

Kinetics of Isothermal Gas Adsorption on Heterogeneous Solid Surfaces: Equations Based on Generalization of the Statistical Rate Theory of Interfacial Transport

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Two generalizations of the statistical rate theory (SRT) approach have been developed for the kinetics of adsorption/desorption on/from heterogeneous surfaces and then compared to each other. The first of them is an improved version of the description based on the condensation approximation (CA) used by us. The other one is an exact generalization for the Langmuir model of adsorption. The latter generalization does not lead to simple analytical expressions for the rate of adsorption/desorption as the CA approach does for typical adsorption energy distributions. The comparison of these two approaches suggests, however, that at small and very high surface coverages the CA approach may not be sufficiently accurate. Very intriguing results are obtained when the developed SRT kinetic equations are applied to describe the kinetics of sorption in carbon molecular sieves. It appears that the fit of experimental data is then equally good as that obtained by assuming that the rate of sorption is controlled by surface diffusion in pores. Also, it is shown that the square-root dependence on time of adsorption at small initial coverages cannot be treated as a definite proof for that sorption proceeds via surface diffusion, as is commonly assumed.

Introduction

The overwhelming majority of the papers treating on gas adsorption on heterogeneous solid surfaces have concerned the properties of these systems at equilibrium.^{1,2} Meanwhile the systems which we have to deal with in the real world are not in equilibrium. So, their properties at nonequilibrium, and their evolution with time, seem to be of great importance. Experimental studies of nonequilibrium properties of adsorption systems usually concern the kinetics of sorption and are more difficult to carry out than experimental studies of adsorption equilibria.³ However, this is only one of the reasons why studies of sorption kinetics are much more rarely carried out. The other well-known reason is the complexity of theoretical description of sorption kinetics in many systems of significant practical importance.⁴ The real systems are more or less porous in which, depending on the pores size, various models of adsorption are believed to be the rate-determining steps.^{4–7}

- When pore diameters are much larger than the mean free path of the adsorbed molecules, the molecular (like in bulk phase) diffusion to surface or transition from free to adsorbed state has commonly been assumed to be the rate-determining steps.

- In the opposite case, when pore diameters are much smaller than the mean free path, the sorption kinetics is commonly believed to be controlled by transport mechanism called Knudsen diffusion.

- Finally, in the case of very narrow pores, the surface diffusion is the rate-controlling step.⁸

Apparently, the kinetics of adsorption on flatlike surfaces where the direct transition from bulk to adsorbed state is the

rate-determining step should be considered most trivial. Such simple adsorption kinetics was considered first in the famous paper by Langmuir published in 1917. This paper initiated a long period of theoretical studies of kinetics in adsorption on flat-like surfaces. The simple approach by Langmuir was further elaborated by adopting the idea of the absolute rate theory (ART) to represent the kinetics of isothermal adsorption/desorption,⁹ first and then in the more and more popular studies of the kinetics of thermodesorption.¹⁰ For the simple Langmuir model of adsorption, (one-site occupancy and no interactions between the adsorbed molecules), the ART kinetic equation takes the well-known form

$$\frac{d\theta}{dt} = K_a p(1 - \theta)e^{-\epsilon_d/kT} - K_d \theta e^{-\epsilon_d/kT} \quad (1)$$

where θ is the fractional coverage of adsorption sites, ϵ_a is the activation energy for adsorption, ϵ_d is the activation energy for desorption, p is the adsorbate pressure, and K_a and K_d are constants.

At equilibrium, when $d\theta/dt = 0$, eq 1 yields the Langmuir isotherm,

$$\theta^{(e)}(p, T) = \frac{Kp^{(e)} \exp\left(\frac{\epsilon}{kT}\right)}{1 + Kp^{(e)} \exp\left(\frac{\epsilon}{kT}\right)} \quad (2)$$

where $K = K_a/K_d$, $\epsilon = (\epsilon_d - \epsilon_a)$, and the superscript (e) refers to equilibrium.

Surprisingly, although Langmuir equation appeared to be a pretty successful expression to describe adsorption equilibria, the related kinetic equation, eq 1, failed to represent the commonly observed kinetics.^{9,11} Further evidence of inapplicability of the ART approach provided more and more

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frequent studies of kinetics of thermodesorption.¹² The inapplicability of the ART approach led scientists to use some empirical equations⁹ and to further modification of ART fundamentals. Thus was introduced the idea of various “precursor states”,^{13–15} considering the interactions between the adsorbed molecules,^{16,17} the energetic heterogeneity of the actual solid surfaces,¹⁸ or both of them.^{19,20}

However, the real breakthrough came with adopting the ideas of the statistical rate theory to represent adsorption/desorption kinetics. The statistical rate theory (SRT) is based on considering the quantum-mechanical transition probability in an isolated many particle system. Assuming that the transport of molecules between phases at thermal equilibrium results primarily from single molecular events, the expression for the rate of molecular transport between two phases “1” and “2”, R_{12} , was developed by using the first-order perturbation analysis of the Schrodinger equation and the Boltzmann definition of entropy.

$$R_{12} = R_e \left[\exp\left(\frac{\mu_1 - \mu_2}{kT}\right) - \exp\left(\frac{\mu_2 - \mu_1}{kT}\right) \right] \quad (3)$$

In eq 3, μ_1 and μ_2 are the chemical potentials of the molecules in phases “1” and “2”, respectively, and R_e is the exchange rate at equilibrium. R_e is only a function of the equilibrium properties which can be calculated using statistical thermodynamics methods.

The SRT approach was first proposed in an elementary form in 1977,²¹ and in 1982, it received firmer theoretical grounds.²²

Soon it was applied to describe successfully the rates of interfacial transports of various kinds, i.e., the rate of exchange at the liquid–gas interface,^{21,23–25} hydrogen absorption by metals,²⁶ electron exchange between ionic isotopes in solution,²⁷ permeation of ionic channels in biological membranes,²⁸ and the rate of liquid evaporation.^{29–31} Very recently it has been successfully applied to describe the kinetics of ion adsorption at the oxide/electrolyte interface.³² That theoretical description made it possible to prove, for the first time, that the kinetics of ion adsorption is the source of the hysteresis frequently observed in both potentiometric and calorimetric titration experiments.

Ward and co-workers were the first to show how the SRT approach can be applied to describe the kinetics of isothermal adsorption at the gas–solid interfaces,^{33–36} and the kinetics of thermodesorption.³⁷ Next, Rudzinski and co-workers proposed a generalization of the SRT kinetic approach to describe the kinetics of isothermal adsorption/desorption on/from energetically heterogeneous solid surfaces,^{38–42} as well as kinetics of thermodesorption.^{43–46} That generalization was aimed at first obtaining simple theoretical expressions of general character and then simple analytical kinetic equations for the systems characterized by some frequently assumed distributions of adsorption energy. That goal has been achieved at expense of accepting certain simplifications in the course of the general treatment of the problem.

The obtained compact analytical expressions were successfully applied for quantitative description of the behavior of some experimental kinetic isotherms of adsorption on nonporous solid surfaces. However, our recent theoretical studies have shown⁴⁷ that, for certain extreme values of physical parameters, very strong surface heterogeneity is observed—for instance, these theoretical expressions predict a behavior that could hardly be observed in real adsorption systems. This has driven us to search for another generalization of the SRT kinetic approach that could lead us to more accurate theoretical expressions for adsorption/desorption kinetics. Here we discuss two such new approaches and apply them to describe the kinetics of sorption in carbon

molecular sieves. This is because the application to such porous systems has led us to the most interesting results.

Theory

I. The Principles of the SRT Approach for Nondissociative One-Site-Occupancy Adsorption. The Langmuir Model and a Homogeneous Solid Surface. For the Langmuir model of adsorption, $d\theta/dt$ takes the following form

$$\frac{d\theta}{dt} = K'_{gs} \left[\exp\left(\frac{\mu_g - \mu_s}{kT}\right) - \exp\left(\frac{\mu_s - \mu_g}{kT}\right) \right] \quad (4)$$

where the subscripts (g) and (s) refer to the bulk (gas) and the adsorbed (surface) phase. The exchange rate at equilibrium will be written as follows,

$$K'_{gs} = K_{gs} p^{(e)} (1 - \theta^{(e)}) \quad (5)$$

where the equilibrium state is defined as the one to which our system would evolve after being closed and equilibrated. Thus, contrary to ART, the new SRT approach also takes into account the technical conditions at which kinetic experiment is carried out. So far we have considered the following three extreme cases.⁴⁸

- The system is “*volume dominated*”, i.e., the amount of the gas in the gas phase strongly dominates over the amount which can be adsorbed. Then, after the system is isolated and equilibrated p does not change substantially, so $p^{(e)} \approx p$. Such a condition seems to be typical of the classical experiments on the isothermal adsorption kinetics.

- The system is “*solid dominated*”. In this case the adsorbed amount dominates so strongly over the amount of gas in the bulk phase, that after closing the system and equilibrating, θ remains practically unchanged, so $\theta \approx \theta^{(e)}$. Such conditions seem to be typical of experiments on the thermodesorption kinetics.

- The system is “*equilibrium dominated*”, so $\theta \approx \theta^{(e)}$ and $p \approx p^{(e)}$

The present publication will focus on the classical experiments on the kinetics of isothermal adsorption, so we will limit our consideration to the case of the *volume dominated* systems.

For the Langmuir model of adsorption

$$\mu_s = kT \ln \frac{\theta}{1 - \theta} - kT \ln q_s \quad (6)$$

The molecular partition function q_s is written usually as the product $q_0 \exp(\epsilon/kT)$. Assuming that μ_g is the chemical potential of an ideal gas phase

$$\mu_g = \mu_0^g + kT \ln p \quad (7)$$

one arrives at the Langmuir isotherm equation,

$$\theta^{(e)} = \frac{K p^{(e)} \exp(\epsilon/kT)}{1 + K p^{(e)} \exp(\epsilon/kT)} \quad (8)$$

in which $K = q_0 \exp(\mu_0^g/kT)$.

Thus, for the Langmuir model of adsorption, the SRT expression for $(d\theta/dt)$ takes the following form:

$$\frac{d\theta}{dt} = K_{gs} p (1 - \theta^{(e)}(p)) \left[K p \frac{1 - \theta}{\theta} \exp\left(\frac{\epsilon}{kT}\right) - \frac{1}{K p} \frac{\theta}{1 - \theta} \exp\left(-\frac{\epsilon}{kT}\right) \right] \quad (9)$$

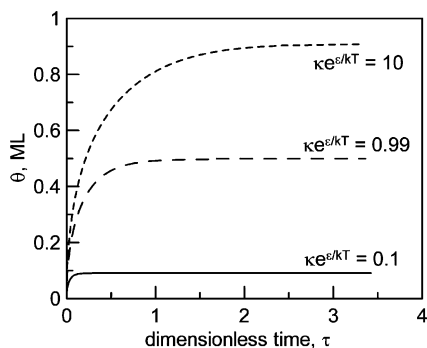


Figure 1. Behavior of the kinetic isotherm (eq 14) for a few values of the dimensionless parameter $\kappa e^{\epsilon/kT}$.

At equilibrium, when $(d\theta/dt) = 0$, eq 9 leads to the Langmuir isotherm (eq 8). Thus

$$1 - \theta^{(e)} = \frac{1}{1 + Kp \exp\left(\frac{\epsilon}{kT}\right)} \quad (10)$$

Thus, for the volume dominated systems, we have

$$\frac{d\theta}{dt} = K_{gs} \frac{p}{1 + Kp \exp\left(\frac{\epsilon}{kT}\right)} \left[Kp \frac{1 - \theta}{\theta} \exp\left(\frac{\epsilon}{kT}\right) - \frac{1}{Kp} \frac{\theta}{1 - \theta} \exp\left(-\frac{\epsilon}{kT}\right) \right] \quad (11)$$

After introducing the following set of dimensionless parameters

$$\begin{aligned} \kappa &= Kp \\ \tau &= K_{gs} p t \end{aligned} \quad (12)$$

eq 11 takes the form

$$\frac{d\theta}{d\tau} = \frac{1}{1 + \kappa \exp\left(\frac{\epsilon}{kT}\right)} \left[\kappa \frac{1 - \theta}{\theta} \exp\left(\frac{\epsilon}{kT}\right) - \frac{1}{\kappa} \frac{\theta}{1 - \theta} \exp\left(-\frac{\epsilon}{kT}\right) \right] \quad (13)$$

Solving the above differential equation with the condition $\theta(\tau = 0) = 0$, one obtains for $\kappa e^{\epsilon/kT} \neq 1$,⁴⁸

$$\tau(\theta) = \frac{\kappa e^{\epsilon/kT} (1 + \kappa e^{\epsilon/kT})}{2(\kappa^2 e^{2\epsilon/kT} - 1)^2} \left[4\kappa e^{\epsilon/kT} \operatorname{arctanh}\left\{ \kappa e^{\epsilon/kT} \right\} + 2(1 + \kappa^2 e^{2\epsilon/kT}) \ln[\kappa e^{\epsilon/kT}] - 2\theta(\kappa^2 e^{2\epsilon/kT} - 1) + 4\kappa e^{\epsilon/kT} \operatorname{arctanh}\left\{ \kappa e^{\epsilon/kT} (\theta - 1) - \frac{\theta}{\kappa e^{\epsilon/kT}} \right\} - (1 + \kappa^2 e^{2\epsilon/kT}) \ln[\kappa^2 e^{2\epsilon/kT} (\theta - 1)^2 - \theta^2] \right] \quad (14)$$

Let us remark that the above isotherm $\theta(t)$ has some small nonphysical region when $\theta \rightarrow 0$. This is because the SRT equation, eq 4, does not apply at some very small surface coverages. This problem was discussed in the fundamental paper by Ward et al.²² Its solution for the region $\theta \rightarrow 0$ has recently been proposed by one of the authors.⁴⁹

Figure 1 shows the behavior of the kinetic isotherm (14) as the function of the dimensionless parameter $\kappa e^{\epsilon/kT}$.

II. Langmuir Model and a Heterogeneous Solid Surface. The Condensation Approximation Approach. Below, we give a brief sketch of the method which we have used so far in our

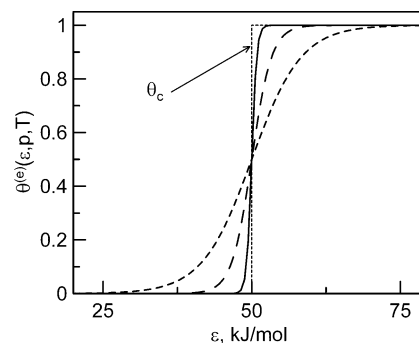


Figure 2. Behavior of Langmuir isotherm considered as a function of ϵ . ($\epsilon_c = 50$ kJ/mol; $T = 50$ K (—), $T = 200$ K (---), and $T = 500$ K (- · -)).

generalizations of the SRT approach for the case of energetically heterogeneous solid surfaces.

Let $\chi(\epsilon)$ denote the differential distribution of the number of adsorption sites among various values of ϵ , normalized to unity. Then, the measured equilibrium isotherm $\theta_t^{(e)}(p, T)$ is given by

$$\theta_t^{(e)}(p, T) = \int_{\epsilon_l}^{\epsilon_m} \theta^{(e)}(p, T, \epsilon) \chi(\epsilon) d\epsilon \quad (15)$$

where ϵ_l and ϵ_m are the lowest (l) and the maximum (m) values of ϵ on a heterogeneous solid surface.

The essential point of the generalization of the SRT kinetic approach proposed previously by us was the application of the condensation approximation (CA) to consider both adsorption equilibria and kinetics.

For the purpose of our further consideration, we will write eq 8 in the following form:

$$\theta^{(e)}(\epsilon, p, T) = \frac{\exp\left(\frac{\epsilon - \epsilon_c^{(e)}}{kT}\right)}{1 + \exp\left(\frac{\epsilon - \epsilon_c^{(e)}}{kT}\right)} \quad (16)$$

Here

$$\epsilon_c^{(e)} = -kT \ln Kp \quad (17)$$

and then

$$\epsilon_c^{(e)} = -\mu_s - kT \ln q_0 \quad (18)$$

Figure 2 shows how the function $\theta^{(e)}(\epsilon, p, T)$ behaves when temperature decreases. One can see, in Figure 2, that when temperature decreases, $\theta^{(e)}$ becomes more and more like the step-function $\theta_c^{(e)}(\epsilon)$, commonly called the “condensation isotherm”

$$\lim_{T \rightarrow 0} \theta^{(e)}(\epsilon) = \theta_c^{(e)}(\epsilon) = \begin{cases} 0 & \text{for } \epsilon < \epsilon_c^{(e)} \\ 1 & \text{for } \epsilon \geq \epsilon_c^{(e)} \end{cases} \quad (19)$$

One can see that also at finite temperatures the adsorption proceeds in a fairly stepwise manner, i.e., we observe a fairly sharp “adsorption front”, on the sites having the adsorption energy ϵ close to $\epsilon_c^{(e)}$.

From Figures 2 and 3 one can deduce that, to a good approximation, the function $\theta_t^{(e)}(\epsilon_c^{(e)})$ can be calculated as follows:

$$\theta_t^{(e)}(\epsilon_c^{(e)}) = \int_{\epsilon_c^{(e)}}^{\epsilon_m} \chi(\epsilon) d\epsilon = -X(\epsilon_c^{(e)}) \quad (20)$$

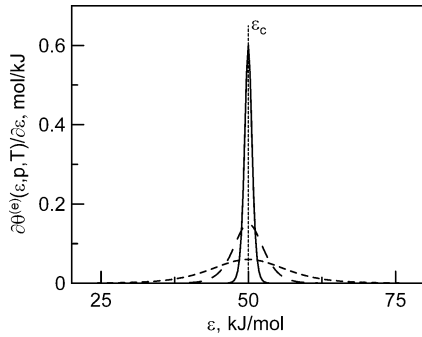


Figure 3. Derivatives of the functions shown in Figure 2.

Here

$$X(\epsilon) = \int \chi(\epsilon) d\epsilon \quad (21)$$

Calculating θ_t in this way is a well-known procedure in the theories of adsorption equilibria and is called the “condensation approximation” (CA). However, one can show that the condition $T \rightarrow 0$ is not the critical one for the CA approach to be applicable. The essential condition is that the variance of the function $\chi(\epsilon)$ is much larger than that of the derivative $(\partial\theta^{(e)}/\partial\epsilon)$. Let us note that

$$\frac{\partial\theta^{(e)}}{\partial\epsilon} = \frac{1}{kT}\theta^{(e)}(1 - \theta^{(e)}) \quad (22)$$

and that the variance of $(\partial\theta^{(e)}/\partial\epsilon)$ is equal to $\pi kT/\sqrt{3}$. When $T \rightarrow 0$, $(\partial\theta^{(e)}/\partial\epsilon)$ tends to the Dirac delta function $\delta(\epsilon - \epsilon_c)$. At $T > 0$, $(\partial\theta^{(e)}/\partial\epsilon)$ reaches its maximum at the point $\epsilon_c^{(e)}$, at which $(\partial^2\theta^{(e)}/\partial\epsilon^2) = 0$

$$\frac{\partial^2\theta^{(e)}}{\partial\epsilon^2} = \frac{1}{(kT)^2}\theta^{(e)}(1 - \theta^{(e)})(1 - 2\theta^{(e)}) = 0 \quad (23)$$

i.e. $\theta^{(e)}(\epsilon_c^{(e)}) = 1/2$.

The function $\chi_c(\epsilon_c)$ calculated from eq 20

$$\chi_c(\epsilon_c^{(e)}) = -\frac{\partial\theta_t}{\partial\epsilon_c} \quad (24)$$

is related to $\theta^{(e)}(\epsilon)$ and $\chi(\epsilon)$

$$\chi_c(\epsilon_c^{(e)}) = \int_0^{+\infty} \left(\frac{\partial\theta^{(e)}}{\partial\epsilon} \right) \chi(\epsilon) d\epsilon \quad (25)$$

and is usually called the “condensation function”. This is a somewhat “diffuse portrait” of the actual adsorption energy distribution $\chi(\epsilon)$. In the limit $T \rightarrow 0$, when the derivative $(\partial\theta^{(e)}/\partial\epsilon)$ tends to the Dirac δ function $[\delta(\epsilon - \epsilon_c^{(e)})]$, the CA function $\chi_c(\epsilon_c^{(e)})$ becomes the exact portrait of $\chi(\epsilon)$.^{2,50,51}

III. A Generalization of the SRT Approach Based on Application of the Condensation Approximation. The first attempts by Rudzinski et al.^{38–42} toward generalizing the SRT approach concerned the case of strongly heterogeneous solid surfaces. The idea was to consider the rate of adsorption kinetics in terms of the rate with which the “adsorption front” moves on the adsorption energy scale.^{49–50}

One essential assumption inhered in the SRT approach is the assumption that the adsorbed phase is in *quasi-equilibrium*. That means, all the correlation functions in the adsorbed phase are practically the same as they would be at equilibrium and the same surface coverage. We have made it a starting point in our

generalization of the SRT kinetic approach. Thus, we assumed that also at nonequilibrium there exists a sharp “adsorption front” on the sites whose adsorption energy $\epsilon = \epsilon_c$, but $\epsilon_c(\theta_t)$ is the same function as in equilibrium, i.e., is given by relation 18. Because ϵ_c and θ are now considered to be under nonequilibrium conditions, we omitted the superscripts (e) . Thus, $\epsilon_c(\theta)$ is determined by the equation

$$\theta_t(\epsilon_c, T) = \int_0^\infty \frac{\exp\left(\frac{\epsilon - \epsilon_c}{kT}\right)}{1 + \exp\left(\frac{\epsilon - \epsilon_c}{kT}\right)} \chi(\epsilon) d\epsilon \quad (26)$$

As we consider now the isothermal adsorption/desorption kinetics, T is a constant, and therefore

$$\frac{d\theta_t}{dt} = \frac{\partial\theta_t}{\partial\epsilon_c} \frac{d\epsilon_c}{dt} = -\chi_c(\epsilon_c) \frac{d\epsilon_c}{dt} \quad (27)$$

Thus, at a certain surface coverage θ_t , the rate of adsorption will depend on the population of the sites having $\epsilon = \epsilon_c$ through $\chi_c(\epsilon_c)$, and on the rate $d\epsilon_c/dt$ with which the adsorption “front” moves on the energy scale when the “front” is on these sites.

We note that ϵ_c is the value of ϵ for the sites whose local coverage $\theta = 1/2$, so we defined the function $F(\epsilon_c, t, T)$:

$$F(\epsilon_c, t, T) = \theta(\epsilon_c, t, T) - \frac{1}{2} = 0 \quad (28)$$

Then

$$\frac{d\epsilon_c}{dt} = -\frac{(\partial F/\partial t)_{\epsilon_c}}{(\partial F/\partial \epsilon_c)_t} = -\left[\frac{(\partial\theta/\partial t)_{\epsilon_c}}{(\partial\theta/\partial \epsilon_c)_t} \right]_{\theta=1/2, \epsilon=\epsilon_c} \quad (29)$$

To represent $(\partial\theta/\partial t)_{\epsilon_c}$ we used eq 11 in which $\epsilon = \epsilon_c$ and $\theta = 1/2$. But then, to represent $(\partial\theta/\partial t)$, one should use eq 14

$$G(\epsilon_c) = \left(\frac{\partial\theta}{\partial\epsilon} \right)_{\epsilon=\epsilon_c, \theta=1/2} = -\left[\frac{\partial\tau(\theta)/\partial\epsilon}{\partial\tau(\theta)/\partial\theta} \right]_{\epsilon=\epsilon_c, \theta=1/2} \quad (30)$$

Taking $\tau(\theta)$ defined in eq 14, we obtain

$$G(\epsilon_c) = -\frac{1}{2kT(\kappa_e^2 - 1)^2} \left[-3 - \kappa_e + 3\kappa_e^2 + \kappa_e^3 - 4\kappa_e(2 + \kappa_e(1 + \kappa_e))\text{arc tanh}\{\kappa_e\} + 4\kappa_e(2 + \kappa_e(1 + \kappa_e))\text{arc tanh}\left\{\frac{1}{2\kappa_e} + \frac{\kappa_e}{2}\right\} - (1 + \kappa_e(1 + \kappa_e(5 + \kappa_e)))\ln\frac{4\kappa_e^2}{\kappa_e^2 - 1} \right] \quad (31)$$

where

$$\kappa_e = \kappa e^{\epsilon_c/kT} = \exp\left(\frac{\epsilon_c(t) - \epsilon_c^{(e)}}{kT}\right) \quad (32)$$

Looking to eq 31, one can see that we have arrived at a complicated expression for $G(\epsilon_c, t)$. Then eq 27 could only be solved by using numerical methods. Trying to arrive at simple

analytical solutions, we made the following approximation:^{38–40,50,51}

$$\left[\frac{\partial \theta(t)}{\partial \epsilon} \right]_{\epsilon=\epsilon_c, \theta=1/2} \approx \left[\frac{\partial \theta(t \rightarrow \infty)}{\partial \epsilon} \right]_{\epsilon=\epsilon_c, \theta=1/2} = \frac{1}{4kT} \quad (33)$$

Then, the equation for $d\epsilon_c/dt$ takes the simple form

$$\frac{d\epsilon_c}{dt} = - \frac{4kTK_{gs}p}{1 + Kpe^{\epsilon_c/kT}} \left[Kpe^{\epsilon_c/kT} - \frac{1}{Kp} e^{-\epsilon_c/kT} \right] \quad (34)$$

One can then proceed by following two pathways:

- One can insert eq 34 into eq 27 and next solve the obtained differential equation with the boundary condition $\theta_i(t=0) = 0$

- One can solve differential equation eq 34 with the boundary condition $\epsilon_c(t=0) = \epsilon_m$, and next calculate $\theta_i(t)$ from the CA equation

$$\theta_i(t) = \int_{\epsilon_c(t)}^{\epsilon_m} \chi(\epsilon) d\epsilon \quad (35)$$

For the volume dominated systems, considered here, the solution of differential equation eq 34 reads:

$$\epsilon_c(p, T, t) = kT \ln \left[\frac{1}{Kp} + \left(e^{\epsilon_m/kT} - \frac{1}{Kp} \right) e^{-4K_{gs}pt} \right] \quad (36)$$

While accepting the approximation in (33), we have arrived at simple analytical solutions for $\theta_i(t)$, in the systems characterized by typical functions $\chi(\epsilon)$ considered so far in the theories of equilibria of adsorption on heterogeneous solid surfaces.² The obtained $\theta_i(t)$ functions could be applied to describe some experimental data for isothermal adsorption kinetics, reported in the literature.^{38,39,41} This made us believe that the applied theoretical procedures are fairly correct, and the approximation in (33) was not discussed in our papers. However, our more recent investigations^{42,47} have brought us to the conclusion that the theoretical procedure accepted by us so far should be reconsidered toward a more accurate generalization of the SRT kinetic approach.

Expression 27 is a fundamental expression for the systems in which stepwise adsorption front exists, or strictly speaking in the limit $\theta(\epsilon) \rightarrow \theta_c(\epsilon)$. In other words, this is the formulation of the adsorption kinetics for the CA approximation accepted ab initio.

So, it is interesting to note that for such a formulation based on ab initio CA approach, $d\epsilon_c/dt$ does not longer depend on the form of the adsorption energy distribution, but only on the mechanistic (Langmuir) model of adsorption. The $d\epsilon_c/dt$ function calculated from eqs 28–30 is a universal function corresponding to the Langmuir model of adsorption and is applicable no matter what the form of the adsorption energy distribution in the Langmuiric system under investigation is. The individual features of the kinetics in a particular adsorption system are taken into account when one uses eq 35 to calculate $\theta_i(t)$.

As the idea of having such an universal form of $\epsilon_c(t)$ for the Langmuiric model of adsorption seems very interesting, we have decided to look for a more accurate form of $\epsilon_c(t)$ than that obtained by us previously by accepting the crude approximation in (33), leading to $\epsilon_c(t)$ expressed in eq 36.

Namely, we have made an interesting observation that the complicated function $G(\epsilon_c)$ in eq 31 can, to a good approxima-

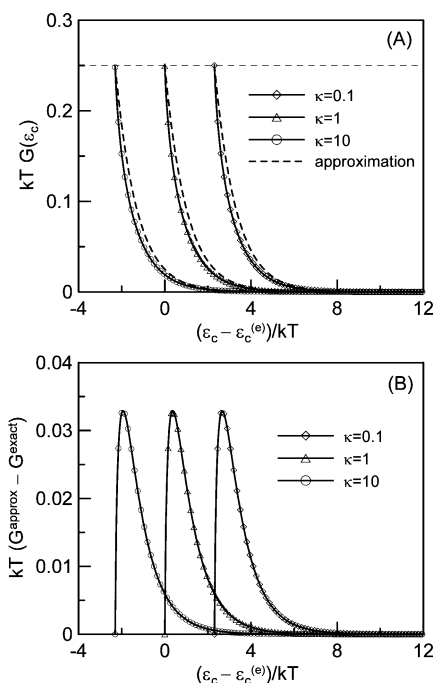


Figure 4. (A) Comparison between the exact function $G(\epsilon_c)$ defined in eq 31 (solid lines) and its approximation defined in eq 37 (dashed lines). (B) Difference between the approximate function $G(\epsilon_c)$ and the exact function $G(\epsilon_c)$.

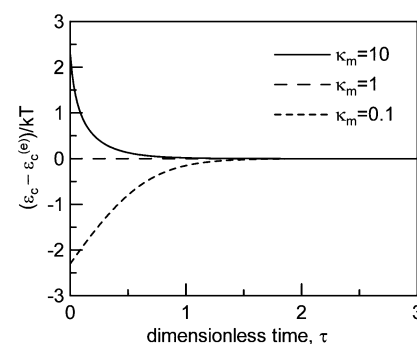


Figure 5. Behavior of the universal function $(\epsilon_c - \epsilon_c^{(e)})/kT$ for a few values of the parameter $\kappa_m = Kpe^{\epsilon_m/kT}$. Negative values of $(\epsilon_c - \epsilon_c^{(e)})/kT$ correspond to the physical situation when at $t=0$ desorption starts in the adsorption system.

tion, be replaced by a simple exponentially decreasing function $\sim \exp(-\epsilon_c/kT)$. This is shown in Figure 4. So

$$G(\epsilon_c) = \frac{1}{4kT} \exp\left(\frac{\epsilon_c^{(e)} - \epsilon_c(t)}{kT}\right) \approx \frac{1}{4\kappa kT} \exp\left(-\frac{\epsilon_c(t)}{kT}\right) \quad (37)$$

While accepting the approximation in (37), the expression $d\epsilon_c/dt$ defined in eq 29 takes the following explicit form:

$$\frac{d\epsilon_c}{dt} = - \frac{4kTK_{gs}p}{1 + Kpe^{\epsilon_c/kT}} [(Kp)^2 e^{2\epsilon_c/kT} - 1] \quad (38)$$

The solution of the differential equation eq 38 with the boundary condition $\epsilon_c(t=0) = \epsilon_m$ yields

$$\epsilon_c(t) = -kT \ln Kp - kT \ln \left[1 + e^{-4K_{gs}pt} \left(\frac{1}{Kpe^{\epsilon_m/kT}} - 1 \right) \right] \quad (39)$$

Figure 5 shows the behavior of the universal function $(\epsilon_c - \epsilon_c^{(e)})/kT$ as a function of the reduced time $\tau = K_{gs}pt$.

The approximation in (33) made in our previous papers, where we used the CA approach, has caused the $\theta_i(\tau)$ functions developed by us for various adsorption energy distributions to be less accurate than the $\theta_i(\tau)$ functions developed in this work.

IV. Comparison with the Exact Generalization of the SRT Kinetic Approach Defined for the Langmuir Model of Adsorption. Application of the CA approach to study the adsorption kinetics is very useful from a practical point of view for the following reason. Namely, we will show soon that, for some $\chi(\epsilon)$ functions commonly considered in the theories of equilibria of adsorption on the actual solid surfaces, the integral in (35) can easily be calculated to yield simple compact analytical expressions. Having such expressions is essential for practical purposes, i.e., for the analysis of experimental data.

However, it seems also necessary to study the range of CA applicability by comparison with a generalization of the SRT approach that would be applicable not only in the case of strongly heterogeneous solid surfaces but also in general.

In the case of the Langmuir model of adsorption, one may consider the whole adsorption system as a collection of subsystems being only in thermal and material contact. Each subsystem corresponds to the sites having identical adsorption energies. While applying the SRT approach to each of these subsystems, we have to note that the expression within the square bracket on the rhs of eq 4 is not a function of ϵ because at the quasi-equilibrium $\mu_s = \mu_s(\theta_i)$. Therefore

$$\frac{d\theta(\epsilon)}{dt} = K_{gs}p(1 - \theta_i^{(e)}(\epsilon, p)) \left[\exp\left(\frac{\mu_g - \mu_s(\theta_i)}{kT}\right) - \exp\left(\frac{\mu_s(\theta_i) - \mu_g}{kT}\right) \right] \quad (40)$$

and for the whole system we have

$$\frac{d\theta_i}{dt} = K_{gs}p(1 - \theta_i^{(e)}(p)) \left[\exp\left(\frac{\mu_g - \mu_s(\theta_i)}{kT}\right) - \exp\left(\frac{\mu_s(\theta_i) - \mu_g}{kT}\right) \right] \quad (41)$$

The explicit expression for $\mu_s(\theta_i)$ depends on the form of the function $\chi(\epsilon)$. It is well-known that, despite the variety of adsorption systems which we may have to deal with, their features can, to the first approximation, be represented by one of the following three adsorption energy distributions:²

- The quasi-Gaussian (LF) function

$$\chi(\epsilon) = \frac{1}{c} \frac{\exp\left(\frac{\epsilon - \epsilon_0}{c}\right)}{\left(1 + \exp\left(\frac{\epsilon - \epsilon_0}{c}\right)\right)^2} \quad (42)$$

centered at $\epsilon = \epsilon_0$, whereas the parameter c describes its variance $\pi^2 c^2/3$.

- The nonsymmetrical DA function

$$\chi(\epsilon) = \frac{r}{\delta} (\epsilon - \epsilon_l)^{r-1} \exp\left(-\left(\frac{\epsilon - \epsilon_l}{\delta}\right)^r\right) \quad (43)$$

where δ affects mainly the variance of $\chi(\epsilon)$, whereas r mainly affects its shape. When $r = 2$, this is a Gaussian-like, rhs widened function.

- When the surface is strongly heterogeneous, its features can well be represented by the following rectangular distribution,

$$\chi(\epsilon) = \begin{cases} (\epsilon_m - \epsilon_l)^{-1}, & \text{for } \epsilon_l \leq \epsilon \leq \epsilon_m \\ 0, & \text{elsewhere} \end{cases} \quad (44)$$

These functions have commonly been considered in the theories of adsorption equilibria. Recently Rudzinski et al. have explained their origin by launching a modified fractal theory of adsorption on real solid surfaces considered as partially correlated surfaces.^{52,53}

Now, let us see to which expressions eq 41 leads in the limit of strongly heterogeneous surfaces, for the three adsorption energy distributions (eqs 42–44). In the limit of strongly heterogeneous solid surfaces, we may apply the CA approximation.

Then, for the LF function $\chi(\epsilon)$, we obtain the Langmuir–Freundlich isotherm

$$\theta_i^{(e)} = \left[1 + \exp\left(\frac{\epsilon_c^{(e)} - \epsilon_0}{c}\right) \right]^{-1} = \frac{[Kpe^{\epsilon_0/kT}]^{KT/c}}{1 + [Kpe^{\epsilon_0/kT}]^{KT/c}} \quad (45)$$

and the corresponding relation

$$\mu_s(\theta_i^{(e)}) = -kT \ln q_0 - \epsilon_0 + c \ln \frac{\theta_i^{(e)}}{1 - \theta_i^{(e)}} \quad (46)$$

which we also accept for the quasi-equilibrium assumed in the SRT.

Equation 41 leads us then to the following expression for $d\theta_i/dt$

$$\frac{d\theta_i}{dt} = \frac{K_{gs}p}{1 + (Kpe^{\epsilon_0/kT})^{KT/c}} \left[Kpe^{\epsilon_0/kT} \left(\frac{1 - \theta_i}{\theta_i} \right)^{c/kT} - \frac{1}{Kp} e^{-\epsilon_0/kT} \left(\frac{\theta_i}{1 - \theta_i} \right)^{c/kT} \right] \quad (47)$$

While considering the nonsymmetrical DA function (eq 43), we arrive at the well-known Dubinin–Astakhov isotherm

$$\theta_i^{(e)} = \exp\left(-\left(\frac{\epsilon_c^{(e)} - \epsilon_l}{\delta}\right)^r\right) = \exp\left[-\left(-\frac{kT}{\delta} \ln Kpe^{\epsilon_l/kT}\right)^r\right] \quad (48)$$

and the related expression

$$\epsilon_c^{(e)}(\theta_i) = \delta(-\ln \theta_i)^{1/r} + \epsilon_l = -\mu_s - kT \ln q_0 \quad (49)$$

Our accurate expression (eq 41) for $d\theta_i/dt$ takes now the following explicit form:

$$\frac{d\theta_i}{dt} = K_{gs}p \left(1 - \exp\left[-\left(-\frac{kT}{\delta} \ln Kpe^{\epsilon_l/kT}\right)^r\right] \right) \left[Kpe^{\epsilon_l/kT} \exp\left(\frac{\delta(-\ln \theta_i)^{1/r}}{kT}\right) - \frac{1}{Kp} e^{-\epsilon_l/kT} \exp\left(-\frac{\delta(-\ln \theta_i)^{1/r}}{kT}\right) \right] \quad (50)$$

Let us finally consider the rectangular function $\chi(\epsilon)$ defined in eq 44. Using the CA approach we arrive at the Temkin isotherm

$$\theta_i^{(e)} = \frac{\epsilon_m}{\epsilon_m - \epsilon_l} - \frac{\epsilon_c}{\epsilon_m - \epsilon_l} = \frac{\epsilon_m}{\epsilon_m - \epsilon_l} + \frac{kT}{\epsilon_m - \epsilon_l} \ln Kp \quad (51)$$

and the related expression for $\epsilon_c^{(e)}(\theta_i)$ reads

$$\epsilon_c^{(e)} = \epsilon_m - \theta_i(\epsilon_m - \epsilon_l) = -\mu_s - kT \ln q_0 \quad (52)$$

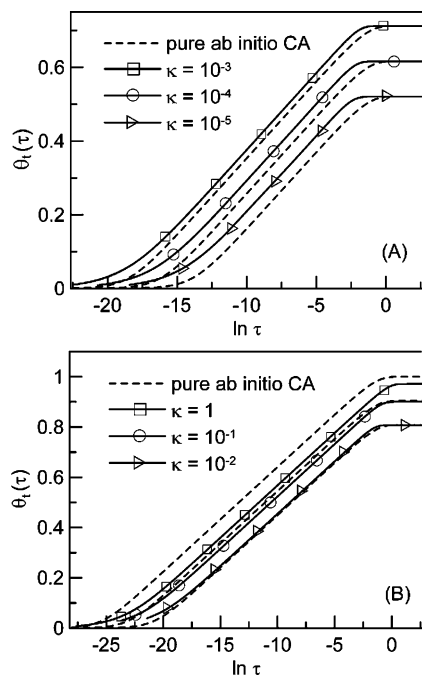


Figure 6. (A) Comparison of $\theta_i(\tau)$ functions calculated from eqs 54 and 55 for three values of the parameter $\kappa = Kp$, i.e., $\kappa = 10^{-5}$, 10^{-4} , and 10^{-3} , with the corresponding $\theta_i(\tau)$ functions calculated by the pure ab initio CA approach from eqs 35, 39, and 51. The parameters of the rectangular function (eq 44) were as follows: $\epsilon_l = 0$ kJ/mol; $\epsilon_m = 60$ kJ/mol. (B) Same calculations made for the other set of parameters: $\kappa = 10^{-2}$, 10^{-1} , and 1. The assumed temperature $T = 300$ K.

Then the accurate generalization yields

$$\frac{d\theta_i}{dt} = K_{gs} p \left(\frac{-\epsilon_l - kT \ln Kp}{\epsilon_m - \epsilon_l} \right) \left[Kp e^{\epsilon_m/kT} \exp\left(\frac{-\theta_i(\epsilon_m - \epsilon_l)}{kT}\right) - \frac{1}{Kp} e^{-\epsilon_m/kT} \exp\left(\frac{\theta_i(\epsilon_m - \epsilon_l)}{kT}\right) \right] \quad (53)$$

Thus, while neglecting the desorption term, we arrive at the Elovich empirical equation, so commonly used to describe the adsorption kinetics on the actual heterogeneous solid surfaces.^{3,11}

To compare the approach represented by eq 41 with the pure ab initio CA approach, one has to apply in eq 41 the exact solutions for $\theta_i^{(e)}(p)$, and $\mu_s(\theta_i)$. This can be done most easily in the case of the rectangular adsorption energy distribution (44). Then $\theta_i(\epsilon_c, T)$ in eq 26 can be integrated analytically to yield

$$\theta_i(\epsilon_c, T) = \frac{kT}{\epsilon_m - \epsilon_l} \ln \frac{1 + \exp\left(\frac{\epsilon_m - \epsilon_c}{kT}\right)}{1 + \exp\left(\frac{\epsilon_l - \epsilon_c}{kT}\right)} \quad (54)$$

From this equation, $\mu_s(\theta_i)$ is calculated using eq 18, and next inserted into eq 41 which we write in the following form:

$$\frac{d\theta_i}{dt} = K_{gs} p (1 - \theta_i^{(e)}(p)) \left[Kp e^{\epsilon_c(\theta_i)/kT} - \frac{1}{Kp} e^{-\epsilon_c(\theta_i)/kT} \right] \quad (55)$$

This equation has to be solved with the boundary condition $\theta_i(t=0) = 0$, and the obtained $\theta_i(t)$ function is to be compared with the $\theta_i(t)$ functions obtained from eqs 35 and 39. Figure 6 shows some examples of such model investigations.

Figure 6 shows a fairly good agreement between the results given by the pure ab initio CA approach, and those obtained by assuming that $d\theta_i/dt$ is given by eq 41 in the region of some

medium surface coverages. The differences become more and more evident below and above this region of medium surface coverages. In this wider region of surface coverages a certain overlapping of the exact and the CA kinetic isotherms can be achieved by using an “effective” value of the constant K_{gs} . That means, the simple expression for the kinetic adsorption isotherms offered by the CA approach will still be fairly applicable, but the determined K_{gs} constants will not be accurate. A similar observation has been made by us in our numerical exercises with other adsorption energy distributions.

For fundamental reasons the behavior of the kinetic isotherms at short times, i.e., when $t \rightarrow 0$ is very essential. Then, the exact kinetic curves are to be considered. This will be an interesting point for discussion in the next section, where the derived kinetic isotherms will be applied to analyze some experimental kinetic data.

V. Comparison with Experiment and Discussion. Application of the SRT approach to represent the kinetics of adsorption on nonporous surfaces has already been demonstrated in our previous papers cited in the references.^{38,40} Also, we have already made an attempt to use that approach to describe the kinetics of benzene sorption by a carbon adsorbent having a porous structure.³⁹ The kinetics of sorption in such systems is a problem of a great practical importance and has, therefore, been a subject of many experimental and theoretical studies.^{4–7} Among carbon sorbents, the CMS sorbents have frequently been studied. Here various theoretical models were used including Fickian diffusion, linear driving force, Langmuir kinetics, and combined barrier resistance/diffusion models.^{54–57} Most commonly it has been assumed that the kinetics of sorption is controlled by micropore diffusion and is therefore, a Fickian kinetics. So, the fractional uptake N_t/N_∞ is described by the equation

$$\frac{N_t}{N_\infty} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp\left(-\frac{Dn^2\pi^2 t}{r^2}\right) \quad (56)$$

where N_t is the amount adsorbed and $N_\infty = N_t(t \rightarrow \infty)$, D is diffusivity and r is the radial coordinate for the particles. At short times, when the fractional uptake is less than around 0.3, the uptake can be expressed as

$$\frac{N_t}{N_\infty} = \frac{6D^{1/2}t^{1/2}}{\pi^{1/2}r} \quad (57)$$

At long times eq 56 simplifies to

$$\frac{N_t}{N_\infty} = 1 - \frac{6}{\pi^2} \exp\left(-\frac{\pi^2 D t}{r^2}\right) \quad (58)$$

The behavior of various adsorption systems exhibited deviations from the kinetics predicted by eq 56. Frequently, the initial uptake at short times was not a linear function of $t^{1/2}$. These deviations were discussed by several authors and were ascribed, for instance, to experimental problems. Next, it was reported that the diffusion coefficient D increases with pressure.^{56,58} That increase was interpreted in terms of irreversible thermodynamics where the driving force for diffusion is the gradient of chemical potential. To account for that the Darken relation was used⁵⁹

$$D = D_0 \frac{\partial(\ln p)}{\partial(\ln N_t)} \quad (59)$$

in which the derivative is calculated from the equilibrium

adsorption isotherm. Thus, it became evident that a proper interpretation of sorption kinetics requires a simultaneous study of both kinetics and adsorption equilibria. Such extensive studies were undertaken by Rutherford and Do.⁵⁸ Having estimated $\partial(\ln p)/\partial(\ln N_s)$ from an equilibrium adsorption isotherm one should predict the behavior of adsorption kinetics just by introducing one more parameter D_0/r^2 . Let us remark that we have the same situation in our theory based on the SRT approach, where all the parameters but K_{gs} can be determined from the equilibrium adsorption isotherm.

However, in the case of porous systems the fundamental problem is the question which model governs the sorption kinetics. Is it Fickian diffusion, is it Knudsen diffusion, or may it still be another kind of kinetics?

There are good reasons to assume, that in many porous systems the transition from free to adsorbed state was the rate-controlling step. In the case of carbon adsorbents, Esseningh⁶⁰ demonstrated the applicability of the Elovich equation to describe the chemisorption of oxygen on carbons. Khan, Everitt, and Lui⁶¹ reported that Elovich equation works for many chars, but not for a high-temperature char, for which the diffusion theory was found to be more successful. As the theoretical origin of the Elovich equation is now clear, this would mean that the Langmuir kinetics of adsorption on a strongly heterogeneous carbon surface might have governed the sorption kinetics in many of the investigated systems.

Very impressive from that point of view is the recent theoretical paper by Feng and Bhatia.⁶² They have demonstrated the applicability of combining Langmuir and other adsorption models with certain adsorption activation energy distributions, to describe the kinetics of sorption of oxygen on various carbon adsorbents. This would mean a fast, presumably Knudsen diffusion to the surface (pore walls), and next a slow chemisorption process. Such conclusion has recently been launched by Rudzinski and Panczyk,³⁹ who found that the simplified condensation approximation SRT approach can represent quite well the kinetics of benzene sorption by an activated carbon.

This would suggest a general, and somewhat trivial, conclusion, that, depending on the nature of an adsorption system (porosity, gas–solid interactions) and the physical conditions at which kinetic experiment is carried out (pressure, temperature), one may face various models governing the sorption kinetics. But then, an intriguing question arises whether analysis of typical adsorption data, i.e., kinetic and equilibrium isotherms, may provide the answer as to which kinetic model is to be accepted in the adsorption systems under investigation.

With this intriguing question in mind we have decided to carry out a comparative analysis of the data recently published by Rutherford and Coons⁶³ for the kinetics and equilibria of carbon dioxide adsorption on a commercially available carbon molecular sieve. These were the equilibrium isotherms measured at 20 °C in the pressure range 0–200 Torr, and the kinetic isotherm measured at 20 °C and at the constant pressure 343 Torr.

The pressure dependence of the mobility parameter D was determined by fitting the experimental equilibrium isotherm by the Toth equation

$$\frac{N_t}{N_m} = \theta_t = \frac{bp}{[1 + (bp)^\alpha]^{1/\alpha}} \quad (60)$$

which yielded $N_m = 3.64$ mmol/g, (N_m is the maximum surface coverage), $b = 4.6 \times 10^{-3}$ Torr⁻¹, and $\alpha = 0.623$. Thus

$$D = D_0[1 + (bp)^\alpha] \quad (61)$$

The Toth equation is frequently used as an empirical isotherm equation to describe gas adsorption by activated carbons. Its formal advantage is the fact that it has Henry's limit when $p \rightarrow 0$. However, it is also known that experimental isotherms of adsorption by activated carbons may not exhibit Henry's region even at very low adsorbate pressures.² Therefore, much more popular here has been the Dubinin–Radushkevich isotherm equation, i.e., the DA isotherm with $r = 2$.

Rutherford and Coons applied also the Dubinin–Radushkevich (DR) equation. By including additionally some equilibrium data found in an independent experiment,⁶⁴ the authors found $N_m = 3.88$ mmol/g, and $\delta = 11.50$ kJ/mol. While applying the DR equation, the authors accepted its traditional interpretation when $K \exp(\epsilon_i/kT) = 1/p_0$, where p_0 is the saturated vapor pressure. They also applied Stoeckli's relation⁶⁵ to estimate from δ the mean pore width as equal to 0.5 nm.

One weak point of that traditional interpretation is the assumption that the state of the adsorbate in micropores is the same as in the bulk phase. Meanwhile, the numerous computer simulations published during the last years show that the state in micropores may be much different. Kaneko et al.⁶⁶ showed that the molecules adsorbed in micropores of carbon adsorbents are localized and that monolayer adsorption exists even in the micropore filling. Of course, the dispersion of micropore dimensions is the main source of the dispersion of adsorption energies. So, in general, $\exp(-\epsilon_i/kT)/K$ cannot be identified with the saturated vapor pressure and should be treated as a free parameter.

Therefore, we have subjected the experimental equilibrium adsorption isotherm to analysis based on eq 48. While choosing properly the value of the monolayer capacity N_m one should make the plot $(\ln 1/\theta_t)^{1/2}$ a linear function of $\ln p$

$$\left[\ln \frac{1}{\theta_t}\right]^{1/2} = -\frac{kT}{\delta} \ln K e^{\epsilon_i/kT} - \frac{kT}{\delta} \ln p \quad (62)$$

from which the other two parameters kT/δ and $\ln K \exp(\epsilon_i/kT)$ are found. So, this is a procedure of determining of just one best-fit parameter. Figure 7 shows the result of our numerical exercises.

Figure 8 shows the comparison of eq 62 with experiment as the function θ_t vs p .

Having estimated the parameters N_m , δ , and $K \exp(\epsilon_i/kT)$, we next fitted the experimental kinetic isotherm of carbon dioxide measured by Rutherford and Coons, by the theoretical isotherm obtained by applying the ab initio CA approach, and assuming that $\epsilon_m = \infty$.

$$\theta_t(t) = \exp\left\{-\left[-\frac{kT}{\delta} \ln K p e^{\epsilon_i/kT} (1 - e^{-4K_{gs} p t})\right]\right\} \quad (63)$$

and next by applying the accurate isotherm $\theta_t(t)$ obtained from numerical solution of eq 50 with the condition $\theta_t(t=0) = 0$. The results of our numerical exercises are shown in Figure 9.

In the next step, we fitted the experimental kinetic isotherm by eq 56, which after introducing the explicit form of D , reads

$$\frac{N_t(t)}{N_\infty} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp\left\{-\frac{D_0}{r^2} [1 + (bp)^\alpha] n^2 \pi^2 t\right\} \quad (64)$$

where (D_0/r^2) is the only unknown best-fit parameter.

With the N_∞ , b , and α values determined by Rutherford and Coons using the Toth isotherm to correlate the experimental

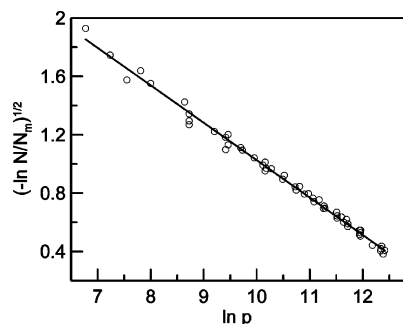


Figure 7. Linear representation (eq 62) for the equilibrium isotherm of carbon dioxide adsorption reported by Rutherford and Coons.⁶³ The experimental data (oooo) were digitized from Figure 2 of their paper,⁶³ whereas the solid line is their best linear regression (eq 62) obtained when $N_m = 2.948$ mmol/g. That linear regression yields the values of the two other parameters; $\delta = 9.50$ kJ/mol and $\ln[K \exp(\epsilon_0/kT)] = -14.00$.

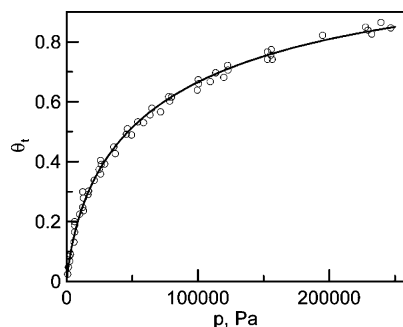


Figure 8. Comparison of the experimental equilibrium isotherm of carbon dioxide with the theoretical isotherm (eq 62) plotted as a function of θ_t vs p . The parameters used are the same as in Figure 7.

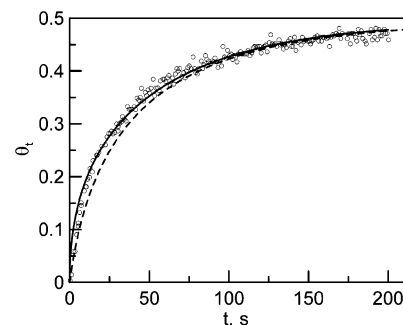


Figure 9. Comparison of the experimental kinetic isotherm of carbon dioxide (○) reported by Rutherford and Coons⁶³ with the theoretical CA best-fit isotherm (eq 63) (---) obtained by assuming $K_{gs} = 6.7 \times 10^{-8}$ Pa⁻¹s⁻¹ and the exact theoretical kinetic isotherm obtained by solving eq 50 and assuming that $K_{gs} = 6.3 \times 10^{-8}$ Pa⁻¹s⁻¹ (solid line). Other adsorption parameters are the same as those in Figure 7. The experimental points (○) were obtained by digitization of data in Figure 4a of the paper by Rutherford and Coons⁶³ for the same region of surface coverages for which the equilibrium isotherm was measured.

equilibrium isotherm, the best fit of $N_t(t)$ is obtained when $D_0/r^2 = 6.62 \times 10^{-4}$ s⁻¹. That fit is shown in Figure 10.

The comparison of the best fits presented in Figures 9 and 10 leads to an intriguing observation. Namely, the fit offered by the diffusion model, i.e., eq 64 is almost the same as the fit given by the kinetic model, i.e., the exact solution obtained from eq 50. In both cases, all the parameters but one were determined from the equilibrium isotherm. Thus, in both cases fitting the kinetic isotherm required adjusting of only one free parameter. This, of course, rises the intriguing question which model of sorption kinetics should be accepted for this adsorption system. A similar problem has already been faced by Bhatia and Arvind

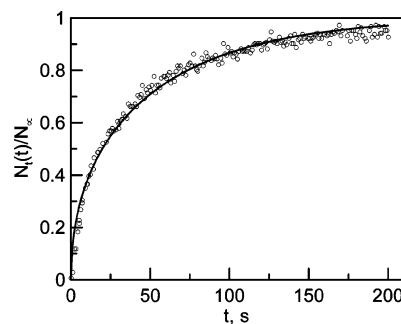


Figure 10. Solid line showing the best-fit of the experimental kinetic isotherm of carbon dioxide adsorption, obtained by assuming $D_0/r^2 = 6.62 \times 10^{-4}$ s⁻¹ in eq 64. The other two constants b and α were those found by Rutherford and Coons using the Toth equation to correlate experimental data for the equilibrium adsorption isotherm. ($bp = 1.58$, $\alpha = 0.62$).

while studying the iodine adsorption kinetics on activated carbon.^{67,68} They found that the kinetic data for that system could be interpreted either by surface diffusion model⁶⁷ or by Langmuir adsorption kinetics model with more consistent parameter values.⁶⁸

A commonly accepted test of applicability of the diffusion model is the square root dependence of $\theta_t(t)$ on time when $t \rightarrow 0$, predicted by eq 57. So, it is interesting to note that the SRT kinetic approach also predicts such behavior for the Langmuir model of adsorption on a homogeneous surface. From the SRT equation, eq 9, it follows that

$$\lim_{\substack{t \rightarrow 0 \\ \theta \rightarrow 0}} \frac{d\theta}{dt} = K_{gs}p \left(1 - \theta^{(e)}(p) \right) Kp \frac{1}{\theta} \quad (65)$$

The solution of this equation with the condition $\theta(t=0) = 0$ yields

$$\theta(t) = (2K_{gs}Kp^2t)^{1/2} \quad (66)$$

So, the square root dependence of $\theta(t)$ on time cannot be treated as a definite proof for the applicability of diffusion model. A similar conclusion can be drawn for energetically heterogeneous solid surfaces. Let us consider, for instance, the accurate expression $d\theta/dt$ in eq 47 for the quasi-Gaussian adsorption energy distribution. Then

$$\lim_{\substack{t \rightarrow 0 \\ \theta \rightarrow 0}} \frac{d\theta_t}{dt} = \frac{K_{gs}pKpe^{\epsilon_0/kT}}{1 + (Kpe^{\epsilon_0/kT})^{kT/c}} [\theta_t(t)]^{-c/kT} \quad (67)$$

The solution of that equation with the condition $\theta_t(t=0) = 0$ yields

$$\theta_t(t) = \left[\left(\frac{c}{kT} + 1 \right) \frac{K_{gs}pKpe^{\epsilon_0/kT}}{1 + (Kpe^{\epsilon_0/kT})^{kT/c}} t \right]^{(kT/c)/(1+(kT/c))} \quad (68)$$

Typical values of kT/c found in analysis of experimental adsorption isotherms vary between 0.5 and 0.9. Application of the LF eq 45 to the equilibrium isotherm measured by Rutherford and Coons yields $kT/c = 0.81$. This value has been found by us from applying the following linear representation for that equilibrium isotherm

$$\ln \frac{N_t/N_m}{1 - N_t/N_m} = \frac{kT}{c} \ln [Ke^{\epsilon_0/kT}] + \frac{kT}{c} \ln p \quad (69)$$

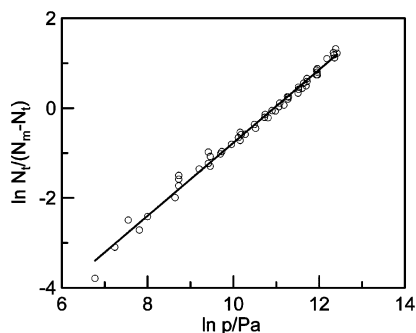


Figure 11. Linear representation (eq 69) for the equilibrium isotherm of carbon dioxide adsorption on the molecular sieve studied by Rutherford and Coons. The best linear regression is obtained when $N_m = 3.23$ mmol/g, $kT/c = 0.81$, and $\epsilon_0/c + (kT/c) \ln K = -8.91$.

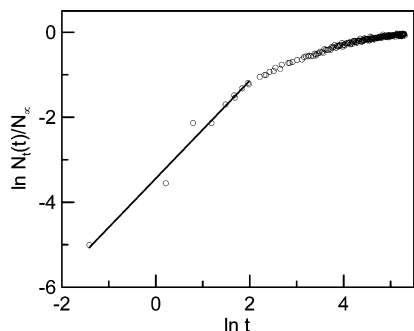


Figure 12. Double logarithmic plot for the kinetic data reported by Rutherford and Coons. The solid line is the best linear regression made for the first 10 experimental points. The tangent of that linear plot is equal to 1.15.

Finding the unknown parameters N_m , kT/c , and $K \exp(\epsilon_0/kT)$ is a simple computer exercise based on finding the N_m value which provides the best linear regression for $\ln[(N_t/N_m)/(1 - N_t/N_m)]$ plotted as a function of $\ln p$. The two other parameters are then found from the tangent and the intercept of that linear plot. Figure 12 shows the result of our numerical exercises for the experimental equilibrium adsorption isotherm.

For the value $kT/c = 0.81$, the time in eq 68 is powered to about 0.44. This is still a value not far from one-half, so also in the case of heterogeneous surfaces the square root dependence on time cannot be treated as a definite proof of the applicability of the diffusion model. The quasi-Gaussian adsorption energy distribution has been used here only as a convenient proof for the above expressed fundamental thesis. Our numerical exercises showed that accepting the DR adsorption energy distribution leads to better description of the equilibrium isotherm and the kinetic isotherm in particular. It means that the right-hand side widened Gaussian-like adsorption energy distribution (eq 43) represents better the actual adsorption energy distribution in this adsorption system than the fully symmetrical Gaussian-like function (eq 42) does.

Much more precise information about the time dependence at the small initial surface coverages is obtained from the plot $\partial(\ln \theta_t)/\partial(\ln t)$. For the Fickian diffusion

$$\lim_{t \rightarrow 0} \frac{\partial(\ln N_t)}{\partial(\ln t)} = \frac{1}{2} \quad (70)$$

Figure 11 shows such a double logarithmic plot for the carbon dioxide adsorption on a molecular sieve reported by Rutherford and Coons.

The linear regression made for the first 10 experimental points has tangent close to unity. Let us remark, however, that these

are the points for which neither the diffusional nor our kinetic approach can give a good fit. In both cases, the experimental data lie below the theoretical curve. In the case of our kinetic approach that effect has already been discussed by us, as being due to nonapplicability of the SRT approach at very small surface coverages.⁴⁹ Namely the “thermodynamic” SRT approach does not apply when the predicted adsorption rate is higher than the flux of molecules to the surface. Let us remark that the SRT eq 11 suggests an infinite value of $d\theta/dt$ in the limit $\theta \rightarrow 0$. Meanwhile, in real physical systems when $\theta \rightarrow 0$, $d\theta/dt$ takes the constant value, determined by the flux of molecules to the solid surface. Thus, in this region of surface coverages $\theta_t(t)$ will be a linear function of time. So, the double logarithmic plot will have tangent equal to unity. This, in fact, can be observed in Figure 12.

Nevertheless, a very similar fit given by the diffusion and the kinetic models still makes the question of their applicability open. Is it the surface diffusion or a fast Knudsen’s diffusion into pores and next a slower adsorption kinetics? The answer will surely require further comparative studies taking into account pressure and temperature dependence of sorption kinetics. A certain problem here is a limited body of available experimental data that would report on simultaneous studies of pressure and temperature dependence of both adsorption kinetics and equilibria. So far, the obvious conclusion which can be drawn from our investigation here is that the common practice to represent the kinetics of sorption in carbon adsorbents by the diffusion models may not always be justified.

Of course, very useful in distinguishing between adsorption kinetics and the diffusion process are such studies as the effect of particle size on the kinetics (useful in identifying the importance of macropore diffusion) or the effect of concentration which may identify the role of micropore diffusion. On the other hand, the exact theories of transport of LJ fluids in micropores can be used to provide theoretical values of diffusivities to help discriminate between models based on adsorption kinetics and diffusion.^{69,70}

Summary

It was only at the beginning of the 1980s when the most substantial progress was made in understanding of the fundamentals of adsorption kinetics. This was when the new fundamental approach to adsorption kinetics based on the statistical rate theory was published.

In a series of papers published during the past few years, we have presented first attempts to generalize that new approach for the case of energetically heterogeneous surfaces. Our attempts were aimed at developing simple analytical expressions, easily applicable to analyze experimental data. This was possible by applying the method known in adsorption theories as the condensation approximation (CA) and also accepting some other additional simplifying assumptions.

In this paper, we are developing a more refined version of that method, and study its applicability by comparing it with a fully exact generalization of the SRT that can be easily defined for the Langmuir model of adsorption. That comparison shows that the CA method is applicable in a wide region of surface coverages but the determined value of the kinetic parameter K_{gs} may not be the exact one. The CA approach is not applicable for the initial region of small times and surface coverages.

While studying the features of adsorption kinetics in this initial region, we have focused our attention on a very intriguing prediction that can be drawn from our kinetic equations based on generalization of the SRT approach. Namely, that for this

initial region and a homogeneous surface, one should observe a square-root dependence on time of the observed surface coverage. Further, a very similar behavior should also be observed in the kinetics of adsorption on a heterogeneous solid surface.

In the studies of kinetics of adsorption on porous surfaces, such square-root dependence has commonly been assumed as a proof for that kinetics of adsorption is to be modeled as surface diffusion. So, we have decided to examine whether our kinetic equations could describe the kinetics of adsorption on porous surfaces as well. Thus, we have carried out a comparative study of kinetics of sorption in a carbon molecular sieve, previously analyzed by assuming the surface diffusion model. Then it appeared that our kinetic equations give an almost identical fit of the experimental kinetic adsorption isotherm as that obtained by assuming that adsorption proceeds via surface diffusion. The fitting procedures were the same and the number of best-fit parameters was the same. This raises the question whether the common practice to represent the kinetics of sorption in porous sorbents as a process of surface diffusion is sufficiently justified.

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