A Statistical Rate Theory Approach to Kinetics of Dissociative Gas Adsorption on Solids

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The reaction rate in some important catalytic systems is governed by kinetics of dissociative adsorption of reactants on a catalyst surface. This, for instance, is the case of ammonia synthesis. Since the beginning of the previous century, the expressions based on the theory of activated adsorption/desorption (TAAD) approach have commonly been attempted to analyze the pressure and coverage dependence of the observed kinetics. However, neither the simple classical TAAD approach nor its further modifications attempted during the last few decades could explain the kinetics observed in many important systems. In particular, it concerned the kinetics of dissociative adsorption in chemisorption systems. For instance, no successful attempt was published to describe quantitatively the pressure and coverage dependence of the kinetics of the dissociative dinitrogen adsorption on iron surfaces, studied for a large part of the previous century, in relation to ammonia synthesis. Here we propose the first successful description of that dissociative adsorption kinetics based on the new statistical rate theory approach, linking the rate of the dissociative kinetics to the chemical potentials in the bulk and the adsorbed phases. The developed theoretical expressions are able to describe quantitatively the kinetic isotherms of dinitrogen dissociative adsorption, recorded experimentally at the pressures ranging from 10^{-6} to 10^2 Torr and the temperatures ranging from 140 to 485 K. These expressions also explain some unusual features of this dissociative kinetics, such as small negative apparent activation energy for the dissociative adsorption and the pressure invariance of the kinetics at high dinitrogen pressures, when considered as a function of exposure.

Introduction

In many adsorption systems, the adsorbing molecule should be considered as consisting of a number of mers (segments), each of them being adsorbed on one adsorption site. When the adsorbed molecule preserves its chemical identity, we call it then the "*multisite-occupancy adsorption*". Sometimes, in the course of adsorption, the molecule undergoes a destruction into a number of smaller chemical species, occupying one or more adsorption sites. We call it then the "*dissociative adsorption*". The dissociative adsorption commonly takes place in catalysis where frequently dissociation of reactants is the first step in a catalytic reaction on a solid surface. In some important catalytic reactions, that dissociation is the step controlling the kinetics of that catalytic reaction. This, for instance, is the case of ammonia synthesis on the Fe catalyst.

Since the beginning of the 20th century, the theory of activated adsorption/desorption (TAAD) approach has, almost exclusively, been used for theoretical interpretation of the adsorption/desorption kinetics.[1,2]

According to TAAD, a molecule taking part in a reaction must first form an activated complex. Its creation can be done by an input of energy, the "*activation energy*". It is assumed that molecules in the activated state are in equilibrium with the reactants and that the rate of reaction is the rate at which molecules pass through the activated state. In the case of adsorption, the reactants are a gas-phase molecule and a certain area of surface. The activation energy for adsorption ϵ_a is the energy difference between the energy of a gas-phase molecule and the energy of molecules in the "*activated*" or "*transition*" state.

For desorption, it is assumed that the desorbing molecule must pass through an activated state before desorbing. The activation energy for desorption, ϵ_d, is defined as the difference in energy between the adsorbed molecules and those being in the activated state for desorption. It is assumed that the adsorbed molecules are in equilibrium with the molecules in the activated state.

The change of the surface coverage θ with time t is given as the difference of the adsorption rate R_a and the desorption rate R_d

$$\frac{d\theta}{dt} = R_a - R_d \tag{1}$$

The classical TAAD approach based on the model of localized adsorption offers the following expression for $d\theta/dt$

$$\frac{d\theta}{dt} = K_a p(1-\theta)^s\, e^{-\epsilon_a/kT} - K_d \theta^s\, e^{-\epsilon_d/kT} \tag{2}$$

where s is the number of adsorption sites involved in an elementary adsorption/desorption process (reaction). In the case $s = 1$, i.e., when one molecule occupies one adsorption site, at the equilibrium when $d\theta/dt = 0$, eq 2 yields the Langmuir isotherm equation

$$\theta^{(e)}(p,T) = \frac{Kp^{(e)} \exp\left(\frac{\epsilon}{kT}\right)}{1 + Kp^{(e)} \exp\left(\frac{\epsilon}{kT}\right)} \tag{3}$$

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

Before equilibrium is reached, the time dependence of the surface coverage, $\theta(t)$, is obtained by solving eq 2 with the appropriate boundary condition. For $s = 1$ and the boundary condition $\theta(t{=}0) = 0$

$$\theta(t) = \frac{Kp\, e^{(\epsilon_d-\epsilon_a)/kT}}{1 + Kp\, e^{(\epsilon_d-\epsilon_a)/kT}}\{1 - \exp(-K_d\, e^{-\epsilon_d/kT}(Kp\, e^{(\epsilon_d-\epsilon_a)/kT} + 1)t)\} \quad (4)$$

whereas for $s = 2$, for instance, and for $Kp\exp((\epsilon_d-\epsilon_a)/kT) < 1$

$$\theta(t) = \frac{Kp\, e^{(\epsilon_d-\epsilon_a)/kT}}{Kp\, e^{(\epsilon_d-\epsilon_a)/kT} - 1} - \frac{(Kp\, e^{(\epsilon_d-\epsilon_a)/kT})^{1/2}}{Kp\, e^{(\epsilon_d-\epsilon_a)/kT} - 1}\tanh\{(Kpe^{(\epsilon_d-\epsilon_a)/kT})^{1/2}K_d\, e^{-\epsilon_d/kT}t + \text{ar}\tanh\{(Kpe^{(\epsilon_d-\epsilon_a)/kT})^{1/2}\}\} \quad (5)$$

When $Kp\exp((\epsilon_d-\epsilon_a)/kT) > 1$, eq 5 takes the form

$$\theta(t) = \frac{Kp\, e^{(\epsilon_d-\epsilon_a)/kT}}{Kp\, e^{(\epsilon_d-\epsilon_a)/kT} - 1} - \frac{(Kpe^{(\epsilon_d-\epsilon_a)/kT})^{1/2}}{Kp\, e^{(\epsilon_d-\epsilon_a)/kT} - 1}\text{ctgh}\{(Kp\, e^{(\epsilon_d-\epsilon_a)/kT})^{1/2}K_d\, e^{-\epsilon_d/kT}t + \text{ar ctgh}\{(Kp\, e^{(\epsilon_d-\epsilon_a)/kT})^{1/2}\}\} \quad (5a)$$

The case $s = 2$ will be the focus of our interest because this is the simplest case of dissociative adsorption. This, for instance, is the case of the numerous catalytic reactions where one of the reactants is the chemisorbed hydrogen.

Studying such a simple case may create a chance to arrive at reliable conclusions about the applicability of various theoretical approaches to represent the kinetics of the above mentioned adsorption/desorption processes. At equilibrium, $t \to \infty$, when $s = 2$ from eq 2 or eq 5, one arrives at the following equilibrium isotherm equation

$$\theta^{(e)}(p,T) = \frac{(Kp)^{1/2}\, e^{(\epsilon_d-\epsilon_a)/2kT}}{1 + (Kp)^{1/2}\, e^{(\epsilon_d-\epsilon_a)/2kT}} \quad (6)$$

In the general case

$$Kp\, e^{(\epsilon_d-\epsilon_a)/kT} = \left(\frac{\theta}{1 - \theta}\right)^s \quad (7)$$

The inapplicability of the classical TAAD approach to represent the observed kinetics of adsorption/desorption in the overwhelming majority of real adsorption systems was known long ago. That failure was observed in both the studies of isothermal adsorption/desorption kinetics and in the studies of the kinetics of thermodesorption.

As a result, the scientists studying the kinetics of isothermal adsorption started to use some empirical expressions such as Elovich or power-law equations.[2-6] The scientists studying the kinetics of thermodesorption assumed that ϵ_d may depend on the surface coverage θ. That failure of the classical TAAD approach led scientists to undertake various attempts to modify that approach. These attempts went toward three directions:

(1) Taking into account the possible interactions between the adsorbed species;

(2) considering the energetic nonequivalence (heterogeneity) of various adsorption sites; and

(3) modifying the fundamentals of TAAD.

In some cases, it was a combination of the concept of energetic surface heterogeneity and of the interactions between the adsorbed species. Sometimes modification of fundamentals was accompanied by adding the concept of interactions between the adsorbed species. Because of the large number of the published works, it would be far beyond the scope of this publication to refer even to the most relevant papers. However, because the main purpose of our present paper is a new theoretical description, based on much different fundamental principles, we shall refer briefly to the fundamental modifications of the classical TAAD approach.

Modifying the fundamentals of the TAAD approach went toward introducing the concept of "*precursor states*". The concept of a precursor state was introduced by Kisliuk[7,8] for adsorption and next adapted by King[9] for desorption. King considered a model assuming existence of two types of precursors, one over filled chemisorption sites and one over an empty site. Next Gorte and Schmidt[10] criticized the expressions developed by King for their complexity and for the fact that they were not generalized for the rate of adsorption. Gorte and Schmidt proposed simpler expressions for dissociative adsorption. A year later (in 1979), Schonhammer[11] published some comments on the treatment by King and by Gorte and Schmidt and proposed still another approach based on the concept of precursor state. With certain assumptions, his expressions reduced to those developed by King and by Gorte and Schmidt. In 1981 Cassuto and King[12] developed other expressions for the rate of dissociative adsorption/desorption.

What was, however, common for all these modifications of TAAD was the fact that they were next rarely used to analyze adsorption/desorption kinetics in real chemisorption systems.[13,14] Experimentalists reporting their results obtained by using various techniques tried as a rule to analyze their results in terms of the simple classical TAAD approach or used even its semiempirical modifications.[15,16] We have had such a situation until now.

While considering the possible reasons for that, one may launch the simple explanation, that the developed expressions were just too complicated to be used in common interpretation of experimental data. This might have been true two or three decades ago but not now. At present, even a complicated function can be easily programmed in a computer, and the parameters characterizing a particular adsorption system can be easily found by using one of the fast commercially available fitting procedures.

Our hypothesis is that it was still small flexibility of the modified TAAD expressions to explain the variety of the data reported for various adsorption systems. And this might be particularly true in the case of chemisorption kinetics, where so many mechanisms (paths) are found for the dissociative adsorption in various chemisorption systems. Meanwhile, even the most elaborated modifications of TAAD consider just a few possible different physical situations.

The purpose of the present publication is to show that the application of the statistical rate theory (SRT) to describe the kinetics of dissociative adsorption leads to very flexible expressions which may account for the variety of physical situations found in these systems. That new SRT approach links the rate of adsorption/desorption kinetics to the chemical potentials in

the bulk and in the adsorbed phase. Therefore, this approach is extremely suitable to study the coverage dependence of the dissociative kinetics. And this was that coverage dependence first for which the classical approaches failed to provide a correct description. At the same time this coverage dependence of the dissociative kinetics is crucial for understanding the rate of catalytic reactions. Moreover, the obtained expressions are almost as simple as the classical ART expressions, so they may be a convenient and attractive tool for the interpretation of experimental data.

Theory

I. Application of the SRT Approach to Describe the Kinetics of Adsorption on the Energetically Homogeneous Solid Surfaces. More and more obvious failure of the classical TAAD approach to represent the adsorption/desorption kinetics in the real adsorption systems inspired some scientists to reconsider theoretical fundamentals of these processes. As a result, in addition to the modifications of the TAAD approach, a family of new approaches challenging the TAAD ones appeared at the beginning of the 80s of the 20th century. These new approaches related the features of the adsorption/desorption processes to the chemical potentials of the free and of the adsorbed molecules.[17−32] A short historical sketch of that development has been given in our previous publications.[33,34] Among these new approaches, the so-called SRT developed by Ward and co-workers[25−32] received the most advanced theoretical background.

The SRT is based on considering the quantum mechanical transition probability in an isolated many-particle system. By assumption that the transport of molecules between two 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

$$R_{12} = R_e\left[\exp\left(\frac{\mu_1 - \mu_2}{kT}\right) - \exp\left(\frac{\mu_2 - \mu_1}{kT}\right)\right] \quad (8)$$

In eq 8, 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 the methods of statistical thermodynamics. The SRT approach was proposed first in an elementary form in 1977[25] and then was placed on firmer theoretical grounds at the beginning of the 80s of the previous century.[26]

Since then it was successfully applied to represent the rates of various interfacial transports, such as the rate of gas absorption at liquid−gas interface, hydrogen absorption by metals, electron exchange between ionic isotopes in solution, permeation of ionic channels in biological membranes, and the rate of liquid evaporation.

Ward and co-workers have also outlined the way in which the SRT approach can be used to describe the kinetics of adsorption at gas−solid interfaces.[27−32] More recently, in a series of papers, Rudzinski and co-workers[33−52] have shown how the SRT approach can be further generalized to analyze quantitatively the kinetics of nondissociative adsorption/desorption on/from energetically heterogeneous solid surfaces.

However, among two dozen of the first papers in the literature treating the application of SRT to describe the kinetics of adsorption at gas−solid interfaces, only two of them dealt with

kinetics of dissociative adsorption.[28,29] Here, we are going to show that the SRT approach may generate a large variety of kinetic equations corresponding to the large variety of physical situations (models of dissociative adsorption), which one may find in the investigated chemisorption systems.

However, the dissociation as a rule is preceded by adsorption from the gas phase into one or more possible weakly bonded molecular states. This, in general, will be a multisite-occupancy adsorption. So the formulation of the kinetics of that kind of adsorption must be the first necessary step in considering the kinetics of dissociative adsorption.

II. The SRT Approach to the Kinetics of Multisite-Occupancy Adsorption. The SRT equation can then be used directly to describe the rate of transfer from the bulk phase into the adsorbed phase $(d\theta/dt)$

$$\frac{d\theta_m}{dt} = K'_{gm}\left[\exp\left\{\frac{\mu^g - \mu^m}{kT}\right\} - \exp\left\{\frac{\mu^m - \mu^g}{kT}\right\}\right] \quad (9)$$

where μ^m is the chemical potential of the adsorbed molecules and K'_{gm} is the exchange rate at equilibrium to which the system would evolve after being isolated and equilibrated. One essential assumption made in the theoretical development of the SRT approach is that the adsorbed phase is in quasi-equilibrium. It means that all the surface correlation functions in the adsorbed phase have values close to their values at a full equilibrium and the same surface coverage θ_m. So, one can apply in eq 9 all the existing expressions for the chemical potential of the adsorbed molecules μ^m, developed so far by applying the methods of statistical thermodynamics to the equilibrium systems.

Let us consider the frequently faced situation when the dissociating molecule consists of identical mers (segments). While applying Flory's approach we have

$$\mu^m = -n\epsilon - kT\ln(q_s\zeta n) + kT\ln\frac{\theta_m}{(1 - \theta_m)^n} \quad (10)$$

where n is the number of adsorption sites occupied by the adsorbing molecule consisting of s atoms (s = n), ϵ is the energy of adsorption of one mer, q_s is the molecular partition function, and ζ is a constant related to the flexibility and symmetry number of a molecule.

Let further μ^g be the expression for the ideal gas

$$\mu^g = \mu^0 + kT\ln p \quad (11)$$

The exchange rate K'_{gm} takes then the form

$$K'_{gm} = K_{gm}p^{(e)}(1 - \theta_m^{(e)})^n \quad (12)$$

where the superscript (e) refers to the above-defined equilibrium state and K_{gm} represents the probability that a molecule striking an ensemble of n available adsorption sites will adsorb. Thus, the SRT theory also assumes the existence of a certain activation energy barrier for adsorptive bond formation, which can be estimated from the studies of the kinetics recorded at various temperatures. We have demonstrated it in our previous publication.[50]

After inserting eqs 10−12 into eq 9, for the multisite-occupancy nondissociative adsorption, the expression $d\theta_m/dt$

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takes the following explicit form

$$\frac{d\theta_m}{dt} = K_{gm}p^{(e)}(1 - \theta_m^{(e)})^n \left[K_m p \frac{(1 - \theta_m)^n}{\theta_m} e^{n\epsilon/kT} - \frac{1}{K_m p} \frac{\theta_m}{(1 - \theta_m)^n} e^{-n\epsilon/kT} \right] \quad (13)$$

where

$$K_m = q_s \zeta n \, e^{\mu^0/kT} \quad (13a)$$

μ^0 is the standard chemical potential of the adsorbate molecules, and q_s is the molecular partition function of the nondissociating adsorbed molecules. At equilibrium, when $d\theta_m/dt = 0$, we have Flory's adsorption isotherm for the multisite-occupancy adsorption

$$K_m p^{(e)} \, e^{n\epsilon/kT} = \frac{\theta_m^{(e)}}{(1 - \theta_m^{(e)})^n} \quad (14)$$

The generalization of eq 13 for the case of energetically heterogeneous surfaces has been the matter of our separate publication on the kinetics of multisite-occupancy adsorption on the heterogeneous solid surfaces.[52]

III. The SRT Approach to the Kinetics of Dissociative Adsorption. Studies of disociative adsorption involve the necessity of considering a great variety of physical situations which one may face in various chemisorption systems. Here, we will limit our consideration to the cases which are frequently assumed. Namely, quantum mechanical calculations of gas−solid interactions, and analysis of experimental kinetic data suggest existence of a certain precursor state which is a weakly adsorbed molecular species. In such a case, two following situations may occur:

(1) The weak molecular adsorption of that precursor is the rate determining step, whereas the forthcoming dissociative adsorption is fast; and

(2) That weak molecular adsorption is fast, whereas the rate determining step is the adsorption of atoms after dissociation.

Now, let us consider the first of the two above-described situations. As the precursor molecules are in equilibrium with the adsorbed atoms, we have $\mu^m = s\mu^a$ where μ^a is the chemical potential of the adsorbed atoms. At the same time, the inequality $\mu^g \neq \mu^m$ exists.

Thus, in the first ever publication on the application of SRT to dissociative adsorption, Ward et al. proposed to replace μ^m by $s\mu^a$ in eq 9 and, next, to express μ^a as a function of θ using the methods of statistical thermodynamics. For the Langmuir model of (one-site-occupancy) adsorption

$$\mu^a = -\epsilon - kT \ln q_a + kT \ln \frac{\theta}{1 - \theta} \quad (15)$$

where q_a now is the molecular partition function of the adsorbed atoms. So, the rate of the dissociative adsorption is then given by the following expression

$$\frac{d\theta}{dt} = K'_{gm} \left[Kp \, e^{s\epsilon/kT} \left(\frac{1 - \theta}{\theta} \right)^s - \frac{1}{Kp} e^{-s\epsilon/kT} \left(\frac{\theta}{1 - \theta} \right)^s \right] \quad (16)$$

where $K = q_a^s \exp(\mu^0/kT)$.

Let us consider now another situation when the rate-determining step is the transition from the precursor state to the adsorbed atoms.

After receipt of a sufficient input of energy, the adsorbed molecule moves to such a configuration on the surface, where it dissociates into single atoms. They have a certain chemical potential μ^*, which, however, is not identical with the potential of adsorbed atoms μ^a. This is because the position of the atoms created in the process of molecule dissociation is different from the positions of the local minima in the atom−surface potential where these atoms finally adsorb. The freshly created atoms reach these minima through the process of surface migration. We assume now that this transition (migration) from the state "*" to the state "a" is the rate-determining step in the whole process of chemisorption.

Then according to the principles of the SRT, we should have under the exponentials the difference $(\mu^* - \mu^a)$ of the (atomic) species before and after adsorption. Next, because the species "*" is in equilibrium with the molecularly adsorbed species "m", we can write $\mu^* = (1/s)\mu^m = (1/s)\mu^g$. Then the SRT equation takes the form

$$\frac{d\theta}{dt} = K'_{gm} \left[\exp\left(\frac{\frac{1}{s}\mu^g - \mu^a}{kT} \right) - \exp\left(\frac{\mu^a - \frac{1}{s}\mu^g}{kT} \right) \right] \quad (17)$$

or, considering eq 15

$$\frac{d\theta}{dt} = K'_{gm} \left[(Kp)^{1/s} e^{\epsilon/kT} \left(\frac{1 - \theta}{\theta} \right) - \frac{1}{(Kp)^{1/s}} e^{-\epsilon/kT} \left(\frac{\theta}{1 - \theta} \right) \right] \quad (18)$$

Also in the case of the above second model of dissociative adsorption, the molecules may either directly enter the precursor state or enter via one of the other possible molecular states. The discussion of the function K'_{gm} will be the same as previously. Both in eqs 16 and 18, the K'_{gm} function describing the exchange rate at equilibrium will acquire various forms depending on the features of the physical system under investigation. We will consider some of the most probable situations in the next section and develop the corresponding expressions for $K'_{gm}(\theta)$. So, we can see that the SRT approach may generate a large variety of kinetic equations, each of them taylored for the particular system (physical situation) under investigation.

At equilibrium, when $d\theta/dt = 0$, eqs 16 and 18 yield the following isotherm equation

$$\theta^{(e)}(p^{(e)}, T) = \frac{(Kp^{(e)})^{1/s} e^{\epsilon/kT}}{1 + (Kp^{(e)})^{1/s} e^{\epsilon/kT}} \quad (19)$$

or

$$Kp^{(e)} e^{s\epsilon/kT} = \left(\frac{\theta^{(e)}}{1 - \theta^{(e)}} \right)^s \quad (20)$$

which is identical with eq 16, obtained by applying the classical TAAD approach.

IV. Exchange Rate at Equilibrium. The explicit form of the expression K'_{gm} for the equilibrium exchange rate will depend on the path of the dissociative adsorption in a particular adsorption system under consideration. Namely, it will depend on the character of the first step of that dissociative adsorption. In general, that first step (molecular adsorption) may not be yet the precursor state. By a fast surface diffusion, the adsorbed molecules may migrate to another state from which they dissociate. Because $K'_{gm} \sim p^{(e)}$, we have to consider K'_{gm} as the following expression, given in eq 12, where $(1 - \theta_m^{(e)})$ is the fraction of the adsorption sites available for molecular

adsorption in the first adsorbed state, and n is the number of these adsorption sites occupied by the adsorbing molecule consisting of s atoms. Let us remark that, in general, these adsorption sites, i.e., local minima in the solid-molecule potential function, may not be the same sites, i.e., local minima for the atom−surface potential function. Let us consider such situation first.

To solve the differential eq 16, $\theta_m^{(e)}$ has to be expressed as the function of θ. For that purpose, $\theta_m^{(e)}$ is expressed first by $\theta^{(e)}$, through comparison

$$\mu^m(\theta_m^{(e)}) = s\mu^a(\theta^{(e)}) \qquad (21)$$

Finally $p^{(e)}$ and $\theta^{(e)}$ are calculated from the known equilibrium isotherm for an isolated system in which the total amount of adsorbate N_t is known from the condition

$$N_t(t) = M_a\theta(t) + \frac{spV}{RT} + sM_m\theta_m(t) \qquad (22)$$

where M_a and M_m are the monolayer capacities for atomic and molecular adsorptions of the solid sample used in the experimental setup and V is the dead volume in that experimental setup. Thus

$$\theta(t) + \frac{spV}{M_aRT} + \frac{sM_m}{M_a}\theta_m(t) = \theta^{(e)} + \frac{sV}{MRT}p^{(e)} + \frac{sM_m}{M_a}\theta_m^{(e)} \qquad (23)$$

However, both quantum mechanical calculations and experimental evidence show that the molecular adsorption is usually much weaker than atomic adsorption. So, to a good approximation we may write

$$\theta(t) + \frac{spV}{M_aRT} = \theta^{(e)} + \frac{sV}{M_aRT}p^{(e)} \qquad (23a)$$

Now, let us consider the other possible situation when the sites for precursor and atomic adsorption are the same adsorption sites. Then, the overwhelming fraction of the occupied sites is due to much stronger atomic adsorption. Strictly speaking, the equilibrium exchange rate should then be proportional to $p^{(e)}(1 - \theta_m^{(e)} - \theta^{(e)})^n$, but because $\theta_m^{(e)} \ll \theta^{(e)}$

$$K'_{gm} \approx K_{gm}p^{(e)}(1 - \theta^{(e)})^n \qquad (24)$$

One will face a similar situation when the adsorption sites are not the same, but the adsorption of atom eliminates in its neighborhood from adsorption the sites that are available for molecular adsorption. Such a situation, of course, must be confirmed by appropriate quantum mechanical calculations, or verified indirectly via a quantitative analysis of kinetic data.

V. Equilibrium Exchange Rate at Some Extreme Experimental Conditions. One of the new fundamental features of the SRT approach is the prediction that many kinetic paths may lead to the same equilibrium state. These different paths may also be related to the technical construction of an experimental setup and to the conditions at which the kinetic experiment is carried out. This follows from eq 23.

However, such complete experimental information such as the monolayer capacity M of the investigated sample and the dead volume V of the experimental setup are not reported as a rule. Thus, Rudzinski et al.[33,34] have proposed that for the experiment under consideration some simplifying assumptions could be attempted. For instance, if the second term on the right-hand side of eq 23a is negligible, compared to the first one,

then after the system is isolated and equilibrated θ does not change much, so we may assume that $\theta^{(e)} \approx \theta$. The above considered situation is probable when the dead volume of an experimental setup is small, whereas the amount of solid phase is large. We call such systems "*solid dominated*" (S) systems. Thus, $p^{(e)}$ is then given by

$$(Kp^{(e)})^{1/s} e^{\epsilon/kT} = \frac{\theta}{1 - \theta} \quad \text{or} \quad p^{(e)} = \frac{1}{K e^{s\epsilon/kT}}\left(\frac{\theta}{1 - \theta}\right)^s \qquad (25)$$

When the molecular states of the molecules entering surface from the gas phase are located on the same sites which are next occupied by atoms, K'_{gm} takes then the following form

$$K'_{gm} = K_{gm}\frac{1}{K e^{s\epsilon/kT}}\left(\frac{\theta}{1 - \theta}\right)^s(1 - \theta)^n \qquad (26)$$

When the sites for the molecular and atomic states are different, we first use eq 21, to express $\theta_m^{(e)}$ by $\theta^{(e)}$

$$-n\epsilon_m - kT \ln(q_s\zeta n) + kT \ln\frac{\theta_m^{(e)}}{(1 - \theta_m^{(e)})^n} = -s\epsilon - kT \ln q_a{}^s +$$
$$kT \ln\left(\frac{\theta^{(e)}}{1 - \theta^{(e)}}\right)^s \qquad (27)$$

or, adding $(-\mu^0)$ to both sides of the above equation, we have

$$\frac{\theta_m^{(e)}}{(1 - \theta_m^{(e)})^n} = \frac{K_m e^{n\epsilon_m/kT}}{K e^{s\epsilon/kT}}\left(\frac{\theta^{(e)}}{1 - \theta^{(e)}}\right)^s \qquad (28)$$

From eq 28, $\theta_m^{(e)}$ is expressed by $\theta^{(e)} = \theta$ and next inserted into eq 20, in which $p^{(e)}$ is expressed by θ using relation 25.

When, on the contrary, the dead volume of the experimental setup is large, whereas the amount of the solid is so small that the first term on the right-hand side of eq 23a can be neglected, then $p^{(e)} \approx p$, whereas $\theta^{(e)}$ is to be calculated as follows

$$1 - \theta^{(e)} = \frac{1}{1 + (Kp)^{1/s} e^{\epsilon/kT}} \qquad (29)$$

We call such systems "*volume dominated*" (V) systems. When the sites for molecular and atomic adsorption are the same then, the K'_{gm} function in eq 24 takes the following explicit form

$$K'_{gm} = K_{gm}\frac{p}{[1 + (Kp)^{1/s} e^{\epsilon/kT}]^n} \qquad (30)$$

When the sites for molecular and atomic adsorption are different, then while considering the expression for K'_{gm} in eq 24, we note that

$$\left(\frac{\theta^{(e)}}{1 - \theta^{(e)}}\right)^s = Kp^{(e)} e^{s\epsilon/kT} \approx Kp e^{s\epsilon/kT} \qquad (31)$$

Thus

$$\frac{\theta_m^{(e)}}{(1 - \theta_m^{(e)})^n} = K_m e^{n\epsilon_m/kT}p \qquad (32)$$

After solving eq 32 with respect to $\theta_m^{(e)}$, the obtained solution is inserted into eq 20.

In our previous publications, we also considered the adsorption processes carried out under the conditions when the system

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is still close to equilibrium, i.e., when $p \approx p^{(e)}$ and $\theta \approx \theta^{(e)}$. For such "*equilibrium dominated*" (E) systems, from eq 24 we obtain

$$K'_{gm} = K_{gm}p(1 - \theta) \tag{33}$$

whereas in eq 20, $\theta_m^{(e)}$ has to be expressed by eq 32.

Kinetics of Dinitrogen Adsorption on a Fe(111) Single-Crystal Face

To illustrate the application of the SRT approach to dissociative adsorption, we consider the kinetics of dinitrogen dissociative adsorption on iron surfaces. This, probably, is the most extensively investigated class of chemisorption systems due to its fundamental importance for the Haber–Bosh industrial synthesis of ammonia developed at the beginning of the previous century. The catalytic ammonia synthesis technology played a central role in the development of chemical industry during the 20th century. Often new techniques, methods, and theories of catalysis have been initially developed and applied in connection with studies of this system.[53] Nevertheless, the kinetics of ammonia synthesis over industrial iron catalysts is still a subject of disscusion despite the fact that it has been studied for most of the previous century.[54] Controversies and unsolved problems still remain.[55] The main unresolved problem here is the theoretical description of the dissociative adsorption of dinitrogen on the iron catalyst surfaces. For many years, this has been known to be the rate-determining step in ammonia synthesis. So, "it is conspicuous that this particular reaction is not yet fully understood", Dahl et al wrote in 2001.[55]

Long-standing controversies accompany the discussion of the mechanism of the dissociative dinitrogen adsorption, and no kinetic equation has been yet developed which could describe the fascinating features of the kinetics of that dissociative adsorption at various pressure and temperature regimes. One of the fundamental questions is why some experiments showed the dissociation of N_2 to be nonactivated,[56–62] whereas some others showed it to be strongly activated.[63–70] No kinetic theory has been yet proposed that could reproduce the temperature and coverage dependence of that dissociative adsorption kinetics.

There is a general agreement now that kinetic modeling of the rate of ammonia synthesis is not able to provide an answer to that intriguing question.[66,70–72] With kinetic modeling, there are many ways to obtain a good fit to a set of experimental data, but such fits definitely do not prove that the assumed mechanism is correct. So, the urgent need to continue both experimental and theoretical studies of the dissociative dinitrogen adsorption on iron surfaces has been realized during the last few decades.

Among the researchers engaged in these studies, one may find the most distinguished names in the area of catalysis. It would be far beyond the scope of this paper to review even the most fundamental achievements and quote even the most relevant reviews and books.

First experiments started with poorly defined iron surfaces (films) or even with typical catalysts for ammonia synthesis. In recent decades, however, a new strategy can be seen to study the kinetics of that dissociative adsorption in the systems with well-defined, single-crystal surfaces.[61,62,73–78]

There were some warnings expressed[65,67,68] that the results from single-crystal studies may be inappropriate to catalysis. Of course, such results cannot be directly applicable but are surely the first necessary step to understand the features of the dissociation processes occurring on the geometrically and
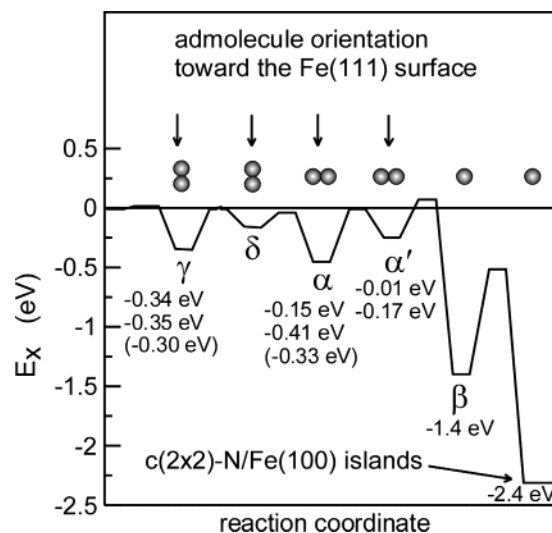
Figure 1. The potential-energy diagram for dissociative dinitrogen adsorption on Fe(111) reported by Mortensen et al. E_x denotes the adsorption energy relative to the energy of the clean surface and gas-phase molecule in the state x ($x = \gamma, \delta, \alpha, \alpha', \beta$). The numbers at the state symbols are the E_x values calculated for 1 ML (the upper value) and for 0.33 ML (the bottom value), respectively. The numbers in parentheses are the values found in some experiments.[62,78,84] In the notation used in this paper, the adsorption energies are the E_x's values taken with the reverse sign.

energetically heterogeneous catalyst surfaces. This is the problem which has long been discussed in the studies of physisorption and was the matter of hundreds of published papers. Finally, several reviews and a few monographs[79] were published, showing how the results obtained for well-defined surfaces can be further generalized for the case of the real adsorption systems with heterogeneous surfaces.

So, like in physisorption, studies of dissociative dinitrogen adsorption on well-defined crystal surfaces should be a key to understanding of the rate of ammonia synthesis.

Therefore, we start our study with the analysis of the kinetics of the dissociative dinitrogen adsorption on the Fe(111) surface, regarded as the most relevant iron face since it has been claimed to be a dominant surface in the multipromoted iron catalyst.[80,81]

The starting point for our consideration will be the recent results of the quantum mechanical calculations of the interaction of dinitrogen with the single Fe(111) surface published by Mortensen et al.[82,83] Their density-functional calculations have shown the existence of four different molecularly adsorbed states and two energetic states for the nitrogen atoms after dissociation. They are shown schematically in Figure 1.

The true precursor for dissociative adsorption appears to be the newly discovered molecular state α' by Mortensen et al. However, this state cannot be directly accessed from the gas phase, perhaps except in some high-energy beam experiments.[85] It has been well established that dissociation proceeds via the α state. From the α state, the molecule makes a transition into the α' state, and from the α' state, it dissociates. Of all the four molecular states, only the γ state has a negligible energy barrier for the transition from the gas phase to the adsorbed state. Thus, Mortensen et al. conclude that the most probable is the complicated dissociation path $\gamma \rightarrow \delta \rightarrow \alpha \rightarrow \alpha' \rightarrow \beta$.

Atomic nitrogen adsorbed on the Fe(111) surface is known to form ordered structures dependent on temperature and coverage. They were revealed by Ertl and co-workers in their LEED experiments,[62] and discussed recently to a great detail by Alstrup et al.[68] Mortensen et al. suggest that one should distinguish basically between two energetic states of adsorbed
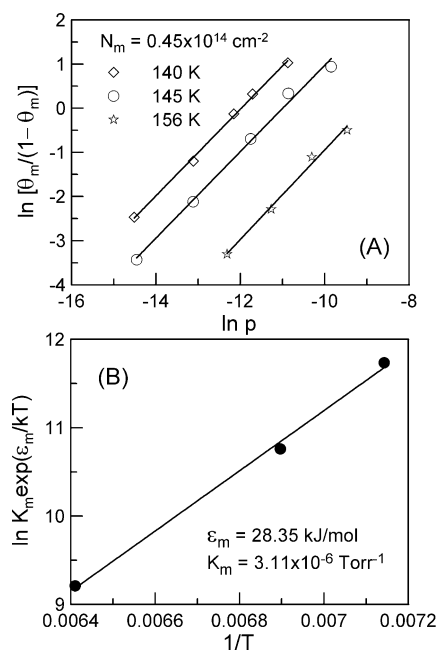
Figure 2. (A) The linear regression (eq 36) for the equilibrium isotherms of dinitrogen adsorption on Fe(111) reported by Ertl et al.[78] (B) The Arrhenius plot. The obtained values of the parameters M_m, K_m, and ϵ_m are displayed in the figure.

atoms. One of them would correspond to a simple (1×1) overlayer structure on the unreconstructed surface with a fairly small binding energy, ϵ_β, and the other one would be a more strongly bounded islands structure being locally (2×2)-N/Fe(100)-like.

The quantum mechanical calculations by Mortensen et al. suggest that either the transition $\alpha \rightarrow \alpha'$ or the $\alpha' \rightarrow \beta$ step might, most probably, be the rate-determining step in the dissociative dinitrogen adsorption on the Fe(111) surface. These two possible rate-controlling steps correspond to the two physical situations considered by us in the previous theoretical section. Thus the $\alpha \rightarrow \alpha'$ slow transition can be classified as the case when the precursor adsorption is the rate controlling step. The kinetics of adsorption should then be described by eq 16. When, on the other hand, the $\alpha' \rightarrow \beta$ would be the slowest step, then the kinetics of adsorption should be described by eq 18.

Mortensen et al. conclude that these two rate-controlling steps are so equally probable and that the "difference between the two barriers is well below the accuracy of the calculation". In a situation like this, we attempted to use both eq 16 and eq 18 to analyze quantitatively the experimentally monitored kinetics of dinitrogen dissociative adsorption on the single (111) crystal face.

However, despite numerous experimental findings which have been published so far, we could find only two papers reporting on such measurements of the isothermal kinetics, which could be subjected to our further quantitative analysis. These are the papers by Bozso et al.[62] and by Alstrup et al.[68] However, although the data in Figure 4 of the paper by Alstrup et al. report on both temperature and pressure dependence of that isothermal kinetics, they can hardly be digitized and show also a considerable experimental scatter. So, we took into consideration the data by Bozso et al.,[62] reporting on temperature dependence of that isothermal kinetics studied at only one pressure 10^{-6} Torr.

For both types of the kinetic eqs 16 and 18, one may have to use a variety of explicit kinetic equations, obtained for different
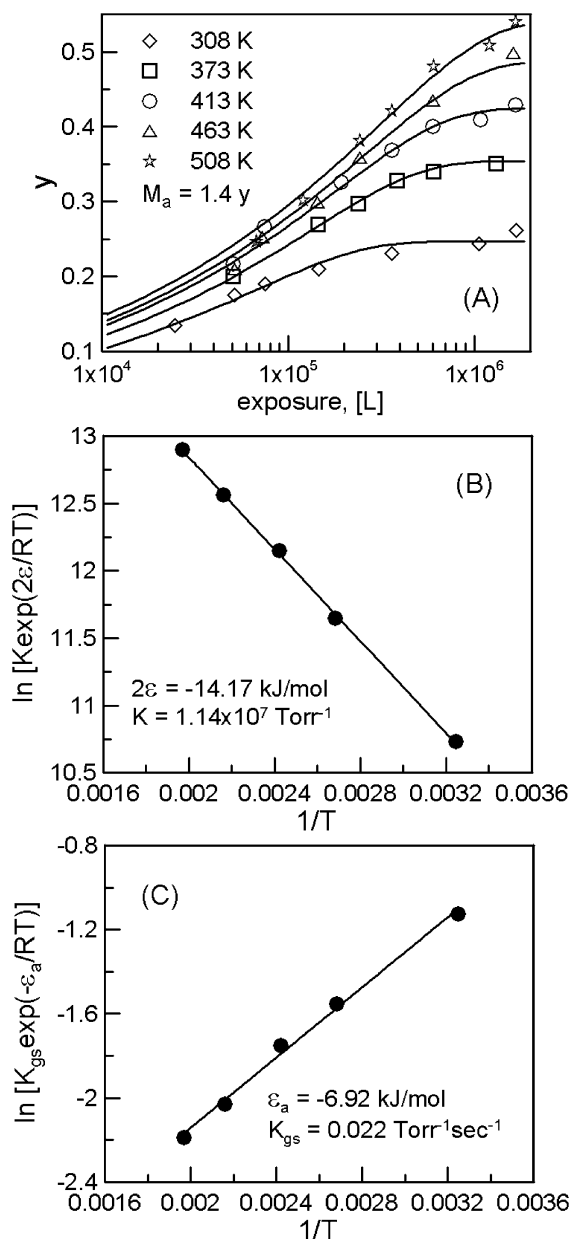
Figure 3. (A) The fit of the experimental kinetic isotherms of dinitrogen dissociative adsorption on Fe(111) reported in Figure 1b in the paper by Bozso et al.[62] The solid lines are the theoretical curves calculated from eq 34, using the best-fit parameters displayed in parts B and C. (B) and (C) show the Arrhenius plots for the parameters $K_{gm} = K_{gs} \exp(-\epsilon_a/kT)$, and $K \exp(2\epsilon/kT)$ used to fit the kinetic curves in a certain temperature. The estimated (best-fit) value of the surface capacity for N atoms on the Fe(111) surface was found to be equal to 1.4 in y units. "y" is the ratio of the Auger peak for N at 380 eV to that of Fe at 650 eV, i.e., the relative surface concentration of nitrogen.

K'_{gm} functions, as it was outlined in the previous theoretical section. Of course, we tried many of them, but only some of them led us to a good agreement with experiment. They corresponded to the assumption that the system studied by Bozso et al. was "volume dominated".

Let us assume first that the $\alpha \rightarrow \alpha'$ transition is the slowest step and that the α state is accessed indirectly via the γ and next the δ steps as suggested by Mortensen et al. Then, we make still the additional assumption that the adsorbed nitrogen atoms do not affect the number of the Fe(111) surface sites available for the first step of molecular adsorption into the γ state. This is because the N atom is adsorbed at a position much

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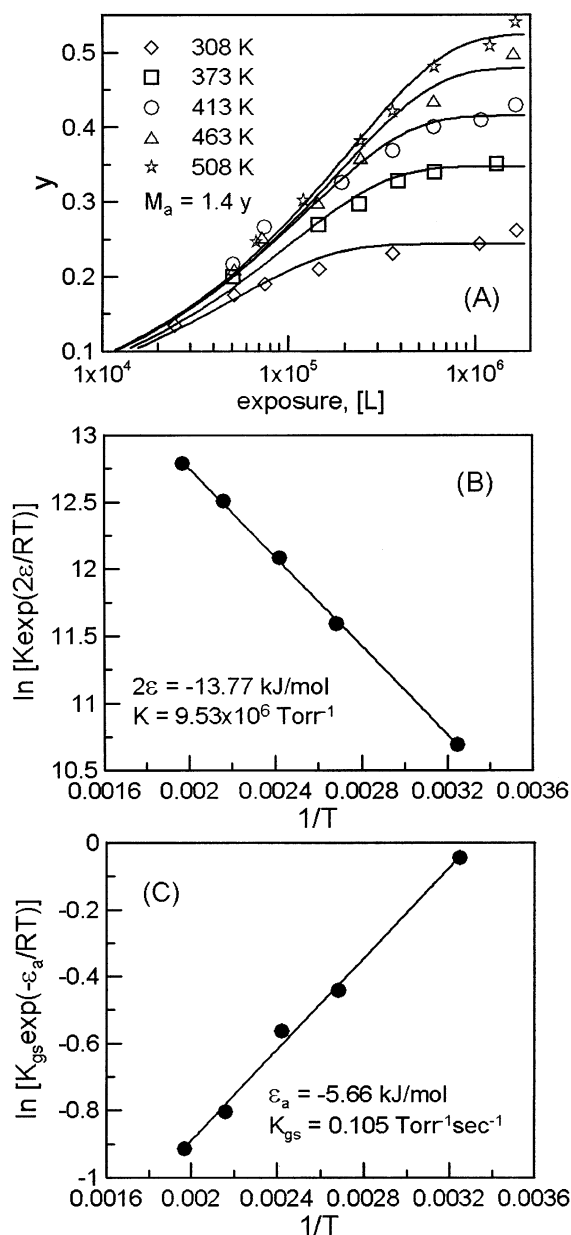
Figure 4. (A) The fit of the kinetic isotherms for N_2 adsorption on Fe(111) reported by Bozso et al., obtained by using eq 35. Other details are the same as in Figure 3.

different from that of the dinitrogen molecule in the γ state. The adsorbed atom is in a hollow site coordinating to a third layer Fe atoms, whereas the molecule in the γ state is coordinated to a single Fe atom, on top of the first layer. While accepting this assumption suggested by the quantum mechanical calculations, from eqs 16, 20, and 31, we arrive at the following explicit expression for $d\theta/dt$

$$\frac{d\theta}{dt} = K_{gm} \frac{p}{1 + K_m p\, e^{\epsilon_m/kT}} \left[Kp\, e^{2\epsilon/kT} \left(\frac{1-\theta}{\theta}\right)^2 - \frac{1}{Kp} e^{-2\epsilon/kT} \left(\frac{\theta}{1-\theta}\right)^2 \right] \quad (34)$$

where $m = \gamma$, and therefore $n = 1$. We notice that in the γ state the dinitrogen molecule is coordinated to a single Fe atom on top of the first layer of Fe atoms and is oriented perpendicularly to the surface. So, this is a one-site-occupancy adsorption, and therefore n was put equal to unity in eq 34.

While assuming that the $\alpha' \rightarrow \beta$ is the slowest step, then, with the above additional assumption made, we have

$$\frac{d\theta}{dt} = K_{gm} \frac{p}{1 + K_m p\, e^{\epsilon_m/kT}} \left[(Kp)^{1/2}\, e^{\epsilon/kT} \left(\frac{1-\theta}{\theta}\right) - \frac{1}{(Kp)^{1/2}} e^{-\epsilon/kT} \left(\frac{\theta}{1-\theta}\right) \right] \quad (35)$$

Our numerical exercises showed that these two kinetic equations (34−35) lead to a good fit of the experimental data reported by Bozso et al.[62] with slightly different values of best-fit parameters.

While fitting the experimental data by eqs 34 and 35, K_m and ϵ_m were not additional best-fit parameters. They were determined independently by fitting the experimental isotherms of dinitrogen molecular adsorption on Fe(111) reported by Ertl et al.[78] for the temperature range 140−156 K. Ertl et al. assumed that the admolecules are in the γ state and discussed the additional supporting arguments coming from the observation of the N−N stretch vibration, angular resolved photoemission, and theoretical calculations. So, we fitted these isotherms by Langmuir isotherm, using the following linear regression

$$\ln \frac{N_m/M_m}{1 - N_m/M_m} = \ln(K_m\, e^{\epsilon_m/kT}) + \ln p \quad (36)$$

By choosing correctly the monolayer capacity M_m, the left-hand side of eq 36 should be a linear function of $\ln p$, at each temperature. Next the Arrhenius plot $\ln(K_m \exp(\epsilon_m/kT))$ vs $1/T$ was made to determine the values of K_m and ϵ_m. The results of these calculations are shown in Figure 2.

The values of K_m and ϵ_m displayed in Figure 2 were next inserted into eqs 34 and 35 to avoid introducing additional best-fit parameters. Then the strategy of our best-fit calculations was the following:

We assumed that with the properly chosen parameter M_a, assumed to be the same for all temperatures, one should fit kinetic isotherms measured at certain temperatures by choosing only two parameters, K_{gm} and $K \exp(2\epsilon/kT)$. We assumed yet that $K_{gm} = K_{gs} \exp(-\epsilon_a/kT)$, where ϵ_a is the energy barrier for the dissociative dinitrogen adsorption. So, in the next step, we made the Arrhenius plots to estimate K, ϵ, K_{gs}, and ϵ_a.

Strictly speaking, we did not fit eqs 34 and 35 but their integral forms obtained by numerical integration and the boundary condition $\theta(t=0) \rightarrow 0$. This is because Bozso et al. reported the integral kinetic isotherms $N(t)$ monitored in their experiments. The kinetics of nitrogen adsorption was followed by means of Auger electron spectroscopy (AES), and the ratio of the Auger peak for N at 380 eV to that of Fe at 650 eV was used as a measure of the relative surface concentration of nitrogen.

In Figure 3, we show the fit of these experimental kinetic isotherms obtained by using eq 34. Then, in Figure 4 we show the fit obtained by applying eq 35.

Under the experimentally studied conditions

$$K_m p \exp\left(\frac{\epsilon_m}{kT}\right) < 1 \quad \text{and} \quad (Kp)^{1/2} \exp\left(\frac{\epsilon}{kT}\right) < 1$$

so, the behavior of the $d\theta/dt$ equations is governed mainly by the expression within the square brackets. The fits of the experimental data in Figures 3A and 4A seem to be equally good. Thus, since the kinetic isotherms were measured at only one pressure, we cannot yet say which one of the two kinetic

equations (34 or 35) should be used to represent the kinetics of the dissociative dinitrogen adsorption. The answer has come from the analysis of the experimental data reported by Alstrup et al.[68] Their data suggest an intriguing conclusion that none of these equations can be used. As we have already mentioned, we could not use the data of Alstrup because they are poorly displayed in small Figure 4 in their paper and could not therefore be digitized for our quantitative analysis. However, there is one important feature that can be seen in Figure 3 of their paper.

Namely, their $\theta(t)$ isotherms studied at 485 K and at the much higher pressures ranging from 10^{-3} to 500 Torr seem to be pressure independent, when plotted against exposure, for the surface coverages below 0.8 ML at which the nitrogen segregation starts. Meanwhile, for the parameters found and displayed by us in Figures 2 and 3, our theoretical isotherms are still strongly pressure dependent. This is demonstrated in Figure 5.

There is, however, one physical model which might explain in a consistent way both the behavior of the data by Bozso et al.[62] measured at the low pressure 10^{-6} Torr and of the data by Alstrup et al.[68] measured at higher pressures $10^{-3}-10^2$ Torr. This is the model which assumes that the α state is accessed directly from the gas phase. We assume then that one adsorbed atom eliminates one site for the molecular adsorption in the α state. Such an assumption seems to be suggested by the results presented by Mortensen et al. in Figure 10 of their paper.[82] One can see there that the adsorbed atom is located roughly at the same place, which is the center for the molecule adsorbed in the α state. Then, to arrive at a rate of dissociative adsorption $d\theta/dt$ that would be pressure invariant at higher pressures, we may still consider two possible explanations. When we assume that the $\alpha \rightarrow \alpha'$ transition is the slowest step, we must necessarily assume that the molecular adsorption in the α state is to be considered as two-sites-occupancy adsorption. The expression for $d\theta/dt$ takes then the following form

$$\frac{d\theta}{dt} = K_{gm}\frac{p}{[1 + (Kp)^{1/2} e^{\epsilon/kT}]^2}\left[Kp\, e^{2\epsilon/kT}\left(\frac{1-\theta}{\theta}\right)^2 - \frac{1}{Kp}e^{-2\epsilon/kT}\left(\frac{\theta}{1-\theta}\right)^2\right] \quad (37)$$

Figure 6 shows the fit of the experimental kinetic isotherms reported by Bozso et al., obtained by us using eq 37.

Now, let us consider the parameters displayed in Figure 6. We note that for the pressures $p > 10^{-3}$ Torr the term Kp exp-$(2\epsilon/kT)$, appearing now in the denominator on the right-hand side of eq 37, is much larger than unity. So, this pressure term will act as a counterbalance to the identical pressure term in the first expression $Kp\, e^{2\epsilon/kT}((1-\theta)/\theta)^2$ within the square bracket. And because the second expression within the square bracket is estimated now to be negligible at these higher pressures, the $d\theta/dt$ becomes pressure invariant.

Now, let us assume the second possible situation when the $\alpha' \rightarrow \beta$ step is the slowest. Then, one may arrive at a pressure invariant (at higher pressures) expression for $d\theta/dt$, only by assuming that the molecular adsorption in the α state should be considered as a one-site-occupancy adsorption. The obtained expression for $d\theta/dt$ takes then the following form

$$\frac{d\theta}{dt} = K_{gm}\frac{p}{1 + (Kp)^{1/2} e^{\epsilon/kT}}\left[(Kp)^{1/2} e^{\epsilon/kT}\left(\frac{1-\theta}{\theta}\right) - \frac{1}{(Kp)^{1/2}}e^{-\epsilon/kT}\left(\frac{\theta}{1-\theta}\right)\right] \quad (38)$$

Figure 7 shows the fit of the kinetic isotherms by Bozso et al. obtained by applying eq 38.
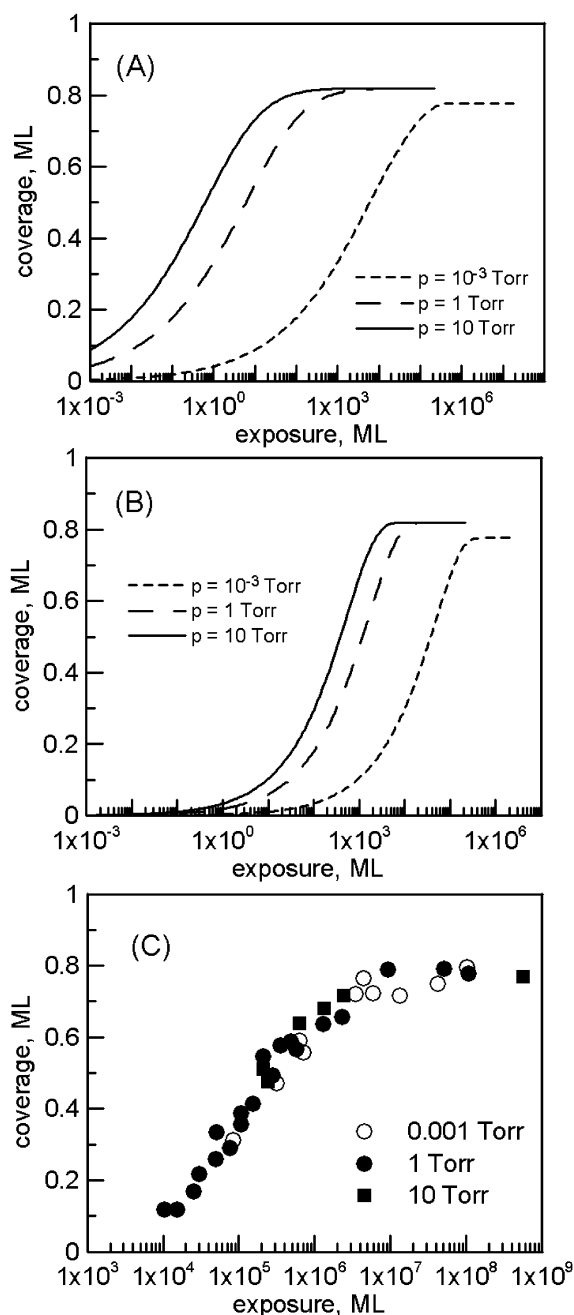
Figure 5. (A) The theoretical kinetic isotherms calculated by eq 34 for the three higher pressures 10^{-3}, 10^0, and 10^1 Torr, using the parameters displayed in Figure 3A. (B) The theoretical kinetic isotherms calculated by eq 35, using the parameters displayed in Figure 4A. (C) The experimental kinetic isotherms of N_2 adsorption on Fe(111) reported by Alstrup et al.,[68] measured at 485 K at three different pressures; 10^{-3} Torr (O), 1 Torr (●), and 10 Torr (■).

Mortensen et al. believe that, at lower temperatures at least, the α state is achieved via the γ state because the sticking probability into the α state is estimated to be around 10^{-2},[62] whereas for the γ state is about 0.7.[84] However, it has also been shown that at higher temperatures a direct channel from the gas phase into the α state is important.[85] So, let us note that the temperature 485 K, at which Alstrup et al. carried out their kinetic experiments, is at the top of the temperatures studied by Bozso et al. So, one cannot exclude the fact that at the lower temperatures in their experiments the α state could be achieved mainly via the γ state as suggested by Mortensen et al. Then, some of the equations (34 and 35) might be correct. Also, it cannot be excluded that we may have to consider a mixed
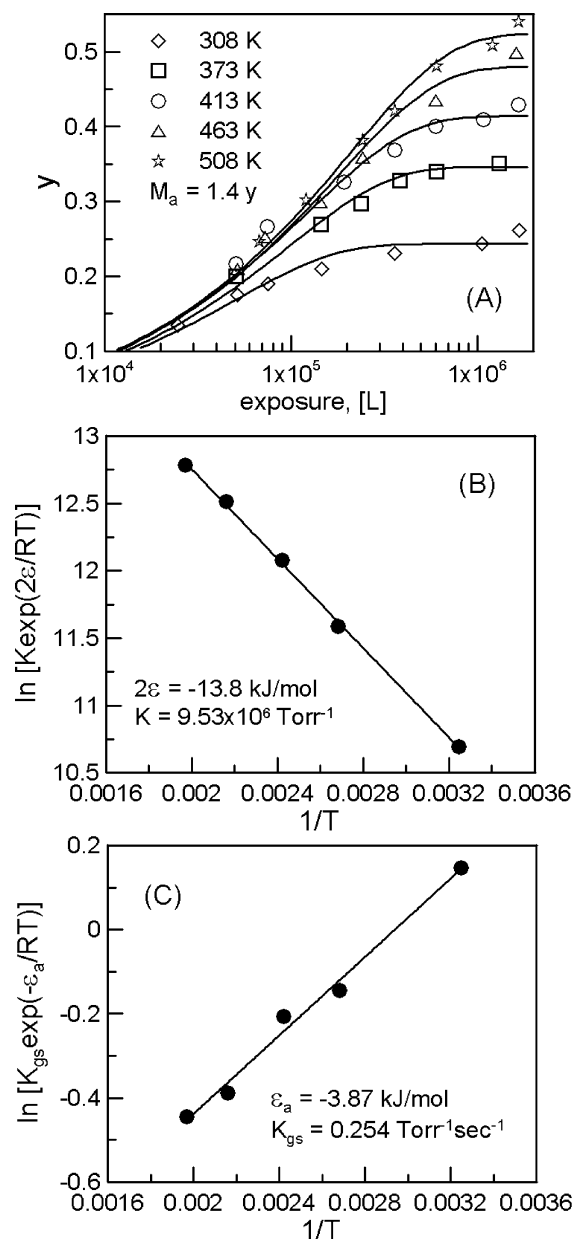
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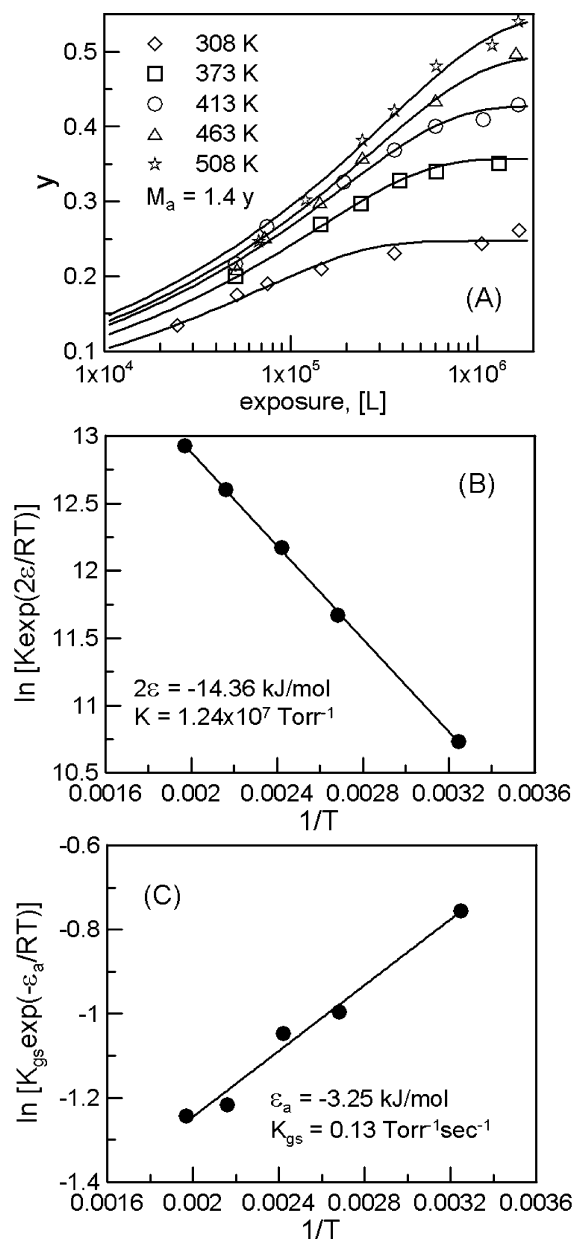
Figure 6. (A) The fit of the kinetic isotherms of N_2 adsorption on Fe(111) reported by Bozso et al.[62] obtained by us using eq 37. (B) and (C) show the Arrhenius plots for the best-fit parameters found at different temperatures. Other details are the same as in Figure 3.

Figure 7. (A) The fit of the kinetic isotherms of N_2 adsorption on Fe(111) reported by Bozso et al., obtained by using eq 38. Other details are the same as in Figure 3.

mechanism in which the α state is accessed partially via the γ state but also directly from the gas phase and that the latter channel prevails at higher temperatures. Such a mixed character of that dissociative kinetics might be suggested by the parameters displayed in Figures 6 and 7. Despite certain differences, they also have some fundamental features in common. All of them suggest that the activation barrier ϵ_a for the dissociative dinitrogen adsorption on Fe(111) is located at negative and small values in agreement with the findings reported by other researchers[62] and in agreement with the results of quantum mechanical calculations.

The apparent negative value of ϵ can easily be explained by assuming a high frequency for the atom−surface vibrations, i.e., that the vibrational partition function reaches its limit $\exp(-h\nu/(2kT))$. Then the apparent value of ϵ, ϵ^{app}, is given by

$$\epsilon^{app} = \epsilon - \frac{h\nu_z}{2} - \frac{h\nu_x}{2} - \frac{h\nu_y}{2} \qquad (39)$$

where ν_z is the frequency of the vibrations normal to surface.

If we accept (from Figure 1) the theoretical value for $\epsilon = -1.4$ eV found by Mortensen et al. in their density functional calculations, we arrive at the frequencies $\nu \approx 10^{14}$ s^{-1}, which justify the approximation of the vibrational partition function by $\exp(-h\nu/(2kT))$. The frequency $\sim 10^{14}$ s^{-1} estimated here should not be seen as controversial to the value 10^{13} s^{-1} generally assumed in the interpretation of temperature-programmed desoprtion (TPD) spectra of nitrogen from iron surfaces. This is because the value 10^{14} estimated here corresponds to the unstable simple (1×1) overalyer structure which reconstructs into other structures at higher nitrogen coverages and temperatures. Meanwhile, TPD experiments are usually started from high surface coverages and carried out at much higher temperatures than those at which the isothermal kinetic experiments, analyzed here by us, were carried out.

On the contrary, much more complicated is the interpretation of the maximum (capacity) value for the atomic adsorption. This is because the problem of nitrogen structures on Fe(111) has not been solved so far. We will comment on the maximum

capacity value found by us after analyzing the $N_2/Fe(100)$ system, where the solution is already well established.

Trying to judge whether eq 37 or eq 38 better represents the investigated kinetics, we turn again to the high-pressure kinetic data published by Alstrup et al. From Figure 3 of their paper, we have digitized the $\theta(t)$ experimental function corresponding to the three pressures 10^{-3}, 1, and 10^2 Torr and to the surface coverages below 0.8 ML at which the segregation starts, not considered in our theoretical treatment. They seem to lie on the same curve, indicating, thus, pressure invariance of that dissociative kinetics at high pressures.

Next we attempted to fit these data using both eq 37 with the parameters displayed in Figure 6 and using eq 38 with the parameters displayed in Figure 7.

To make such a fit possible, first we had to "translate" the coverages expressed in y units (monitored by AES in the experiments by Bozso et al.) to ML units displayed in Figure 3 of the paper by Alstrup et al.

By use of a combination of various techniques, Alstrup et al. have been able to determine the (saturation) capacity for N atoms M_a as equal to 0.85 in the monolayer units ML. So, this value should correspond to $1.4y$ found by us, while fitting our kinetic equations (37 and 38) into the low-pressure kinetic data reported by Bozso et al. It is, therefore, interesting to notice the following observation. Namely, for the well-established c(2 × 2) structure of the Fe(100) surface, the surface capacity M_a was determined to be 0.5 ML, which corresponds to $y = 0.9$ as reported by Bozso et al. Assuming, thus, a similarity of the Fe(111) and Fe(100) surface structures, our best-fit value 1.4 would suggest the surface capacity value $M_a = 0.8$, compared to 0.85 found by Alstrup et al.

While assuming that $1.4y = 0.85$, and using the parameters displayed in Figures 6 and 7, along with the corresponding kinetic equations (37 and 38), we arrived at the fits of the high-pressure kinetic data by Alstrup et al. presented in Figure 8.

Looking to Figure 8, one can see much better agreement between theory and experiment in Part B, obtained by applying the kinetic eq 38. We would even call this agreement a very impressive one taking into account the fact that with the same set of parameters eq 38 fits the data measured in the pressure range 10^{-6}–10^2 Torr and at different temperatures. Moreover, one has to realize that the two experiments by Bozso et al. and by Alstrup et al. were not identical. Also, the quantum mechanical calculations by Mortensen et al.[82,83] suggest that the adsorption energy of atoms may change to some extent with the increasing surface coverage θ. We ignored it in our best-fit exercises.

The fact that only one of the studied kinetic equations, i.e., eq 38, can fit so well the data measured in such different pressures, coverages, and temperatures must be viewed as very optimistic. This means that application of the new SRT approach to the dissociative kinetics creates a chance to verify the assumed models through the quantitative analysis of the experimental kinetic data.

Finally, we would like to emphasize the importance of the new SRT approach for catalytic studies. Namely, there have been published many theoretical papers on the rate of transition of a single molecule from the bulk phase to a precursor state and next the rate of its dissociation. It would be far beyond the scope of this publication to refer even to the most important ones, so let us mention only the very recent paper by German et al.[86] The theoretical predictions can be verified, for instance, by studying experimentally the behavior of the sticking coefficient at the zero surface coverage. Such studies provide
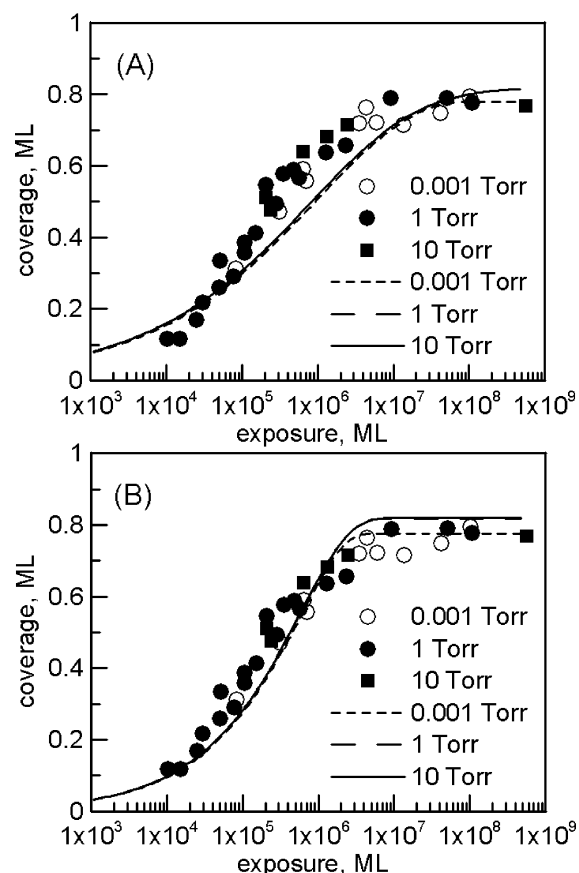
Figure 8. The comparison between the theory and the experimental kinetics of dinitrogen dissociative adsorption on Fe(111) measured by Alstrup et al.[68] at 485 K and at the three pressures: 10^{-3} Torr (○), 1 Torr (●), and 10 Torr (■). (A) The theoretical $d\theta/dt$ curves (solid line, dashed line, dot-dashed line) were calculated by using eq 37 along with the parameters displayed in Figure 6. (B) The fits obtained by eq 38 along with the parameters are displayed in Figure 7. The exposure of ML unit used by Alstrup et al. means twice the number of N_2 molecules hitting the surface during the exposure divided by the number of surface iron atoms (7.05×10^{18} m^{-2}).

important information about the mechanism of catalytic reactions. However, as catalytic reactions do not take place at the zero surface coverage, also the coverage dependence of the kinetics of dissociative adsorption is crucial for understanding catalytic reactions. So, next, a "thermodynamic" approach must be applied to consider that many body problem. The new SRT approach is essentially such a kind of thermodynamic approach, referring to the chemical potentials of the bulk and the adsorbed molecules (atoms).

At the same time our present theoretical treatment is not particularly suitable to study the behavior of the kinetics of dissociative adsorption at very low (close to zero) surface coverage. The reason for that is following:

The SRT approach takes into account the whole adsorption systems composed of both the adsorbed and the nonadsorbed molecules. Meanwhile, in the statistical development of the expressions for $d\theta/dt$, the adsorption system was considered as a lattice of adsorption sites covered partially by adsorbed molecules, for which the nonadsorbed molecules act only as a thermodynamic "bath" composed of identical molecules having a certain temperature T and a chemical potential μ. When $\theta \to 0$, one should consider at least the effect of the presence on the surface of the species which are not adsorbed, but then the theoretical treatment becomes very complicated. We will consider that case in our future publications. The main goal of

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this present publication was to provide a simple but efficient solution for one of the great unresolved problems, the pressure and coverage dependence of the kinetics of dissociative chemisorption.

We finish our discussion by emphasizing one of the fundamental features of the dissociative adsorption kinetics. Namely, it has been common in the kinetic studies to consider the adsorption kinetics as a function of the "exposure", i.e., of the product of time and adsorbate pressure. This is a consequence of using the classical TAAD approach, i.e., the simple eq 2 in which the desorption term $K_d\theta^s \exp(-\epsilon_d/kT)$ is neglected. Then the function θ depends on the product pt. The new SRT approach shows clearly that t and p should be treated as independent variables. Various pairs of (p,t) may yield the same value of exposure, but the corresponding values of θ will be different. The new SRT approach shows clearly that the above fundamental conclusion is true even when the desorption term is neglected. This simple but fundamental conclusion should influence the way in which the future kinetic experiments will be performed.

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