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The Langmuirian Adsorption Kinetics Revised: A Farewell to the XXth Century Theories?

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Abstract. A brief historical review of the development of the theoretical approaches to the kinetics of gas adsorption/desorption on/from the solid surfaces is presented. The attention is focused on new approaches, challenging the classical theories based on the ideas of Absolute Rate Theory (ART). These new approaches relate the adsorption/desorption kinetics to the chemical potentials of the molecules in the gas and adsorbed states. Among them the so-called Statistical Rate Theory (SRT) has the most rigorous theoretical foundations. That new approach predicts that depending on experimental conditions one can have a variety of kinetic equations corresponding to the Langmuir equilibrium adsorption isotherm.

Keywords: gas adsorption, adsorption kinetics, langmuirian kinetics, statistical rate theory

Introduction

In the case of many adsorption systems which are crucial for life, technology and science, the time dependence of these adsorption process is at least as important as the features of these systems at equilibrium.

For decades, beginning from the twenties of the XXth century, the Absolute Rate Theory (ART) was, almost exclusively used for interpretation of the data on the kinetics of gas adsorption/desorption on/from solid surfaces. Although it was a kind of a rough transfer of some ideas from the field of chemical reactions, the principles of that approach were rarely questioned. The ART approach has, for instance, commonly been applied to describe the adsorption/desorption kinetics also in physisorption systems where the gas/solid interactions can hardly be interpreted as chemical reactions.

Although the inapplicability of the ART kinetic equations leading to Langmuir isotherm, was dramatically demonstrated in the reported kinetic studies, the fundamentals of ART remained untouched. Instead, various attempts were made to improve the ART by taking into account the energetic heterogeneity of the actual solid surfaces, or possible interactions between the adsorbed molecules. Introducing the concept of the precursor states was also an attempt to save the fundamentals of ART.

Looking at the historical development of kinetic studies one can see that experimental studies have proceeded along two separate paths which hindered the progress in the experimental part.

The scientists studying isothermal adsorption kinetics in the first half of the XX century focused mainly on the initial stage of adsorption, when the simultaneously appearing desorption can be safely ignored. Consequently, the related theoretical interpretation of isothermal adsorption kinetics neglected, as

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a rule, the desorption term in the related theoretical expressions.

Studies of desorption kinetics so rigorously developed from the sixties were mainly oriented toward thermodesorption, where the related theoretical interpretation ignored, as a rule, the simultaneously occurring re-adsorption. As a result, the theoretical interpretations involving the complete ART expression were scarce.

This situation delayed bringing to light several inconsistencies and fundamental difficulties which appear only when the full form of ART equations is taken into consideration, i.e., when the theoretical interpretation takes into account both adsorption and desorption occurring simultaneously.

This can be seen clearly when adsorption on energetically heterogeneous surfaces is considered. However, in spite of the growing evidence that the fundamentals of the existing kinetic theories need to be revised, the ART approach and its various modifications are still commonly applied. It was only 15 years ago, when the first papers were published challenging that approach. They related the features of the adsorption/desorption kinetics to the chemical potentials of gas molecules in the equilibrium and the adsorbed state.

The appearance of this new view aroused immediately heated discussions and did not receive common acceptance. There were various reasons for that. First, because at the beginning the new approach had a semi-empirical character. The second reason was the obvious inertia arising from the fact that the ART approach was used for so long. Finally, it might also be fear of some scientists that their well-established views and existing interpretations might have to be seriously reconsidered. Although at the beginning of the eighties the new approach received a solid theoretical background in a series of papers published in J. Chem. Phys., only a few advanced papers were published based on that new approach, called the Statistical Rate Theory (SRT).

The few advanced papers dealt with the kinetics of adsorption/desorption on/from well-defined, (energetically homogeneous) solid surfaces. It has been only the last few years when this new approach was generalized to handle the kinetics of adsorption/desorption on/from energetically heterogeneous solid surfaces. These papers have provided an impressive support for the applicability of that new approach.

The purpose of the present publication is to give a brief sketch of the historical development of the kinetic research, its current state, and the perspectives of a further development based on using the SRT approach. Also certain fundamental features of that approach, not investigated systematically yet, will be brought into light. This is, how the experimental conditions may affect seriously the observed adsorption/desorption kinetics. That feature of adsorption kinetics was not predicted by the classical ART approach.

Theory

The Classical Absolute Rate Theory (ART) Approach and its Further Modifications

The principles of the ART approach are generally known. However, before discussing more recent approaches challenging the ART, we will briefly review the application of those principles to the adsorption/desorption kinetics (Clark, 1970; Elliot and Ward, 1997a), for further comparison.

Thus, the adsorbing or desorbing molecule must first form an activated complex. The molecules in the activated state are in equilibrium with the gas molecules and the rate of adsorption is the rate at which molecules pass through the activated state. The activation energy for adsorption ε_a is the difference between energies in the gaseous and "activated" states. The rate of adsorption R_a, is then given by,

$$R_a = \alpha \nu F(\theta) \exp\left(\frac{-\varepsilon_a}{kT}\right) \tag{1}$$

where $\nu = p/\sqrt{2\pi mkT}$ is the rate of collision of the gas molecule of mass m with the surface, $F(\theta)$ is the fraction of surface available for adsorbing molecules, p is the pressure and k and T are the Boltzmann constant and absolute temperature respectively.

The activation energy for desorption, ε_d, is defined as the difference in energies of the adsorbed molecules and those in the activated state for desorption. The desorption rate, R_d, is given by the expression,

$$R_d = \gamma G(\theta) \exp\left(\frac{-\varepsilon_d}{kT}\right) \tag{2}$$

where γ is a constant, and $G(\theta)$ is another unspecified function of the surface coverage θ. The time dependence of the surface coverage $(d\theta/dt)$ is, thus, given by,

$$\frac{d\theta}{dt} = R_a - R_d \tag{3}$$

The ART alone does not make it possible to develop explicit expressions for the functions $F(\theta)$ and $G(\theta)$ and does not provide an answer for the question whether α, γ, ε_a, ε_d might depend on the surface coverage θ (Elliot and Ward, 1997a). The coverage dependence was introduced first on a semi-empirical basis, and the expression for $(d\theta/dt)$ has, usually been written in the following form,

$$\frac{d\theta}{dt} = K_a p(1-\theta)^s\, e^{\frac{-\varepsilon_a}{kT}} - K_d \theta^s\, e^{\frac{-\varepsilon_d}{kT}} \tag{4}$$

where s is the number of adsorption sites involved into an elementary adsorption-desorption process. In the case $s = 1$, at the equilibrium when $(d\theta/dt) = 0$, Eq. (4) yields the Langmuir isotherm equation

$$\theta^{(e)}(p, T) = \frac{Kp^{(e)} \exp(\varepsilon/kT)}{1 + Kp^{(e)} \exp(\varepsilon/kT)} \tag{5}$$

where $K = K_a/K_d$ and $\varepsilon = (\varepsilon_d - \varepsilon_a)$, and where the superscript (e) refers to equilibrium.

For that reason Eq. (4) has been frequently called in literature "*Langmuirian adsorption kinetics*". Paradoxically, the Langmuir isotherm equation appeared to be much more successful formula to describe gas/solid equilibria than the kinetic equations by which the Langmuir equation was developed.

The experimentally measured equilibrium adsorption isotherms followed commonly the "*Langmuirian shape*" to a more or lesser extent. The reported deviations could be easily explained by possible effects of multilayer adsorption at high surface coverages, or effects of surface energetic heterogeneity of the actual solid surfaces at lower coverages in particular (Rudzinski and Everett, 1992). Some of the observed deviations from the "*Langmuirian behavior*" could easily be explained based on interactions between the adsorbed molecules.

Meanwhile, the commonly observed dramatical inapplicability of the "*Langmuirian kinetics*" Eq. (4) could hardly be explained in a simple way. Nevertheless, attempts to interpret the observed data on the adsorption/desorption kinetics went, almost exclusively, towards improving the ART approach for that purpose. Progress in revising its fundamentals was delayed by the historical development of experiment. Let us have a brief look at it.

Thus, studies of the adsorption/desorption kinetics which were carried out during the first half of the previous XX-th century, concerned isothermal adsorption kinetics. They have been reviewed in the excellent detailed article by Low, published in 1960 (Low, 1960). Those studies of isothermal adsorption kinetics focused on the initial character of adsorption kinetics, measured at low surface coverages. Although desorption kinetics could be safely neglected under these conditions, the inapplicability of the Langmuirian adsorption term,

$$R_a = K_a p(1-\theta)^s e^{-\frac{\varepsilon_a}{kT}} \tag{6}$$

was so dramatically visible, that it was practically never used for correlation of experimental kinetic data. Instead, the empirical Elovich equation appeared as a very successful formula (Low, 1960),

$$\frac{d\theta_t}{dt} = a\, e^{-b\theta} \tag{7}$$

where a and b are constants, characteristic for the adsorption system under investigation.

The Elovich equation gained so enormous popularity, that even the analysis by Low of the experimental data collected during the first half of the previous century, was based on accepting the fundamental character of the Elovich equation.

Attempts to explain the theoretical origin of Elovich equation went toward assuming that the actual solid surfaces are energetically heterogeneous. Such an assumption seemed to be obvious because neither desorption nor interactions between the adsorbed molecules could substantially affect the kinetics of adsorption at low surface coverages. Also, from the beginning of the forties, numerous papers brought more and more convincing evidence regarding the crucial effect of the surface energetic heterogeneity on the equilibria of adsorption in the gas/solid systems (Rudzinski and Everett, 1992).

The Elovich equation was developed from the ART adsorption term (6) assumming that there is dispersion of the activation energy for adsorption ε_a, on various adsorption sites described by the rectangular distribution (Aharoni and Tompkins, 1970),

$$\chi(\varepsilon_a) = \begin{cases} \dfrac{1}{\varepsilon_{am} - \varepsilon_{al}} & \text{for } \varepsilon \in (\varepsilon_{al}, \varepsilon_{am}) \\ 0 & \text{elsewhere} \end{cases} \tag{8}$$

where ε_{al} and ε_{am} are the lowest (l), and the maximum (m) values of ε_a, on the investigated solid surface.

However, neglecting the simultaneously occurring desorption led scientists to missing (on purpose or not) the answer to the very fundamental question which then appeared. Namely, if distribution of activation energies exists for adsorption, ε_a, $\chi_a(\varepsilon_a)$ then, there must also exist a distribution of the activation energies for desorption, ε_d, $\chi_d(\varepsilon_d)$. So, is there a correlation between ε_a and ε_d on various adsorption sites? Consequently, a rigorous description of the adsorption/desorption kinetics based on the complete Eq. (4) would consequently involve introduction of three functions:

- the distribution of the activation energies for adsorption, $\chi_a(\varepsilon_a)$,
- the distribution of the activation energies for desorption, $\chi_d(\varepsilon_d)$,
- the correlation function, $\chi_c(\varepsilon_a, \varepsilon_d)$.

Such a rigorous description of the adsorption/desorption kinetics based on ART has never been attempted in open literature. The inconsistencies of the theoretical descriptions, based on the ART approach to kinetics of isothermal adsorption, have been analyzed recently in the review by Rudzinski and Panczyk (1999).

When Low published in 1960 his exhaustive review and analysis of the existing experimental data on the isothermal kinetics of adsorption, another kind of kinetic experiments started, which soon gained an enormous popularity among the scientists working on adsorption and catalysis. It was the programmed thermodesorption (TPD), first described in the papers by Cvetanovic and Amenomiya (Amenomiya and Cvetanovic, 1963; Cvetanovic and Amenomiya, 1972). These experiments provided even more impressive evidence of the inapplicability of Eq. (4) to interpret the recorded thermodesorption spectra. The commonly accepted method of TPD spectra analysis involved the concept of surface energetic heterogeneity, and sometimes also interactions between the adsorbed molecules. However, all more or less advanced interpretations were based on neglecting re-adsorption, i.e., on the truncated form of Eq. (4) including only the desorption term. This has been discussed in the recent reviews by Rudzinski and Panczyk (Rudzinski et al., 1998; Rudzinski et al., 2000).

Thus neglecting re-adsorption led again scientists to missing the answer to the fundamental question of the ART approach concerning the correlations between ε_a and ε_d on various adsorption sites. Attempts to solve that question would have surely added more doubts concerning the fundamentals of the ART approach when applied to the adsorption/desorption kinetics. However, it was not only the energetic heterogeneity of the majority of the actually existing solid surfaces, which put into question the validity of the ART approach.

Progress in the preparation of relatively homogeneous solid surfaces, (single crystal faces, etc.) created also interest in investigating the kinetics of adsorption on such surfaces. And, again, the experiments on isothermal adsorption kinetics provided further evidence for inapplicability of the ART approach. However, the idea of abandoning that approach did not emerge quickly. First numerous attempts were made to improve the fundamentals of that approach.

Thus Kisliuk (1957) introduced his idea of *precursor states* to derive a coverage dependent equation for the sticking probability which he defined as the number of molecules being adsorbed divided by the number of molecules striking the surface. The equation which Kisliuk worked out in 1957 was following (Elliot and Ward, 1997a)

$$\frac{S}{S_0} = \left(1 + \frac{\theta}{1-\theta}\aleph\right)^{-1} \tag{9}$$

where S is the sticking probability, S_0 is the sticking probability at the initial time, and $\aleph$ is a new parameter. Note that if $\aleph$ equals unity, the sticking probability reduces to the Langmuirian form:

$$S = S_0(1-\theta) \tag{10}$$

Twenty years later in 1977 King (1977) considered two types of precursor states: one type existing over a filled adsorption site and the other one over an unfilled site.

One year later, Gorte and Schmidt (1978) assumed that adsorption is a two step process in which the molecules first form a weakly bound precursor phase before being adsorbed. Gorte and Schmidt found that the desorption rate could be written as follows,

$$R_d = \frac{k^* k_d}{k_a}\frac{\theta}{1-\theta} \tag{11}$$

where k^*, k_d, and k_a are the rate coefficients for the transition from the activated state to the gas, from the adsorbed state to the activated state and from the activated state to the adsorbed state respectively. Gorte and Schmidt admitted that the only evidence for the existence of the precursor states was a better agreement of their new equation with experiment.

New Approaches Based on Considering Chemical Potentials of the Bulk and the Adsorbed Molecules

At the beginning of the eighties a certain feeling started to grow that the fundamental features of the adsorption/desorption kinetics should be related to the chemical potential of the adsorbed molecules μ^s. For historical reasons the approach proposed by Nagai (1985) in 1985 could be considered first. This is because the idea behind that approach can be traced back to de Boer in 1956 (de Boer, 1956). In this approach the rate of desorption R_d is represented by,

$$R_d = \xi \exp\left(\frac{\mu^s - \varepsilon_d}{kT}\right) \tag{12}$$

where μ^s is the chemical potential of the adsorbed molecules and ξ is a constant.

Nagai's proposal raised objections and heated discussion (Zhdanov, 1986; Nagai, 1986; Cassuto, 1988; Nagai, 1988), but finally, Nagai presented proof (Nagai, 1991) that his expression (12) is superior to the R_d expression derived from the ART approach. Using the hard hexagon adsorption model Nagai showed that the ART approach underestimates the role of entropy changes as a factor affecting the kinetics of adsorption/desorption processes.

Since we have taken the Langmuir model for consideration, the chemical potential μ^s of the adsorbed molecules is given by the expression:

$$\mu^s = kT \ln\frac{\theta}{1-\theta} - kT \ln q^s \tag{13}$$

where q^s is the molecular partition function of the adsorbed molecules. It is commonly written in the following form,

$$q^s = q_0^s \exp\left(\frac{\varepsilon}{kT}\right) \tag{14}$$

where q_0^s is the molecular partition function of the adsorbed molecules which include all internal degrees of freedom.

So, R_d in Eq. (12) takes now the following form,

$$R_d = \frac{\xi}{q_0^s}\frac{\theta}{1-\theta}\exp\left(-\frac{\varepsilon + \varepsilon_d}{kT}\right) \tag{15}$$

The approach proposed by Kreuzer and Payne in 1988 (Kreuzer, 1988; Payne, 1989; Kreuzer, 1991, 1997) can also be classified as relating the features of adsorption/desorption kinetics to the chemical potential of adsorbed molecules, μ^s. Although they failed to mention it, they followed the assumption made by Kubokawa (1938) that the rate of adsorption should be proportional to the difference between the actual (nonequilibrium) pressure p, and the equilibrium pressure $p^{(e)}$ corresponding to the same surface coverage. On this basis they wrote the expressions for R_a and R_d in the following form,

$$R_a = S(\theta) p \frac{\alpha_s}{(2\pi mkT)^{1/2}} \tag{16}$$

$$R_d = S(\theta) p^{(e)} \frac{\alpha_s}{(2\pi mkT)^{1/2}} \tag{17}$$

where $S(\theta)$ is the "sticking coefficient" and α_s is the surface area associated with one adsorption site. The equilibrium pressure $p^{(e)}$ is now expressed in terms of the gas-phase chemical potential, μ^g

$$p^{(e)} = kT\left(\frac{2\pi mkT}{h^2}\right)^{3/2} q_0^g \exp\left(\frac{\mu^g}{kT}\right) \tag{18}$$

where q_0^g is the partition function of gas molecules related to their internal degrees of freedom. At equilibrium, $\mu^g = \mu^s$, so, R_d takes the following form,

$$R_d = S(\theta)\alpha_s kT \frac{2\pi mkT}{h^3} q_0^g \exp\left(\frac{\mu^s}{kT}\right) \tag{19}$$

which is similar to Nagai's expression (12). The coverage dependence of the sticking coefficient $S(\theta)$ cannot be obtained from thermodynamic arguments. If it is postulated that $S(\theta) = S_0(1-\theta)$ the Kreuzer–Payne expressions for R_a and R_d take the form of the classical ART expressions, with zero activation energy for adsorption. For the rate of adsorption we have,

$$R_a = \frac{S_0 \alpha_s p(1-\theta)}{(2\pi mkT)^{1/2}} \tag{20}$$

By replacing μ^s in Eq. (19) by expression (13), we obtain,

$$R_d = S_0 \alpha_s kT \frac{2\pi mkT}{h^3}\frac{q_0^g}{q_0^s}\theta \exp\left(\frac{-\varepsilon}{kT}\right) \tag{21}$$

On the other hand, since the physical meaning of the sticking coefficient is obscure, one may arbitrarily assign a value of unity. Then, R_d in Eq. (21) has the same coverage dependence as the Nagai's expression (12). In both cases, Kreuzer's approach leads to the Langmuir isotherm at equilibrium, i.e. when $R_a = R_d$.

One important feature of the new approaches discussed above (Nagai and Kreuzer) is that they relate the rate of adsorption/desorption to the features of equilibria of adsorption. This is because the adsorption energy ε, is inhered in the expression for μ^s. The additional appearance of ε_d in Nagai's equation (12) can be related to its semi-empirical character. Similarly, the appearance of ε_d in Kreuzer's papers is the result of seeking relations between ε and ε_d, to follow (unnecessarily) the ideas of ART so commonly accepted at that time.

Finally, in 1982 there appeared a publication describing the adsorption/desorption kinetics solely in terms of the same quantities and functions which have been used to describe adsorption equilibria. This was the paper by Ward and Findlay (1982) introducing a new approach called the Statistical Rate Theory (SRT). The fundamentals of that new approach have, recently been reviewed by Elliot and Ward (1997b).

The objective of SRT approach was to obtain explicit dependence of the rate expressions on coverage. Based on quantum mechanics and thermodynamics for isothermal adsorption they have developed the following rate expressions,

$$R_a = K'_{gs} \exp\left(\frac{\mu^g - \mu^s}{kT}\right) \tag{22}$$

$$R_d = K'_{gs} \exp\left(\frac{\mu^s - \mu^g}{kT}\right) \tag{23}$$

where K'_{gs} is a constant for an isolated system.

The physical meaning of K'_{gs} was discussed in the first paper by Ward and Findlay (1982), as well as in the recent publications by Ward and co-workers (Elliot and Ward, 1997a, b). K'_{gs} is the exchange rate between the gas phase and the solid surface once an isolated system has reached equilibrium. To a good approximation, K'_{gs} can be written as the following product, (Elliot and Ward, 1997a, b)

$$K'_{gs} = K_{gs} p^{(e)} \left(1 - \theta^{(e)}\right) \tag{24}$$

where the equilibrium state (e) is defined as the one to which a system isolated at the surface coverage θ and gas phase concentration with the partial pressure p would evolve.

So far, Ward and coworkers have put into analysis only a few adsorption systems with well-defined solid surfaces. Their analysis has proved the superiority of the SRT approach over the classical ART approach to describe the recorded kinetic data quantitatively. Meanwhile, very recently, an even more impressive proof has come from considering the kinetics of adsorption/desorption on/from the energetically heterogeneous solid surfaces of the actual solids.

In the recent series of papers Rudzinski and coworkers have generalized the SRT approach to describe kinetics of adsorption/desorption on/from eneregtically hetrogeneous solid surfaces. (Rudzinski and Panczyk, 1999; Rudzinski et al., 2000a; Rudzinski and Aharoni, 1997; Rudzinski, 1996; Rudzinski and Aharoni, 1995; Rudzinski et al., 1996, 1997, 1998, 1999, 2000b; Rudzinski and Panczyk, 2000; Rudzinski et al., 2000c). That generalization concerned both the isothermal adsorption kinetics and the kinetics of thermodesorption. It has been shown, that the well-known empirical kinetic equations like Elovich or Power-Law, describe the kinetics of isothermal adsorption in the systems where the adsorption equilibria are described by some well-known isotherm equations like Temkin or Freundlich equation. (Rudzinski and Everett, 1992). Moreover, a more general form of these kinetic equations has been developed by taking rigorously into account both the adsorption and desorption terms.

The Statistical Rate Theory (SRT) Approach and Langmuir Model of Adsorption

While considering the kinetics of thermodesorption from energetically heterogeneous surfaces, in one of our very recent publications (Rudzinski et al., 2000c), we put into consideration still another important physical factor brought into light by the SRT approach. Namely, depending on the conditions under which the experiment is carried out, one may observe somewhat different behaviour of the adsorption/desorption kinetics. Since at equilibrium (e) the ART rate expressions (22, 23) yield the Langmuir isotherm (5), it would be interesting to see first, which rate expressions are obtained on the ground of the SRT approach, when the Langmuir model of adsorption is accepted. To see to what extent the experimental conditions (including the technical characteristics of the experimental set-up) may affect the observed adsorption/desorption kinetics, we will study here the features of the following three extreme kinds of adsorption system, considered in one of our recent publications focused on thermodesorption kinetics. (Rudzinski et al., 2000c):

1. The adsorption process is essentially a non-equilibrium one, and the features of a gas/solid system are "volume dominated," i.e., the amount of the gas in the gas phase above the surface dominates strongly over the adsorbed portion. In that case, after the system is isolated and equilibrated, the gas pressure p does not change much, so that $p^{(e)} \approx p$.
2. The process is a non-equilibrium one, but the features of a gas/solid system are "solid dominated". In the case of the "solid dominated" system the adsorbed amount prevails so strongly over the amount in the bulk gas phase, that after isolating the system and equilibrating, θ remains practically unchanged, so that $\theta \approx \theta^{(e)}$.
3. The process is carried out under such conditions that the gas/solid system is close to equilibrium. We will call such system—"equilibrium dominated," i.e., the process is carried out under such conditions, that one may assume $\theta \approx \theta^{(e)}$ and $p \approx p^{(e)}$.

Then in view of Eq. (24) the expression for $(d\theta/dt)$ now takes the form,

$$\frac{d\theta}{dt} = \left[K_a p \frac{1-\theta}{\theta} \exp\left(\frac{\varepsilon}{kT}\right) - K_d \frac{1}{p} \frac{\theta}{1-\theta} \times \exp\left(-\frac{\varepsilon}{kT}\right)\right] \left[1-\theta^{(e)}\right] p^{(e)} \tag{25}$$

where

$$K_a = K_{gs} q_0^s \exp\left(\frac{\mu_0^g}{kT}\right), \quad K_d = \frac{K_{gs}}{q_0^s} \exp\left(-\frac{\mu_0^g}{kT}\right) \tag{26}$$

At equilibrium, when $(d\theta/dt) = 0$, Eq. (26) yields the Langmuir isotherm (5), in which

$$K = \sqrt{K_a/K_d} = q_0^s \exp\left(\mu_0^g/kT\right). \tag{27}$$

Thus,

$$1 - \theta^{(e)} = \frac{1}{1 + Kp^{(e)} \exp\left(\frac{\varepsilon}{kT}\right)}. \tag{28}$$

Thus, for the "volume dominated" (V) systems we have,

$$\frac{d\theta}{dt} = \left[K_a p^2 \frac{1-\theta}{\theta} \exp\left(\frac{\varepsilon}{kT}\right) - K_d \frac{\theta}{1-\theta} \times \exp\left(-\frac{\varepsilon}{kT}\right)\right] \left[1 + Kp \exp\left(\frac{\varepsilon}{kT}\right)\right]^{-1}, \tag{29}$$

whereas for the "solid dominated" (S) systems, we obtain

$$\frac{d\theta}{dt} = \frac{K_a}{K} p(1-\theta) - \frac{K_d}{K} \frac{1}{p} \frac{\theta^2}{(1-\theta)} \exp\left(-\frac{2\varepsilon}{kT}\right). \tag{30}$$

Finally, for the "equilibrium dominated" (E) systems we arrive at the following expression,

$$\frac{d\theta}{dt} = K_a p^2 \frac{(1-\theta)^2}{\theta} \exp\left(\frac{\varepsilon}{kT}\right) - K_d \theta \exp\left(-\frac{\varepsilon}{kT}\right). \tag{31}$$

Equations (29–31) describe the kinetics of adsorption/desorption on a hypothetical energetically homogeneous solid surface, where all the adsorption sites are characterized by the same adsorption energy ε. While considering the dependence of $(d\theta/dt)$ on the surface coverage θ, none of them is identical with the ART rate expression (4). The striking differences and apparently an unusual form of these kinetic equations may arise the question of their physical significance. Furthermore we are going to demonstrate that they predict typical features of the gas adsorption/desorption kinetics, observed in experiment.

The reported experimental data are usually shown as the coverage θ is changing with time. So, it is desirable to have integral forms of these kinetic equations. Let us consider E-systems first (Eq. 31).

To arrive at the function $\theta(t)$ we apply the integration by parts,

$$\int \frac{d\theta}{K_a p^2 \frac{(1-\theta)^2}{\theta} \exp\left(\frac{\varepsilon}{kT}\right) - K_d \theta \exp\left(-\frac{\varepsilon}{kT}\right)} = \int dt = t + C \tag{32}$$

where C is an integration constant. The integral on the left hand side of Eq. (32) can be evaluated analytically. While assuming that $\theta(t=0)=0$, we arrive at the following integral form of this kinetic equation.

$$t(\theta) = \frac{1}{2\left(K_a p^2 e^{\frac{\varepsilon}{kT}} - K_d e^{-\frac{\varepsilon}{kT}}\right)} \ln\left|K_a p^2 e^{\frac{\varepsilon}{kT}} - 2K_a p^2 e^{\frac{\varepsilon}{kT}} \theta + \left(K_a p^2 e^{\frac{\varepsilon}{kT}} - K_d e^{-\frac{\varepsilon}{kT}}\right)\theta^2\right| - \frac{\sqrt{\frac{K_a}{K_d}}\, p e^{\frac{\varepsilon}{kT}}}{K_a p^2 e^{\frac{\varepsilon}{kT}} - K_d e^{-\frac{\varepsilon}{kT}}}$$

$$\times \operatorname{ar\,tanh}\left[\frac{\sqrt{K_a K_d}\,p}{\left(K_a p^2 e^{\frac{\varepsilon}{kT}} - K_d e^{-\frac{\varepsilon}{kT}}\right)\theta - K_a p^2 e^{\frac{\varepsilon}{kT}}}\right] + C \tag{33}$$

where,

$$C = \frac{\sqrt{\frac{K_a}{K_d}}\,p e^{\frac{\varepsilon}{kT}}}{K_a p^2 e^{\frac{\varepsilon}{kT}} - K_d e^{-\frac{\varepsilon}{kT}}} \operatorname{ar\,tanh}\left[-\sqrt{\frac{K_d}{K_a}\,\frac{e^{-\frac{\varepsilon}{kT}}}{p}}\right] - \frac{1}{2\left(K_a p^2 e^{\frac{\varepsilon}{kT}} - K_d e^{-\frac{\varepsilon}{kT}}\right)} \ln\left|K_a p^2 e^{\frac{\varepsilon}{kT}}\right| \tag{34}$$

In a similar way we arrive at the θ(t) function for the volume dominated (V) (Eq. 29) systems

$$\begin{aligned} t(\theta) = {} & \theta \frac{1 + Kpe^{\frac{\varepsilon}{kT}}}{K_d e^{-\frac{\varepsilon}{kT}} - K_a p^2 e^{\frac{\varepsilon}{kT}}} \\ & - \frac{\left(K_a p^2 e^{\frac{\varepsilon}{kT}} + K_d e^{-\frac{\varepsilon}{kT}}\right)\left(1 + Kpe^{\frac{\varepsilon}{kT}}\right)}{2\left(K_a p^2 e^{\frac{\varepsilon}{kT}} - K_d e^{-\frac{\varepsilon}{kT}}\right)^2} \\ & \times \ln\left|\frac{K_a p^2 e^{\frac{\varepsilon}{kT}}}{1 + Kpe^{\frac{\varepsilon}{kT}}} - 2\theta \frac{K_a p^2 e^{\frac{\varepsilon}{kT}}}{1 + Kpe^{\frac{\varepsilon}{kT}}} + \frac{K_a p^2 e^{\frac{\varepsilon}{kT}} - K_d e^{-\frac{\varepsilon}{kT}}}{1 + Kpe^{\frac{\varepsilon}{kT}}}\theta^2\right| \\ & + \frac{2\left(1 + Kpe^{\frac{\varepsilon}{kT}}\right)\sqrt{K_a K_d}\,p}{\left(K_a p^2 e^{\frac{\varepsilon}{kT}} - K_d e^{-\frac{\varepsilon}{kT}}\right)^2} \\ & \times \operatorname{ar\,tanh}\left[\frac{\sqrt{K_a K_d}\,p}{\left(K_a p^2 e^{\frac{\varepsilon}{kT}} - K_d e^{-\frac{\varepsilon}{kT}}\right)\theta - K_a p^2 e^{\frac{\varepsilon}{kT}}}\right] \\ & + C \end{aligned} \tag{35}$$

where the integration constant corresponding to the condition $\theta(t = 0) = 0$, takes now the following form

$$\begin{aligned} C = {} & -\frac{2\left(1 + Kpe^{\frac{\varepsilon}{kT}}\right)\sqrt{K_a K_d}\,p}{\left(K_a p^2 e^{\frac{\varepsilon}{kT}} - K_d e^{-\frac{\varepsilon}{kT}}\right)^2} \\ & \times \operatorname{ar\,tanh}\left[-\sqrt{\frac{K_d}{K_a}\,\frac{e^{-\frac{\varepsilon}{kT}}}{p}}\right] \\ & + \frac{\left(K_a p^2 e^{\frac{\varepsilon}{kT}} + K_d e^{-\frac{\varepsilon}{kT}}\right)\left(1 + Kpe^{\frac{\varepsilon}{kT}}\right)}{2\left(K_a p^2 e^{\frac{\varepsilon}{kT}} - K_d e^{-\frac{\varepsilon}{kT}}\right)^2} \\ & \times \ln\left|K_a p^2 e^{\frac{\varepsilon}{kT}}\right| \end{aligned} \tag{36}$$

Finally for the S-systems (Eq. 30) we have

$$\begin{aligned} t(\theta) = {} & \frac{K}{2\left(K_d \frac{1}{p} e^{-\frac{2\varepsilon}{kT}} - K_a p\right)} \ln\left|\frac{K_a}{K} p - 2\frac{K_a}{K} p\theta + \left(\frac{K_a}{K} p - \frac{K_d}{K}\frac{1}{p} e^{-\frac{2\varepsilon}{kT}}\right)\theta^2\right| \\ & + \frac{e^{-\frac{\varepsilon}{kT}}}{K_a p^2 - K_d e^{-\frac{2\varepsilon}{kT}}} \\ & \times \operatorname{ar\,tanh}\left[\frac{\sqrt{K_a K_d}\,e^{-\frac{\varepsilon}{kT}}}{\left(K_a p - K_d \frac{1}{p} e^{-\frac{2\varepsilon}{kT}}\right)\theta - K_a p}\right] + C \end{aligned} \tag{37}$$

and the integration constant is now given by

$$C = -\frac{e^{-\frac{\varepsilon}{kT}}}{K_a p^2 - K_d e^{-\frac{2\varepsilon}{kT}}} \operatorname{ar\,tanh}\left[-\sqrt{\frac{K_d}{K_a}\frac{1}{p} e^{-\frac{\varepsilon}{kT}}}\right] - \frac{K}{2\left(K_d \frac{1}{p} e^{-\frac{2\varepsilon}{kT}} - K_a p\right)} \ln\left|\frac{K_a}{K} p\right| \tag{38}$$

The above consideration shows that one may have to deal with a variety of kinetic equations corresponding to the same Langmuirian model of adsorption. (localized one-site-occupancy adsorption by only one molecule, and no interactions between the adsorbed molecules). Therefore calling Eq. (4) the "Langmuirian kinetics" is not justified, because various kinetic equations may lead to the Langmuir isotherm equation at equilibrium. Moreover, the ART expression (4) seems to have an even less defined theoretical background than the others, developed using the SRT approach.

The classical ART approach does not predict that the experimental conditions may affect the recorded kinetic data i.e. the measured $\theta(t)$ function. The very recent paper by (Rudzinski et al., 2000c) showed how the experimental conditions affect the kinetics of thermodesorption. However, even on the ground of SRT approach no systematic investigation has been reported yet showing how the experimental conditions may affect the isothermal adsorption kinetics. Thus, we have decided to carry out some model investigation based on Eqs. (33–38) to see, how for the same thermodynamic parameters, K_a, K_d, ε, T, p, the kinetics of adsorption may look like for the E, V, and S-systems. Some examples of our model investigation are shown in Figs. (1–4).

Looking to the calculated $\theta(t)$ functions, one can see their obvious similarities to the experimental data reported in various papers. (Rudzinski and Panczyk, 2000) Thus, although the SRT kinetic equations (29–31) may look strikingly different than the classical equation (4), they correctly predict the observed physical features.

As an example we show in Fig. 5 a certain selection of experimental data available in Literature. These are the cases where the kinetic isotherms were measured

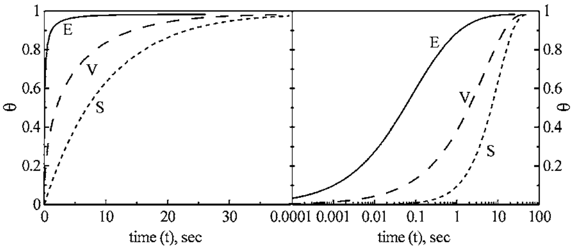

Figure 1. Comparison of the $\theta(t)$ functions calculated for the E, V, and S-systems, for the same set of parameters: $\varepsilon = 50$ kJ/mol, $p = 101325$ Pa, $T = 298$ K, $K_a = 9.74 \times 10^{-15}$ Pa^{-2} s^{-1}, $K_d = 10^6$ s^{-1}. The solid line (———) was calculated for the E-systems, using Eqs. (33) and (34), the slightly broken line (— — —) was calculated for the V-systems using Eqs. (35) and (36), whereas the strongly broken line (– – –) was calculated for the S-systems using Eqs. (37) and (38).

from very short times (i.e. from small surface coverages), up to coverages close to their equilibrium values.

However, we do not carry out a quantitative analysis of these data using the SRT kinetic equations developed here. The reason for that is following.

Langmuir isotherm equation describes adsorption equilibria in the systems with energetically equivalent

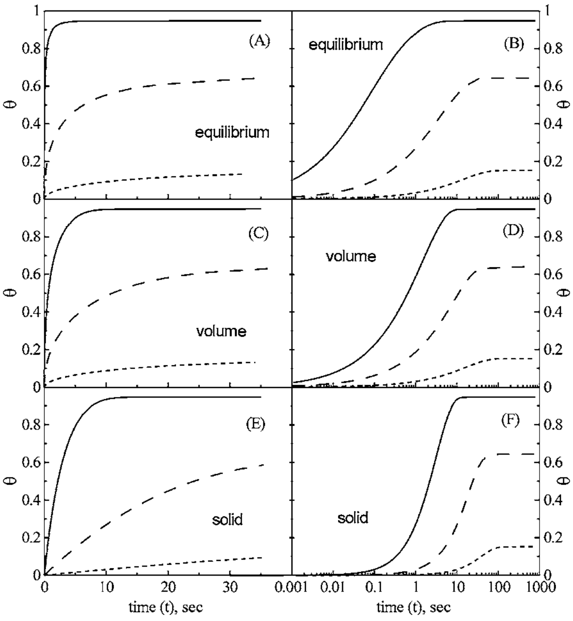

Figure 2. Comparison of $\theta(t)$ functions calculated for the E-systems (A, B), V-systems (C, D) and S-systems (E, F), for the same set of the parameters: $\varepsilon = 50$ kJ/mol, $T = 298$ K, $K_a = 9.74 \times 10^{-15}$ Pa^{-2} s^{-1}, $K_d = 10^7$ s^{-1}, and for three different values of pressure p: 101325 Pa (———), 10132.5 Pa (— — —), and 1013.25 Pa (– – –).

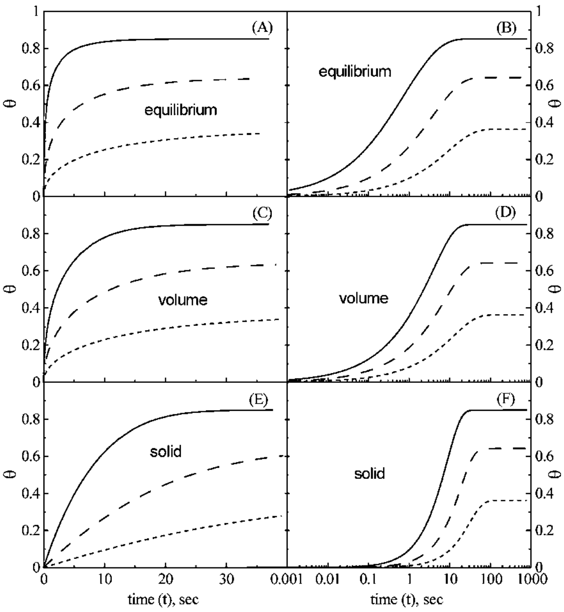

Figure 3. Comparison of $\theta(t)$ functions calculated for the E-systems (A, B), V-systems (C, D) and S-systems (E, F), for the same set of the parameters: $\varepsilon = 50$ kJ/mol, $p = 10132.5$ Pa, $T = 298$ K, $K_d = 10^7$ s^{-1}, and for three different values of the parameter K_a: 9.74×10^{-14} Pa^{-2} s^{-1} (———), 9.74×10^{-15} Pa^{-2} s^{-1} (— — —), and 9.74×10^{-16} Pa^{-2} s^{-1} (– – –).

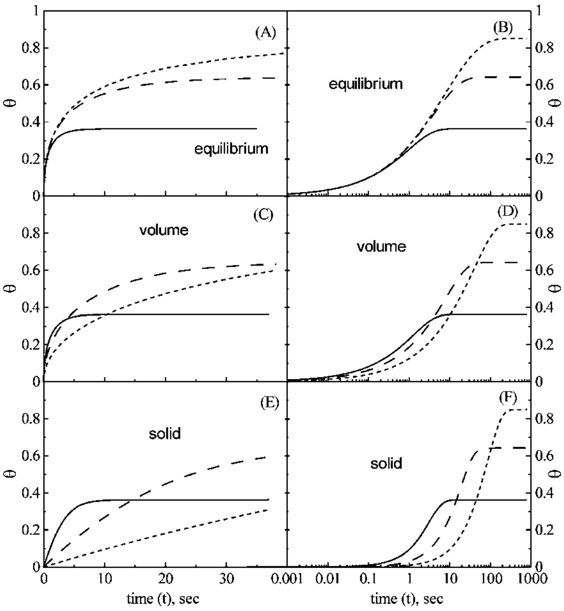

Figure 4. Comparison of $\theta(t)$ functions calculated for the E-systems (A,B), V-systems (C,D) and S-systems (E,F), for the same set of the parameters: $\varepsilon = 50$ kJ/mol, $p = 10132.5$ Pa, $T = 298$ K, $K_a = 9.74 \times 10^{-15}$ Pa^{-2} s^{-1}, and for three different values of the parameter K_d: 10^8 s^{-1} (———), 10^7 s^{-1} (— — —), and 10^6 s^{-1} (– – –).

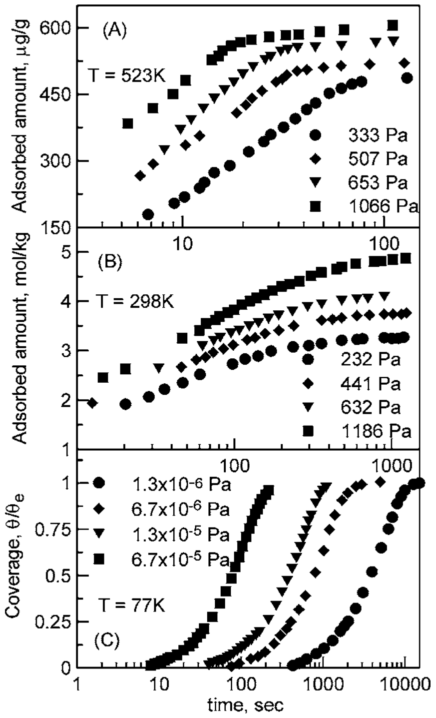

Figure 5. (A) Kinetics of CO_2 adsorption on Sc_2O_3 (Pajares, 1978), (B) kinetics of benzene adsorption on activated carbon (Wojsz, 1989) and (C) kinetics of O_2 adsorption on pollycrystalline tungsten (θ_e is the corresponding equilibrium coverage) (Lopez-Sancho, 1972).

adsorption sites. Meanwhile, in majority of the studied gas/solid systems this assumption is too crude for to be accepted in a quantitative analysis of adsorption equilibria. This, of course, will also be true for a quantitative analysis of adsorption kinetics in the real adsorption systems.

Among the important physical factors the energetic surface heterogeneity but also interactions between the adsorbed molecules have to be considered first. The way in which they can be incorporated into the SRT approach has been outlined in one of our very recent publications dealing with kinetics of thermodesorption. (Rudzinski et al., 2000c) In the case of isothermal adsorption kinetics only the equilibrium dominated systems have been considered so far by us. (Rudzinski and Panczyk, 2001) Applications of the presently developed equations to quantitatively analyze some already reported experimental data on isothermal kinetics will be a subject of our future publications. The purpose of the present publication was to discuss the fundamentals of the isothermal adsorption kinetics corresponding to the Langmuir model of adsorption.

The presented model investigation seems to suggest that the experimental conditions may have pronounced effects on the observed kinetics of isothermal adsorption. Thus, while considering other physical factors which may considerably affect adsorption kinetics, the conditions at which the experiment is carried out must also be considered.

Conclusions

Since the beginning of the XXth century, Langmuir isotherm equation was commonly associated with certain equations describing the kinetics of adsorption. Adsorption was viewed as a kind of surface reaction considered in terms of the Absolute Rate Theory. This approach led to various difficulties in the theoretical interpretation of the observed adsorption kinetics. Attempts to improve that approach led to more and more complicated expressions, but certain fundamental difficulties still remained unsolved.

A breaking moment was publication in the last decade of the last century of a new approach relating the kinetics of adsorption/desorption to the chemical potentials of the molecules in the adsorbed and the bulk phase. Recently a series of papers has been published showing a successful application of that new approach to the theoretical interpretation of both the isothermal adsorption kinetics, and the kinetics of thermodesorption.

The purpose of the present publication was to show which kinetic equations, obtained by using this approach, correspond to Langmuir equation at equilibrium.

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Nomenclature

a	Coefficient in Eq. (7) (s^{-1})
b	Coefficient in Eq. (7)
R_a	Rate of adsorption (mol/s)
$F(\theta)$	Fraction of surface available for adsorbing molecules
$G(\theta)$	Fraction of surface occupied by adsorbed molecules
k	Boltzmann constant (J/(mol K))

k^*, k_d, k_a	The rate coefficients for the transition from the activated state to the gas, from the adsorbed state to the activated state and from the activated state to the adsorbed state, respectively (s^{-1})
K	Langmuir constant (Pa^{-1})
K_a	Pre-exponential factor for adsorption (Pa^{-1} s^{-1} (ART) or Pa^{-2} s^{-1}(SRT))
K_d	Pre-eksponential factor for desorption (s^{-1})
K'_{gs}	Parameter defined in Eq. (24)
K_{gs}	Constant in Eq. (24)
m	Mass of molecule
p	Non-equilibrium pressure (Pa)
$p^{(e)}$	Equilibrium pressure (Pa)
q^s	The molecular partition function of the adsorbed molecules
q_0^g	The partition function of gas molecules related to their internal degrees of freedom
s	Order of adsorption/desorption
S	Sticking probability
S_0	Sticking probability at the initial time
T	Absolute temperature (K)
α	Sticking coefficient
α_s	The surface area associated with one adsorption site (m^2)
γ	Coefficient in Eq. (2)
χ_a	Distribution of activation energy for adsorption (mol/kJ)
χ_d	Distribution of activation energy for desorption (mol/kJ)
χ_c	Correlation function
ν	Rate of collisions (s^{-1})
ε	Energy for adsorption/desorption (kJ/mol)
ε_a	Activation energy for adsorption (kJ/mol)
ε_d	Activation energy for desorption (kJ/mol)
ε_{am}	Maximum value of activation energy for adsorption (kJ/mol)
ε_{al}	The lowest value of activation energy for adsorption (kJ/mol)
μ^s	Chemical potential for adsorbed molecules (kJ/mol)
μ^g	Chemical potential for gas phase molecules (kJ/mol)
μ_0^g	Standard chemical potential for perfect gas (kJ/mol)
θ	Non-equilibrium surface coverage
$\theta^{(e)}$	Equilibrium surface coverage
ξ	Constant in Eq. (12)
$\aleph$	Parameter in Eq. (9)

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