concentration

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We present and discuss a model that describes the rate of adsorption coverage in active porous samples under continuous variation of the gas phase concentration. It is basically a Langmuir adsorption model, modified to account for the nanostructured porous nature of the sample surface and the possible presence of dissociative molecular adsorption phenomena. A non-linear differential rate equation is obtained and when solved numerically exhibits steady state oscillations.

**Keywords:** Gas adsorption, surface physics.

Se presenta y discute un modelo para la velocidad de adsorción en muestras porosas activas sometidas a la acción de una fase gaseosa cuya concentración varía continuamente. En lo fundamental se trata de un modelo tipo Langmuir modificado para incluir estructuras nanoporosas en la superficie de la muestra, donde se admite igualmente la posibilidad de que ocurran fenómenos de adsorción molecular disociativa. La ecuación diferencial no lineal resultante que se resuelve numéricamente indica la presencia de oscilaciones para tiempos suficientemente largos.

**Descriptores:** Adsorción de gases, física de superficies.

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The wide acceptance of photoacoustic (PA) and photothermal (PT) methods to investigate materials properties can be appreciated from the published literature in the past few years (Refs. 1 and 2 and references therein for a review). They have in fact become rather versatile experimental tools for research in materials science [1, 3–6, 8]. However, little attention has been given to the study of transient phenomena with PA and PT. In this paper, we report on a effective-sample model description for the kinetics of the gas sorption on active porous materials.

We have worked with Pd:Ag nano-clustered powders, with average colloidal cluster radii around 10 nm, highly compressed ( $10^3 \text{ kg/cm}^2$ ) to form 270  $\mu\text{m}$  thick, 10 mm diameter wafers. The details of the technique used in the preparation of these colloidal powders and the PA experimental setup is described elsewhere [7, 9]. We have performed sequential dehydration experiments on our samples, at a fixed modulation frequency of 10 Hz, following its kinetics by recording the time evolution of both the PA signal and the correlated relative humidity (RH) variations within the humidity reservoir.

In Fig. 1a we show the time evolution of the PA signal amplitude for a freshly produced sample during its first ( $n=1$ ) dehydration cycling, starting immediately after replacing water by dry silica-gel in the humidity reservoir. The corresponding data for RH time evolution is given in Fig. 1b. In figures 1c and 1d we show the corresponding results for the fourth ( $n=4$ ) dehydration cycling with the same sample.

The solid curves in Figs. 1b and 1d, represent the RH data least squares fitting to an exponential decay. The values for the decay time  $\tau_r$ , in these fittings, were found to be 1.9 and 4.0 min, respectively, with a fitting error of 4%. We notice from these figures that in a matter of a few minutes while the RH decreases sharply from the wet into the dry situation, the PA signal accomplishes simultaneously a dramatic jump. Such jump is accompanied by oscillations, whose period increases with repeated dehydration cycling. These oscillations are quite possibly traceable, at least in part, to kinetic effects in water vapor reactive sorption due to the catalytic action of the Pd:Ag surface towards water molecule dissociation. An adequate modification of the standard PA model is necessary to deal with the case of damp porous samples. We did that and got for the pressure fluctuation in the PA cell the expression

$$\delta P = \frac{P_{amb}\beta' I_o (\alpha_g)^{1/2}}{T_o \ell_g \omega (k\rho c)^{1/2}} e^{j(\omega t - \pi/4)} \quad (1)$$

in which  $P_{amb}$ ,  $T_o$  and  $\alpha_g$  are the ambient pressure, temperature and the thermal diffusivity of the gas in the PA cell,  $\beta'$  is the sample surface optical absorption coefficient,  $I_o$  is the light intensity of the incident beam, modulated at frequency  $\omega$ , while the thermal conductivity and the thermal capacity per unit volume of the effective-sample is given by  $k$  and  $\rho c$  respectively. Here  $P_{amb} = P_o + P_v$ , where  $P_o$  is the dry air atmospheric pressure and  $P_v$  is the water vapor pressure at temperature  $T_o$ . In terms of the relative humidity,  $P_{amb}$  can then be written as  $P_{amb} = P_o + (P_s/P_o)RH(t)$ ,

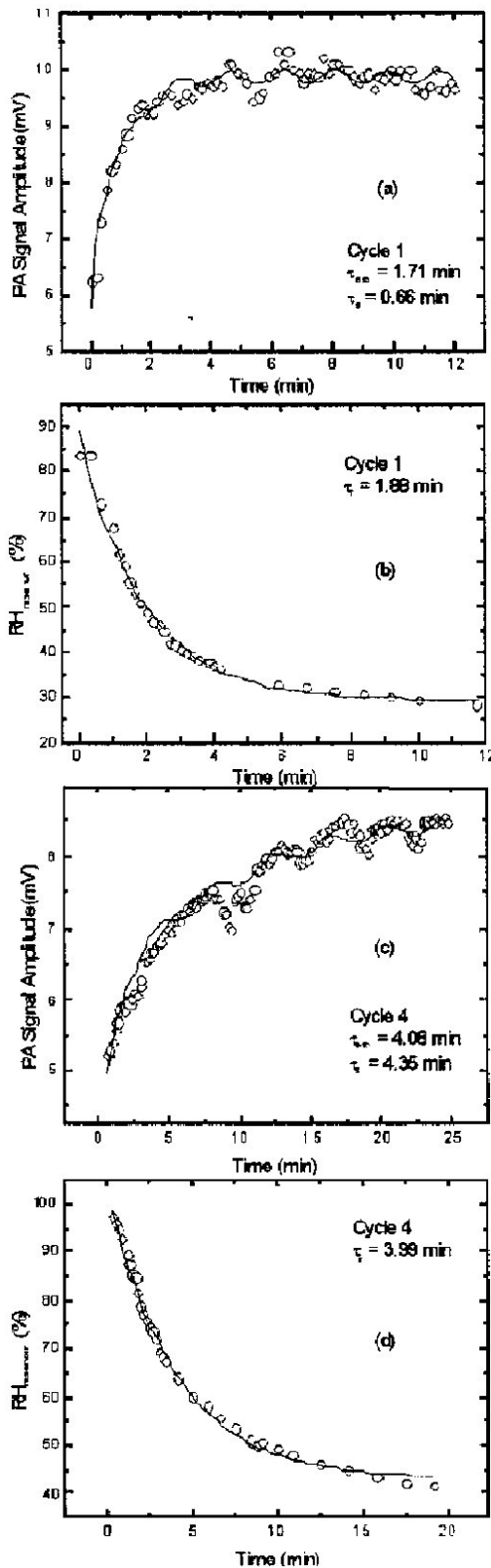


FIGURE 1. PA (a and c), RH (b and d) data at 22 °C for the first (a and b) and fourth (c and d) wet-dry cycling. Solid lines are least-squares fits to the data. In both cases (a, c) sinusoidal-like oscillations prevail after a time lapse  $t_o$  of about 16 min, corresponding quite approximately to the levelling off in the exponential RH decay and to the end of the transient evolution in a wet-into-dry transition.

where  $P_s$  is the saturation pressure for water vapor and  $RH(t)$  is the time-dependent relative humidity exponential decay function, with characteristic decay time  $\tau_r$ , obtained from a least squares fit to the measured RH data. To calculate in the effective-sample approach the thermal conductivity  $k$  and volumetric heat capacity  $\rho c$  of our damp porous sample we assume the heat transfer process in it to be a combination of heat conduction in the solid portion, molecular heat conduction in dry pores and heat conduction in damp pores. Let  $\varepsilon$  be the sample porosity and  $x(t)$  the moisture content in the sample. Then  $k$  and  $\rho c$  are given by

$$k = (1 - \varepsilon)k_s + k_v x(t) + (\varepsilon - x(t))k_a$$

$$\approx (1 - \varepsilon)k_s + k_v x(t)$$

and

$$\rho c = (1 - \varepsilon)(\rho c)_s + (\rho c)_v x(t) + (\varepsilon - x(t))(\rho c)_a$$

$$\approx (1 - \varepsilon)(\rho c)_s + (\rho c)_v x(t)$$

where  $k_i$ , and  $(\rho c)_i$  are the thermal conductivity and volumetric heat capacity of the solid portion ( $i = s$ ) of the sample (in our case, Pd-Ag compacts), of the water vapor ( $i = v$ ) and dry air ( $i = a$ ), respectively. As to  $x(t)$ , we took its time-dependence to be adequately described by BET [10] isothermal curve, that is

$$x(t) = \frac{Cu(t)}{(1 - u(t))[1 + (C - 1)u(t)]}$$

in which  $C$  is a constant dependent on the net heat of desorption for water vapor and  $u(t)$  is the time-dependent relative humidity ( $RH$ ) function within the sample. We assume that  $u(t)$  as a function of time is given by

$$u(t) = (RH)_o \exp(-t/\tau_s) \quad (2)$$

where  $(RH)_o$  is the initial  $RH$  value in the dehydration cycle under consideration and  $\tau_s$  is the cycle number dependent characteristic response time for the humidity change within the sample. At this point, we recall the experimental results shown in Figs. 1a. and 1c where it is seen that the oscillations in the PA signal associated to the desorption process become more conspicuous after an rapidly increasing initial transient in the PA signal essentially levels off, what occurs for times larger compared to  $\tau_r$  and much larger compared to  $\tau_s$ . In this time scale  $u(t) \ll 1$  and the above equation for  $x(t)$  becomes

$$x(t) \approx \frac{Cu(t)}{1 + Cu(t)}.$$

As we recognize, this expression recalls the time honored Langmuir adsorption isotherm

$$\theta = v/v_m = \frac{Cu}{1 + Cu}.$$

Here  $\theta$  measures the fraction of the surface covered with adsorbed molecules, known as the surface coverage,  $v$  is the

volume of the gas adsorbed and  $v_m$  is the volume of gas which, under the same conditions, is necessary to cover the entire surface with a unimolecular layer of adsorbed gas,  $C$  is a constant dependent upon the net heat of desorption for the gas and  $u = P/P_s$  is the ratio of the observed vapor pressure to the saturation pressure. But, here  $u = u(t)$  is a function of time. As we recall that around the rear surface of the sample the RH variation is an exponential decay. We shall then assume the same to hold for the RH within the sample, *i.e.* (2), leaving  $\tau$  as an adjustable model parameter. Under such circumstances, we get

$$\frac{dx(t)}{dt} = -A[1 - x(t)]^2 \exp(-t/\tau)$$

where

$$A = \frac{C}{\tau}(RH)_o.$$

This is a non-linear equation for  $x(t)$ . We have solved it numerically using the Mathematica<sup>R</sup> non-linear differential equation numerical solver. The results were that, whatever the values of  $A$ , for a sufficiently large time,  $x(t)$  would always exhibit oscillations. Figure 2 shows a typical result of our calculations for the numerical solution of the non-linear equation for  $x(t)$ . As a consequence, in view of our model such a time behavior for  $x(t)$  directly translates into a corresponding oscillatory time behavior of the PA signal amplitude, in such kind of desorption experiments, in agreement with what we observe in the experimental curves given in Figs. 1.a and 1.c

Our model description of the gas sorption phenomena in porous surface active samples, when the gas phase is allowed rapid variation in concentration, can be summarized as

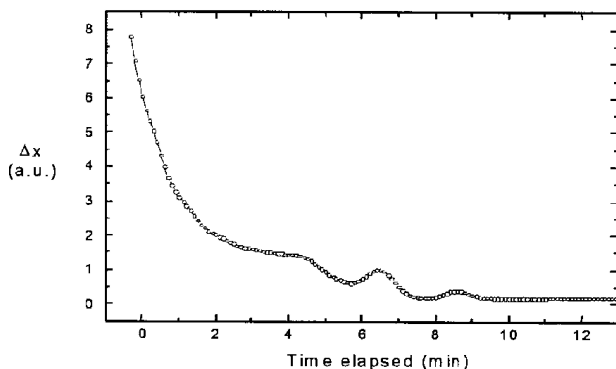


FIGURE 2. Variation  $\Delta x$  of the adsorption coverage (sample humidity content) function  $x(t)$  as a function of the elapsed time  $(t - t_o)$ , where  $t_o$  is the time lapse referred to in Fig. 1.

corresponding to a Langmuir-like desorption with time a dependent sticking probability. It gave a consistent description when we applied it, as reported here, to a situation of the kind described above, which we have recently observed when studying water vapor desorption from Pd:Ag highly compacted nano-colloidal powders using the PA time scan technique [9].

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