

# Kinetics of Multisite-Occupancy Adsorption on Heterogeneous Solid Surfaces: A Statistical Rate Theory Approach

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The theoretical approach to kinetics of adsorption on heterogeneous surfaces, developed recently by using the statistical rate theory (Rudzinski, W.; Panczyk, T. *J. Phys. Chem. B* 2000, 104, 9149) is generalized here for the case of multisite-occupancy adsorption. Theoretical kinetic isotherms are developed for the systems with quasi-Gaussian distribution of adsorption energies and when all of the segments (mers) of the adsorbing molecule are identical. The two extreme cases of surface topography, that is, patchwise and random topography, are considered. The obtained theoretical equations are used to correlate successfully experimental data for kinetics of oxygen adsorption on polycrystalline tungsten. Six experimental isotherms, measured at different pressures, can be successfully fitted by appropriate choice of only three parameters. The analysis of the estimated best-fit parameters makes drawing certain conclusions possible, concerning the energetic topography of the polycrystalline tungsten surface.

## Introduction

In many adsorption processes of a great importance for life, science, and technology, the adsorbing molecule should be considered as consisting of a number of mers (segments), each of them being adsorbed on one adsorption site. Thus, the adsorbed molecule occupies then a number of neighboring adsorption sites. When the adsorbed molecule preserves its chemical identity, we call it then the “multisite-occupancy adsorption”.

The existing literature shows how impressive progress has already been made toward applying lattice formalism to describe such adsorption on hypothetical, energetically homogeneous solid surfaces, creating a lattice of energetically equivalent adsorption sites. On the contrary, because of the complexity of the problem, much lesser progress has been made, so far, toward further generalizing of the existing approaches to describe that kind of adsorption on the energetically heterogeneous lattices of sites created by the real solid surfaces.<sup>1–5</sup>

In particular, the most challenging problem is to arrive at compact analytical solutions, which are so much preferred for both their elegance and the easy way of their application. Despite the complexity of the problem, some attempts have already been made.<sup>3</sup>

However, the above-mentioned progress concerns, almost exclusively, the description of adsorption equilibria. On the contrary, very little has been done so far toward developing a simple theoretical description of the kinetics of multisite-occupancy adsorption on energetically heterogeneous solid surfaces.<sup>6</sup> Here, we present some attempts to develop such compact simple expressions by applying for that purpose the statistical rate theory (SRT), developed by Ward and co-workers to describe the rate of interfacial transport in various systems.<sup>7–25</sup>

In the series of our recent works, we have applied that approach to describe successfully both the kinetics of isothermal adsorption/desorption on/from energetically heterogeneous surfaces<sup>26–30</sup> and the kinetics of thermodesorption.<sup>31–36</sup> Here, we are going to generalize some of the expressions developed for isothermal adsorption/desorption kinetics for the case when the adsorbed molecule occupies more than one site. We will do it for the adsorption systems characterized by a quasi-Gaussian dispersion of adsorption energies and when the adsorbing molecule consists of identical segments (mers).

## Theory

In the systems in which the interactions between the adsorbed molecules cannot be ignored or when one adsorbed molecule occupies more than one site, another important physical factor comes into play. This is the way in which adsorption sites characterized by different adsorption energies are distributed on a heterogeneous solid surface. In other words, this is the topography of a heterogeneous solid surface. So far, two extreme models of surface topography have, most commonly, been considered in theoretical works on adsorption.

The first one was the “random” model, introduced in the literature by Hill.<sup>37</sup> It assumes that adsorption sites characterized by different adsorption energies are distributed on a solid surface completely at random. The other extreme model of surface topography was the “patchwise” model, introduced to literature by Ross and Olivier.<sup>38</sup> It assumes that adsorption sites having the same adsorption energy are grouped on a heterogeneous surface into “patches”. These patches are large enough so that the states of an adsorption system in which two interacting molecules are adsorbed on different patches, could be neglected. Thus, the adsorption system can be considered as a collection of independent subsystems, being only in a material and thermal contact.

Similarly to the case of adsorption equilibria, considered by Rudzinski and Everett,<sup>3</sup> the starting point of our consideration

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will be Nitta's approach to the multisite-occupancy adsorption.<sup>1</sup> Here, we repeat only its principles for reader's convenience.

When  $N_t$  molecules are adsorbed on a heterogeneous surface, the system partition function  $Q(N_t, M, T)$ , may be written as<sup>1</sup>

$$Q = q_s^{N_t} \sum_{\{N_{ij}\}} g(N_t, M, \{N_{ij}\}) \exp \left\{ \sum_i \sum_j N_{ij} \frac{\tilde{\epsilon}_{ij}}{kT} \right\} \quad (1)$$

where  $\epsilon_{ij}$  is the energy of adsorption of  $j$ th group (mer) on the  $i$ th kind of sites.  $N_{ij}$  is the number of adsorption pairs of sites  $i$  and a group  $j$ ;  $\{N_{ij}\}$  is a distribution of these adsorption pairs, the subscript  $i0$  being used for the empty site;  $g(N_t, M, \{N_{ij}\})$  is a combinatorial factor expressing the number of the distinguishable ways of distributing the  $N_t$  molecules on  $M$  sites under the condition of a special distribution  $\{N_{ij}\}$ ;  $q_s$  is the product of internal and vibrational partition functions of an adsorbed molecule. As emphasized by Nitta, it is difficult to find a rigorous expression for  $g(N_t, M, \{N_{ij}\})$  by taking into consideration the mutual correlations between neighboring sites and neighboring groups in a molecule. A simple expression is obtained by assuming that all pairs of site-mer  $\{ij\}$  are independent, under the constraints imposed by the distribution  $\{N_{ij}\}$ .

To evaluate  $\theta_t$ , three kinds of surface coverages,  $\theta_t$ ,  $\{\theta_{ij}\}$  and  $\{\theta_{ij}\}$  are to be defined:  $\theta_t = nN_t/M$  is the fraction of sites occupied ( $n$  is the total number of sites occupied by one adsorbed molecule);  $\theta_{ij} = n_j N_t/M$  ( $j = 1, \dots, s$ ) is the fraction of sites occupied by the segment of type  $j$  ( $n_j$  is the number of sites occupied by the segments of type  $j$ );  $\theta_{ij} = N_{ij}/M_i$  ( $i = 1, \dots, W$ ;  $j = 1, \dots, s$ ) is the fraction of sites of type  $i$  occupied by the segments of type  $j$ .

The problem of evaluating  $\theta_t$  is not trivial, and Nitta<sup>1</sup> proposed a complicated numerical procedure, in which only a discrete distribution of adsorption energy can be applied. Then, Rudzinski and Everett<sup>3</sup> have shown that this problem becomes much more easily tractable when all of the segments of an admolecule are of the same kind. Nitta's approach leads then to the following expression for the chemical potential,  $\mu^s$ , of the adsorbed (surface) molecules:<sup>3</sup>

$$\mu^s = -\epsilon_{ni} - kT \ln(q_s \zeta n) - (n-1)kT \ln \theta_t + nkT \ln \frac{\theta_i}{1-\theta_i} \quad (2)$$

where

$$\theta_i = \frac{N_i}{M} \quad (3)$$

$$\epsilon_{ni} = n\epsilon_{1i} \quad (4)$$

and  $\zeta$  is a constant related to the flexibility and symmetry number of a molecule. Thus, when all of the segments are identical, the Nitta's assumption that all the pairs  $\{ij\}$  are independent is true only if the  $i$ th values are independent. This means a lack of spatial correlations between  $i$ th values on various sites, which is true only in the case of random topography. This means that Nitta's expression (eq 2) is valid for the surfaces having random topography.

When the surface becomes homogeneous, that is,  $\theta_i, \theta_t \rightarrow \theta$ , eq 2 reduces to the well-known Flory's isotherm for the multisite-occupancy adsorption on homogeneous solid surfaces,

$$\mu^s = -\epsilon_n - kT \ln(q_s \zeta n) + kT \ln \frac{\theta}{(1-\theta)^n} \quad (5)$$

In the case of patchwise topography,  $\epsilon_n$  will contain the additional index  $i$  referring to the  $i$ th patch,  $\epsilon_{ni}$ . Thus, in the case of patchwise topography, the isotherm equation reads

$$\mu^s = -\epsilon_{ni} - kT \ln(q_s \zeta n) + kT \ln \frac{\theta_i}{(1-\theta_i)^n} \quad (6)$$

Rudzinski and Everett<sup>3</sup> have also proposed an easy method to calculate  $\theta_t$  for both patchwise and random topography. They applied for that purpose the condensation approximation (CA) method, which has appeared so successful in theoretical descriptions of one-site-occupancy adsorption on energetically heterogeneous solid surfaces.<sup>3,39</sup> The CA method can be applied when the variance of the isotherm derivative ( $\partial\theta/\partial\epsilon$ ) is smaller than the variance of the adsorption energy distribution,  $\chi(\epsilon)$ .<sup>3,40-45</sup> The numerous theoretical papers published so far suggest that this was true for the overwhelming majority of the investigated adsorption systems.<sup>3,39</sup> In the case of multisite-occupancy adsorption, our particular attention is focused here on the adsorption systems that, in the case of one-site-occupancy adsorption, are characterized by the Gaussian-like adsorption energy distribution,  $\chi(\epsilon)$ ,

$$\chi(\epsilon) = \frac{1}{c} \frac{\exp\left(\frac{\epsilon - \epsilon_0}{c}\right)}{\left[1 + \exp\left(\frac{\epsilon - \epsilon_0}{c}\right)\right]^2} \quad (7)$$

centered at  $\epsilon = \epsilon_0$ . Its variance,  $\delta$ , is given by  $c\pi/\sqrt{3}$ , so the parameter  $c$  is a measure of the degree of surface energetic heterogeneity. The variance of the corresponding derivative of the Langmuir isotherm is then given by  $kT\pi/\sqrt{3}$ . Thus, the applicability of the CA method means that for the investigated adsorption system the inequality  $c > kT$  must hold.

The CA expression for  $\theta_t$  is then given by

$$\theta_t = \int_{\epsilon_c}^{\infty} \chi(\epsilon) d\epsilon \quad (8)$$

where the  $\epsilon_c$  function is found from the condition

$$\left(\frac{\partial^2 \theta}{\partial \epsilon^2}\right)_{\epsilon=\epsilon_c} = 0 \quad (9)$$

Let us assume further that the potential of the gas-phase  $\mu^g$  is given by the ideal gas expression,

$$\frac{\mu^g}{kT} = \ln \left[ \frac{p\Lambda^3}{q_g kT} \right] \quad (10)$$

in which  $\Lambda$  is the thermal de Broglie wavelength and  $q_g$  is the internal molecular partition function of the molecules in the bulk phase. Then, the expression for  $\theta_t$  takes the form of the commonly applied Langmuir-Freundlich isotherm,

$$\theta_t = \frac{(K e^{\epsilon_0/(kT)} p)^{kT/c}}{1 + (K e^{\epsilon_0/(kT)} p)^{kT/c}} \quad (11)$$

where  $K = q_s \zeta \Lambda^3 / (q_g kT)$ .

In the case of multisite-occupancy adsorption and the particular case of identical segments considered here,  $\theta_i$  is to be considered as a function of  $\epsilon_{ni}$ , and the application of the CA method leads then to the following expressions for  $\epsilon_{nc}$ . For the random topography, we have<sup>3</sup>

$$\epsilon_{nc} = \epsilon_{nc}^{(r)} = -\mu_s - kT \ln(q_s \xi n) - (n-1)kT \ln \theta_t \quad (12a)$$

whereas for the patchwise topography, we obtain

$$\epsilon_{nc} = \epsilon_{nc}^{(p)} = -\mu_s - kT \ln(q_s \xi n) + kT \ln \left( \frac{(1 + \sqrt{n})^{n-1}}{n^{n/2}} \right) \quad (12b)$$

Then, the related expression,  $\theta_t$ , for the patchwise topography reads

$$\theta_t^{(p)}(p, T) = \frac{\left( \frac{n^{(n+2)/2}}{(\sqrt{n} + 1)^{n-1}} K e^{\epsilon_{o'}/(kT)} p \right)^{kT/c}}{1 + \left( \frac{n^{(n+2)/2}}{(\sqrt{n} + 1)^{n-1}} K e^{\epsilon_{o'}/(kT)} p \right)^{kT/c}} \quad (13a)$$

whereas for the random surface topography, we obtain

$$\theta_t^{(r)}(p, T) = \frac{(nK e^{\epsilon_{o'}/(kT)} p)^{kT/c} (\theta_t^{(r)})^{[(n-1)kT/c]}}{1 + (nK e^{\epsilon_{o'}/(kT)} p)^{kT/c} (\theta_t^{(r)})^{[(n-1)kT/c]}} \quad (13b)$$

Thus, we can see, that even in the absence of interactions between the adsorbed molecules, surface topography will affect the equilibria of multisite-occupancy adsorption on a heterogeneous solid surface.

Now, we are going to show that surface topography also affects the kinetics of multisite-occupancy adsorption/desorption on/from an energetically heterogeneous solid surface. Our considerations will be based on the statistical rate theory developed by Ward and co-workers. That approach leads to the following equation for the rate of adsorption,  $(\partial\theta/\partial t)$ :<sup>27–29</sup>

$$\frac{\partial\theta_i}{\partial t} = K'_{gs} \left[ \exp \left\{ \frac{\mu^g - \mu^s}{kT} \right\} - \exp \left\{ \frac{\mu^s - \mu^g}{kT} \right\} \right] \quad (14)$$

where  $t$  is time, and  $K'_{gs}$  is defined as the exchange rate at equilibrium, to which the system would evolve after being closed and isolated. This parameter is proportional to the frequency of collisions of adsorbing molecules with the surface. To a good approximation,  $K'_{gs}$  may be expressed as follows:<sup>16,20</sup>

$$K'_{gs} = K_{gs} p^{(e)} (1 - \theta_i^{(e)})^n \quad (15)$$

where the superscript (e) means that the quantity is related to the above-defined equilibrium state. The parameter  $K_{gs}$  is only a function of temperature. Like in our previous publications,<sup>26–36</sup> we assume that the kinetic process is not far from equilibrium at any instant of time. Such assumption enables us to accept the following approximate relations,

$$p^{(e)} \approx p \quad \text{and} \quad \theta_i^{(e)} \approx \theta_i \quad (16)$$

For multisite-occupancy adsorption and an energetically heterogeneous solid surface, we must still consider the effects of surface topography. For random topography, the chemical potential of the adsorbed phase is defined in eq 2. If we assume that gaseous phase behaves like an ideal gas, then, after inserting

the expressions for chemical potentials of adsorbed and bulk phases into the Ward's eq 14, we obtain the following equation:

$$\frac{d\theta_i}{dt} = K_{gs} K p^2 n \theta_t^{n-1} \frac{(1 - \theta_i)^{2n}}{\theta_i^n} e^{\epsilon_{ni}/(kT)} - \frac{K_{gs}}{Kn \theta_t^{n-1}} \theta_i^n e^{-\epsilon_{ni}/(kT)} \quad (17a)$$

where  $K = \zeta q_s e^{\mu_0^g/(kT)}$  and  $\mu_0^g$  is the standard chemical potential of an ideal gas.

Similar considerations carried out for the patchwise surface topography model yield the following equation for the rate of adsorption/desorption:

$$\frac{d\theta_i}{dt} = K_{gs} K p^2 n \frac{(1 - \theta_i)^{2n}}{\theta_i^n} e^{\epsilon_{ni}/(kT)} - \frac{K_{gs}}{Kn} \theta_i^n e^{-\epsilon_{ni}/(kT)} \quad (17b)$$

In the CA picture of the kinetics of adsorption on a heterogeneous surface, the change of the overall surface coverage with time  $(\partial\theta_t/\partial t)$  depends on the speed of moving the sharp “adsorption front” with time  $(d\epsilon_{nc}/dt)$  and on the population of the adsorption sites on which that sharp front is currently located. One can see it when considering the following formal relation:

$$\frac{d\theta_t}{dt} = \frac{\partial\theta_t}{\partial\epsilon_{nc}} \frac{d\epsilon_{nc}}{dt} = -\chi_c(\epsilon_{nc}) \frac{d\epsilon_{nc}}{dt} \quad (18)$$

The function  $\chi_c$  is the condensation approximation of the real energy distribution function  $\chi$  and is connected with  $\chi$  via the relation

$$\chi_c(\epsilon_{nc}) = \int_0^\infty \left( \frac{\partial\theta_i}{\partial\epsilon_{ni}} \right) \chi(\epsilon_{ni}) d\epsilon_{ni} \quad (19)$$

The function  $\chi_c(\epsilon_{nc})$  is a diffuse portrait of  $\chi(\epsilon_n)$ , which becomes an exact portrait when the variance of  $\chi(\epsilon_n)$  is much larger than the variance of the isotherm derivative. This problem has been discussed to a much detail in previous papers.<sup>43–45</sup> It appears that for typical heterogeneous surfaces replacing  $\chi_c(\epsilon_{nc})$  by  $\chi(\epsilon_n)$  leads to successful description of both the adsorption equilibria and the kinetics of the adsorption/desorption processes.<sup>3,27,39</sup> So, as in our previous papers on the kinetics of one-site-occupancy adsorption, we will assume here that  $\chi_c \approx \chi$ .

Now, let us note that  $\epsilon_{nc}$  is the value of  $\epsilon_{ni}$  on the adsorption sites of which the local coverage  $\theta_c = 1/2$  for random topography and  $(1 + \sqrt{n})^{-1}$  for patchwise topography. And now, we apply a similar procedure to that used in our previous papers on the kinetics of one-site-occupancy adsorption on heterogeneous solid surfaces. So, we define the function  $F(\epsilon_{nc}, t, T)$ :

$$F(\epsilon_{nc}, t, T) = \theta_i(\epsilon_{nc}, t, T) - \theta_c = 0 \quad (20)$$

for random and patchwise topography, respectively.

Then,

$$\frac{d\epsilon_{nc}}{dt} = - \frac{(\partial F/\partial t)_{\epsilon_{nc}}}{(\partial F/\partial \epsilon_{nc})_t} = - \left[ \frac{(\partial\theta_i/\partial t)_{\epsilon_{ni}}}{(\partial\theta_i/\partial\epsilon_{ni})_t} \right]_{\theta_i=\theta_c, \epsilon_{ni}=\epsilon_{nc}} \quad (21)$$

To represent  $(\partial\theta_i/\partial t)_{\epsilon_{nc}}$ , we use SRT eqs 17a and 17b with  $\epsilon_{ni} = \epsilon_{nc}$  and  $\theta_i = \theta_c$ . Thus, for random topography, we have

$$\left(\frac{d\theta_i}{dt}\right)_{\theta_i=\theta_c, \epsilon_{ni}=\epsilon_{nc}} = K_{gs} K p^2 n \theta_t^{n-1} \frac{1}{2^n} e^{\epsilon_{nc}/(kT)} - \frac{K_{gs}}{Kn \theta_t^{n-1}} \frac{1}{2^n} e^{-\epsilon_{nc}/(kT)} \quad (22a)$$

whereas for patchwise topography, we obtain

$$\left(\frac{d\theta_i}{dt}\right)_{\theta_i=\theta_c, \epsilon_{ni}=\epsilon_{nc}} = K_{gs} K p^2 \frac{n^{n+1}}{(1+\sqrt{n})^{2n-1}} e^{\epsilon_{nc}/(kT)} - \frac{K_{gs}}{Kn} \frac{1}{(1+\sqrt{n})} e^{-\epsilon_{nc}/(kT)} \quad (22b)$$

Now, because the adsorption/desorption runs at quasi-equilibrium, we can calculate  $\partial\theta_i/\partial\epsilon_{ni}$  from the related isotherm eqs 2 and 6. So, for the random topography model, we have

$$\left(\frac{\partial\theta_i}{\partial\epsilon_{ni}}\right)_{\theta_i=(1/2), \epsilon_{ni}=\epsilon_{nc}} = \frac{1}{4nkT} \quad (23a)$$

whereas for patchwise topography, we obtain

$$\left(\frac{\partial\theta_i}{\partial\epsilon_{ni}}\right)_{\theta_i=(1/(1+\sqrt{n})), \epsilon_{ni}=\epsilon_{nc}} = \frac{1}{kT(1+\sqrt{n})^2} \quad (23b)$$

In this way, we arrive at the expressions describing the rate of moving the adsorption front on the energy scale for both random and patchwise topographies

$$\frac{d\epsilon_{nc}}{dt} = -2^{2-n} kTK_{gs} K p^2 n^2 \theta_t^{n-1} e^{\epsilon_{nc}/(kT)} + \frac{2^{2-n} kTK_{gs}}{K \theta_t^{n-1}} e^{-\epsilon_{nc}/(kT)} \quad (\text{random}) \quad (24a)$$

$$\frac{d\epsilon_{nc}}{dt} = -kTK_{gs} K p^2 \frac{n^{n+1}}{(1+\sqrt{n})^{2n-3}} e^{\epsilon_{nc}/(kT)} + \frac{kTK_{gs}}{K} \frac{(1+\sqrt{n})}{n} e^{-\epsilon_{nc}/(kT)} \quad (\text{patchwise}) \quad (24b)$$

The preceding equations are first-order differential equations, which can be solved analytically to give the functions  $\epsilon_{nc}(t)$ :

$$\epsilon_{nc}(t) = -kT \ln[Kpn \theta_t^{n-1} \tanh\{2^{2-n} K_{gs} pnt + C\}] \quad (\text{random}) \quad (25a)$$

$$\epsilon_{nc}(t) = -kT \ln \left[ Kp \frac{n^{(n+2)/2}}{(1+\sqrt{n})^{n-1}} \tanh \left\{ \frac{n^{n/2}}{(1+\sqrt{n})^{n-2}} K_{gs} pt + C \right\} \right] \quad (\text{patchwise}) \quad (25b)$$

The integration constant  $C$  is determined from the appropriate boundary condition, imposed on the function  $\theta_i(t)$ , obtained by inserting the  $\epsilon_{nc}$  values into the CA expression

$$\theta_i(t) = \int_{\epsilon_{nc}(t)}^{\infty} \chi(\epsilon_{ni}) d\epsilon_{ni} \quad (26)$$

For both kinetic isotherms of adsorption corresponding to the two limiting cases of surface topography considered here, we accept as the boundary condition the situation when at  $t = 0$  no preadsorbed amount exists, that is,  $\theta_i(t=0) = 0$ .

Then, for the quasi-Gaussian adsorption energy distribution (eq 7),  $C = 0$ , and we arrive at the following kinetic isotherms of adsorption:

$$\theta_i(t) = \frac{[Kp e^{\epsilon_0/(kT)} n \theta_t^{n-1} \tanh\{2^{2-n} K_{gs} pnt\}]^{(kT)/c}}{1 + [Kp e^{\epsilon_0/(kT)} n \theta_t^{n-1} \tanh\{2^{2-n} K_{gs} pnt\}]^{(kT)/c}} \quad (\text{random}) \quad (27a)$$

$$\theta_i(t) = \frac{\left[ Kp e^{\epsilon_0/(kT)} \frac{n^{(n+2)/2}}{(1+\sqrt{n})^{n-1}} \tanh \left\{ \frac{n^{n/2}}{(1+\sqrt{n})^{n-2}} K_{gs} pt \right\} \right]^{(kT)/c}}{1 + \left[ Kp e^{\epsilon_0/(kT)} \frac{n^{(n+2)/2}}{(1+\sqrt{n})^{n-1}} \tanh \left\{ \frac{n^{n/2}}{(1+\sqrt{n})^{n-2}} K_{gs} pt \right\} \right]^{(kT)/c}} \quad (\text{patchwise}) \quad (27b)$$

Let us remark that in the limit  $n \rightarrow 1$ , eqs 27a,b reduce to the expression

$$\theta_i(t) = \frac{[Kp e^{\epsilon_0/(kT)} \tanh\{2K_{gs} pt\}]^{(kT)/c}}{1 + [Kp e^{\epsilon_0/(kT)} \tanh\{2K_{gs} pt\}]^{(kT)/c}} \quad (28)$$

developed in our previous paper<sup>27</sup> on the kinetics of one-site-occupancy on heterogeneous solid surfaces. Equation 28 has been used to correlate successfully the experimental kinetic isotherms of CO adsorption on Scandia, measured at various (constant) pressures and temperatures.<sup>27</sup> Next, in the limit  $t \rightarrow \infty$ , eqs 27a,b reduce to the eqs 13 developed earlier by Rudzinski and Everett<sup>3</sup> to describe the equilibria of multisite-occupancy adsorption on heterogeneous solid surfaces.

## Analysis of Experimental Data and Discussion

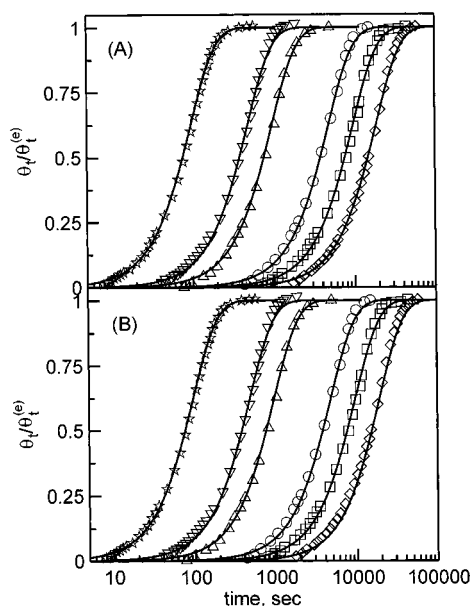
Looking for convincing verification of the developed equations for adsorption/desorption kinetics, we had the following three requirements in mind for such data selection: (1) The experimental kinetic isotherms should be measured from very low adsorption times (surface coverages), up to the coverages close to the one corresponding to equilibrium. (2) These kinetic isotherms should be measured at various pressure regimes. (3) The reported data should contain a possibly large number of experimental points. The last obvious condition was that the adsorbing molecule could be considered as consisting of identical fragments (mers).

Such sharp criteria dramatically decrease the choice of the reported experimental data. After having made a search in the existing literature, we have selected one system for our theoretical-numerical analysis. These are the data on the kinetics of O<sub>2</sub> adsorption on polycrystalline tungsten, reported by Lopez-Sancho and de Segovia at the beginning of the 1970s.<sup>46</sup> The reported set of experimental data contains kinetic isotherms measured at six different nonequilibrium pressures. Altogether, more than 100 experimental points were recorded in the reported experiment.

Their theoretical interpretation was based on the absolute rate theory (ART) approach and on an extensive use of the concept of sticking coefficient introduced to ART by Kisliuk<sup>47</sup> and Ehrlich.<sup>48</sup> Such analysis led them to interesting speculations on the existence of various adsorption states, but they did not present a quantitative (simultaneous) fit of all of their six experimental kinetic isotherms.

What cannot be questioned at all is the fact that their polycrystalline tungsten represented a heterogeneous surface.





**Figure 1.** The results of fitting by eqs 27a,b the experimental data for O<sub>2</sub> adsorption kinetics reported by Lopez-Sancho.<sup>46</sup> Panel A represents the fit by eq 27a, corresponding to random topography, whereas panel B represents the fit by eq 27b for patchwise topography. The kinetic data were recorded at constant temperature  $T = 77$  K and at six different but constant pressures: ( $\star$ )  $5 \times 10^{-7}$ ; ( $\nabla$ )  $1 \times 10^{-7}$ ; ( $\Delta$ )  $5 \times 10^{-8}$ ; ( $\circ$ )  $1 \times 10^{-8}$ ; ( $\square$ )  $5 \times 10^{-9}$ ; ( $\diamond$ )  $2.6 \times 10^{-9}$  Torr. The solid lines represent the theoretical curves calculated for the values of the best-fit parameters collected in Table 1. The assumed number of segments in the molecule is  $n = 2$ .

**TABLE 1: The Parameters Used to Fit by Eqs 27a and 27b the Experimental Data for Adsorption Kinetics Reported by Lopez-Sancho<sup>46 a</sup>**

$K \exp(\epsilon_0/kT)$ [Torr <sup>-1</sup> ]	$K_{gs}$ [Torr <sup>-1</sup> s <sup>-1</sup> ]	$kT/c$
Random Topography		
36 500	9344	0.583
Patchwise Topography		
44 059	9370	1.405

<sup>a</sup> The experiment was carried out at the temperature  $T = 77$  K, and the assumed value of the parameter  $n = 2$ .

As such, it should serve as a good material for our theoretical studies. Provided that our theoretical kinetic isotherms (eqs 27a,b) are correct, one of them should fit all of the six experimental isotherms, by appropriate choice of only three best-fit parameters;  $K \exp(\epsilon_0/kT)$ ,  $K_{gs}$ , and  $kT/c$ . This is because their experimental kinetic isotherms were reported as normalized to their equilibrium values,  $\theta_t(t)/\theta_t^e$ .

The results of our best-fit computer exercises are shown in Figure 1, and the related best-fit parameters are collected in Table 1. Looking to Figure 1, one can see a strikingly similar good fit given by both eq 27a developed for random topography and by eq 27b developed for patchwise topography. On the contrary, one can see in Table 1 strikingly different values of the best-fit parameters deduced from experiment for these two kinds of surface topography assumed in the corresponding theoretical derivations of these two kinetic isotherm equations. And here, the most striking is the value of the parameter  $kT/c = 1.4$  deduced for patchwise topography.

As we have already emphasized in the theoretical section, the condition for the application of the condensation approximation (CA) in the case of the quasi-Gaussian adsorption energy distribution is that  $kT/c < 1$ . So, because both eqs 27a,b were developed by using the CA approach, only the value  $kT/c =$

0.583 can be considered as having a physical meaning. That means that only eq 27a developed for random topography can be assumed to be applicable for this adsorption system. Equation 27b is to be considered as a good working theoretical formula, but not having a physical background, in this case.

One might eventually raise the question whether considering O<sub>2</sub> adsorption in terms of one-site occupancy could not lead to another physically acceptable interpretation. So, let us remark that the related eq 28 has, essentially, the same form as the eq 27b for patchwise topography. Thus, we would arrive at the same fit as for patchwise topography with somewhat different values of the best-fit parameters  $K$  and  $K_{gs}$ .

$$K \rightarrow K \frac{n^{(n+2)/2}}{(1 + \sqrt{n})^{n-1}} \quad \text{and} \quad K_{gs} \rightarrow K_{gs} \frac{1}{2} \frac{n^{n/2}}{(1 + \sqrt{n})^{n-2}} \quad (29)$$

Of course, the really existing surfaces are never perfectly patchwise or lacking any degree of surface organization, that is, random. While considering the two extreme surface topographies, we can only say that the investigated surface is a random-like rather than a patchwise.

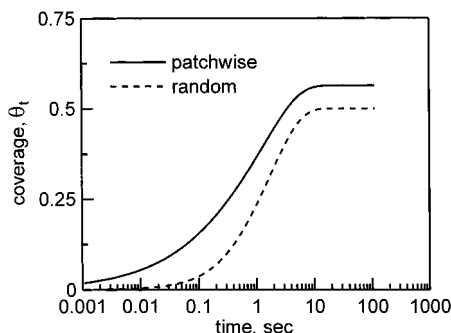
The really existing surfaces are partially correlated, that is, possess a certain degree of surface organization, as can be seen by using the STM or AFM microscopies. This is also demonstrated by the numerous computer simulations of the formation of the real solid surfaces. There has been used a variety of methods of which the description would deserve a review article. Very recently Rudzinski et al.<sup>49,50</sup> have published an analytical proof for that based on considering the deviations in the behavior of the real adsorption systems from the one predicted by the fractal approach.

While considering our eqs 27a,b, we can see that the essential difference between the patchwise and the random topography lies in the factor  $\theta_t^{(n-1)}$  appearing in the equations developed for random topography. So, while considering adsorption equilibria, Rudzinski and Everett<sup>3</sup> proposed that in the case of partially correlated surfaces one might still use eq 27a, except that the factor  $\theta_t^{(n-1)}$  should be replaced by  $\theta_t^{(n-1)\tau}$ , where  $\tau$  is a parameter characterizing the degree (lack) of surface organization.

In the case of random topography,  $\tau = 1$ , whereas when  $\tau = 0$ , equations reduce essentially to those developed for patchwise topography. In some adsorption systems, the parameter  $\tau$  can be estimated from experimental data. This was demonstrated by Rudzinski and Everett<sup>3</sup> by analyzing isotherms of adsorption of the first three  $n$ -alkanes on an activated carbon. For that particular case of multisite-occupancy adsorption, the estimated parameter was  $\tau = 0.55$ .

This parameter cannot be determined here by us having at disposal only one isotherm for two-site-occupancy adsorption. However, it is reasonable to introduce that correlation parameter also to our kinetic isotherm eqs 27a,b. The equally good fit of the experimental data presented in Figure 1 suggests that while assuming  $0 < \tau < 1$  we would arrive every time at a good fit of experimental data with different sets of the three parameters  $K \exp(\epsilon_0/kT)$ ,  $K_{gs}$ , and  $kT/c$ . Decreasing the correlation parameter would yield still higher and higher values of the parameter  $kT/c$ . Of course, only the values  $kT/c < 1$  would have a physical meaning, together with the related (assumed) values of the correlation parameter  $\tau$ . In Figure 2, we show how surface topography affects the behavior of kinetic adsorption isotherms.

We finish our discussion in this section by emphasizing the advantages of using the SRT approach to describe the kinetics of adsorption. Let us remark that of all of the three parameters,



**Figure 2.** The function  $\theta_t(t)$  calculated from (—) eq 27a for patchwise surface topography and (---) eq 27b for random topography. The calculations were done for  $n = 2$  by accepting  $Kp \exp(\epsilon_0/(kT)) = 1$  and  $K_{gs}p = 1 \text{ s}^{-1}$ .

$K \exp(\epsilon_0/(kT))$ ,  $kT/c$ ,  $K_{gs}$ , the first two can be determined from the analysis of equilibrium adsorption isotherms. Application of the classical ART approach introduces more best-fit parameters and leads to some inconsistencies in the theoretical interpretation of the determined best-fit parameters. We have shown it in our previous paper on the much simpler case of one-site-occupancy adsorption on heterogeneous solid surfaces.<sup>29</sup>

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