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Modified quasi-chemical approximation in the lattice-gas theory allowing for the internal partition functions of adatom groups in an adsorbed layer

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Abstract

The quasi-chemical approximation of the lattice-gas theory is widely used for description of adsorption–desorption processes. In its present form, however, it is incapable of describing some experimental results: wide ranges of variation of the pre-exponential factor in the desorption-rate constant with changing coverage, the compensation effect, the shift of thermal desorption spectra toward lower temperatures with increasing initial coverage for some systems with lateral attraction between adatoms, etc. In the present paper a modification of the quasi-chemical approximation is proposed, which, in the authors' opinion, significantly increases its capabilities of describing experimental results. This is achieved by including an entropy factor α_0, which reflects a change of the internal partition functions of adsorbed particles by their interactions with nearest neighbors. This parameter is interpreted as the ratio of the internal partition function of a dimer to that of two isolated monomers on the surface. It always differs from unity. The introduction of the parameter α_0 in the lattice-gas theory leads to replacing the quantity $\eta = \exp(-u/kT)$ by the quantity $\eta_1 = \alpha_0 \exp(-u/kT)$ in all formulae of the theory, their analytical form being unchanged. However, this involves cardinal changes of the coverage dependence of the Arrhenius pre-exponential factor in the desorption rate constant, of the thermal desorption spectra behavior with varying the initial coverage, as well as of the critical temperature of the first-order phase transition.

1. Introduction

The lattice-gas model [1–4] is widely used to describe kinetics of various processes on solid surfaces. In particular, it allows to describe the splitting of thermal desorption (TD) spectra, the dependence of the desorption activation energy on the surface coverage θ of an adsorbate, and phase diagrams in an adlayer [1–12]. A comparison of the theory with experiments allows to obtain the lateral interaction energy, which is a parameter of the theory.

However, the lattice-gas theory in its present form cannot account for some experimental results. For example, the authors of the articles [13–15] have noted that this model has failed to explain some experimental results concerning the thermal desorption of Nd and Sm atoms from W(100) face. According to recent reviews [16,17], the lattice-gas theory cannot describe the monotonic dependence of the desorption-rate pre-ex-

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ponential factor $C(\theta)$ on θ. Such monotonic dependence (either increase or decrease) is frequently observed in experiment. In Refs. [14,15, 18–20] shifts of maxima of TD spectra towards lower temperatures were revealed when the initial coverage θ_0 increases for systems with lateral attraction between adatoms. The theory predicts a shift towards higher temperatures for such systems, thus being at variance with the experiment.

We believe that these shortcomings of the lattice-gas theory arise from the lack of a parameter allowing for a variation of the internal partition function of adatoms due to their interaction with neighbors. Indeed, in most papers [1–12] the lateral interactions are included in the grand partition function Ξ only by shifting the ground level of each configuration by the energy of the full interaction of particles constituting the configuration. Various approaches are used to take into account all possible configurations. The simplest of them is the cluster model, which describes a system as a small cluster, consisting of a two-dimensional lattice cell and its nearest neighbors. This approach embraces Bethe–Peierls, quasi-chemical, and mean-field approximations. In recent years, Monte-Carlo [10,11] and transfer-matrix [9,21–23] methods are more widely used in the grand partition function Ξ calculations. These methods enable one to take into account more accurately different sets of adatom configurations and many-particle interactions. A specific feature of all above-mentioned approaches is that the summation in Ξ is made over all configurations only for the ground state of the adlayer. This follows from an assumption that electronic and vibrational spectra of an adatom do not depend on the number of its nearest neighbors. The result is that the sum over the total spectrum of all excited states for each configuration, i.e. the internal partition function of n interacting particles in the ith configuration $F(T, n, i)$ (where T is the surface temperature), is approximately replaced in the theory by the partition function of n free particles, which is equal to the nth power of the internal partition function $f_{1S}(T)$ of a single atom:

$$F(T, n, i) \approx (f_{1S}(T))^n. \tag{1}$$

A change of the internal partition functions of adatoms when they form a cluster mainly influences the adlayer entropy and related quantities. One of these quantities is the pre-exponential factor $C(\theta)$ in the Arrhenius law for desorption rate constants. That is why the existing lattice-gas theory (which neglects such changes) fails most frequently to describe experimental dependences of $C(\theta)$, especially in the case of lateral attraction between adatoms, when they can form real associations on the surface.

We shall show that the experimental results can be understood in the framework of the quasi-chemical approximation, if to take into account the dependence of internal partition functions on the number of particles in a cluster. Let us write the grand partition function in the form

$$\Xi = \sum_n \exp\left(\frac{n\mu_s}{kT}\right) Q(T, n), \tag{2}$$

where k is the Boltzmann constant, μ_s is the chemical potential of the adlayer, and $Q(T, n)$ is the partition function of a group consisting of n particles,

$$Q(T, n) = \sum_i \exp\left(-\frac{E_0(n, i)}{kT}\right) F(T, n, i). \tag{3}$$

Here $E_0(n, i)$ is the ground-state energy of the ith configuration, and $F(T, n, i)$ is its internal partition function, which includes the summation over electronic-vibrational states of this configuration. The thermal equilibrium of all adatom groups is assumed in the adlayer. In the pair-interaction approximation

$$E_0(n, i) = nE_{1S} + \sum_{k \neq l}^{n} u_{kl} n_k n_l, \tag{4}$$

where n_k, n_l are the occupation numbers (0 or 1) of k, l sites in a lattice cluster at the ith configuration of particles, and E_{1S} is the ground-state energy of an isolated particle. As noted above, the existing lattice-gas theory fully includes in Ξ only the first multiplier in Eq. (3), whereas for $F(T, n, i)$ the approximation (1) is accepted. Only Asada [24] does not use this approximation when describing 2D-condensation in physisorbed layers in the frames of a "registered cell model", and calculates the single-atom partition function for

(i)-local atomic configuration by the use of the semi-empirical potentials of Lennard–Jones.

In our previous papers [25–27] a new simple approximation has been proposed, which enables one to abandon the relation (1). Without any complication, this approximation extends significantly the applicability of the lattice-gas theory to the description of desorption processes and the absorption–desorption equilibrium. A brief exposition of the new approach is given in Section 2. Sections 3–5 present its applications to a description of first-order phase transitions, θ-dependence of the pre-exponential factor in the reaction rate constant for desorption, and the thermal desorption spectra shifting with the initial coverage θ_0 increasing. In Section 6 physical causes are discussed of the difference of an entropy parameter α_0 from 1 introduced in our approach. Section 7 contains concluding remarks.

2. Formalism

Let us write the grand partition function Ξ of the adsorbed layer in the Bethe–Peierls approximation [1–5]. In this approximation, interactions of an adsorbed particle with its nearest neighbors only are explicitly taken into account. The interactions of these neighbors with other adatoms in the layer are calculated in the mean-field approximation. The occupation of all the sites in a two-dimensional lattice cluster, consisting of a central cell and Z nearest ones, is defined by a set of numbers $n_0, n_1, \ldots, n_Z$, each of them taking the values 0 or 1. In the Ξ calculation, summing is made over all possible sets of the numbers. This corresponds to summing over n and i in Eqs. (2) and (3). In contrast to Refs. [1–7], we shall take into account the factor $F(T, n, i) = F(n_0, \ldots, n_Z)$ in Eq. (3), which reflects that the internal partition functions of particles change because of their association. Then the grand partition function Ξ will take the form

$$\Xi = \sum_{n_0, \ldots, n_Z} F(n_0, \ldots, n_Z) \times \exp\left(\frac{\mu_s}{kT}(n_0 + \ldots + n_Z)\right) \times \exp\left(-\frac{u n_0}{kT}(n_1 + \ldots + n_Z)\right) \times \exp\left(\frac{-\bar{u}}{kT}(n_1 + \ldots n_Z)\right), \qquad (5)$$

where u is the interaction energy of nearest neighbors (its positive value corresponds to the repulsion), and $\bar{u}$ is the average field of all adatoms at given coverage θ. We shall write the factor $F(n_0, \ldots, n_Z)$ under the assumption that each newly formed bond with a nearest neighbor changes the partition function of the central particle by a factor of α_0,

$$F(n_0, \ldots, n_Z) = f_A^{n_0 + \ldots + n_Z} \alpha_0^{n_0(n_1 + \ldots + n_Z)}. \qquad (6)$$

Here $f_A = f_{1S} \exp(-E_{1S}/kT)$ is the partition function of an isolated atom, and E_{1S} is the ground-state energy. In principle, α_0 may be different for different configurations of a given number of bonds, but we neglect this difference. The assumption made in Eq. (6) is indirectly confirmed by the numerical results of Ref. [24c], which have shown that the single-atom free energy $f(n_1, n_2, \ldots, n_Z)$ is approximately linear in the number of periphery atoms $N_p = \Sigma_j n_j$,

$$f(n_1, n_2, \ldots, n_Z) \approx f_0 + \frac{w_{in}}{2} N_p \qquad (7)$$

(Eq. (4.4) of Ref. [24c]), where $w_{in}(T) \approx w_0 T$. This numerical result is equivalent to our approximation (6) with $\alpha_0 \equiv \exp(-w_0/2) = \text{const}$.

Eq. (5) for Ξ, with the aid of Eq. (6), takes the same form as in Refs. [1,2,4], but with the quantities

$$\lambda \equiv \exp(\mu_s/kT), \quad \eta \equiv \exp(-u/kT),$$
$$\mathscr{E} \equiv \lambda \exp(-\bar{u}/kT) \qquad (8)$$

replaced by

$$\lambda_1 = f_A \lambda, \quad \eta_1 = \alpha_0 \eta, \quad \mathscr{E}_1 = \lambda_1 \exp(-\bar{u}/kT). \qquad (9)$$

That is,

$$\Xi = \sum_{n_0, \ldots, n_Z} \lambda_1^{n_0} \eta_1^{n_0 + (n_1 + \ldots + n_Z)} \mathscr{E}_1^{(n_0 + \ldots + n_Z)}$$
$$= \lambda_1 (1 + \eta_1 \mathscr{E}_1)^Z + (1 + \mathscr{E}_1)^Z. \qquad (10)$$

Thus, in the description of a state of the adlayer all equations of the quasi-chemical approximation [1–9] keep satisfying, but with parameters (9) instead of (8). We shall present these equations for the sake of clarity.

With the aid of Eq. (10), we define the average occupation probability of one adsorption lattice center,

$$\bar{\theta} = \theta = \lambda_1(1+\eta_1\mathscr{E}_1)^Z/\Xi;$$

$$1-\theta = (1+\mathscr{E}_1)^Z/\Xi. \tag{11}$$

From the self-consistency condition [2,5] $\bar{\theta}(n_0 = 1) = \bar{\theta}(n_1 = 1) = \theta$ we find

$$\lambda_1 = \mathscr{E}_1[(1+\mathscr{E}_1)/(1+\eta_1\mathscr{E}_1)]^{Z-1}. \tag{12}$$

Substituting Eq. (12) into Eq. (11), we obtain the parameter $\mathscr{E}_1$:

$$\mathscr{E}_1 = (2\theta - 1 + \gamma_1)/[2\eta_1(1-\theta)],$$

$$\gamma_1 = [1 + 4(\eta_1 - 1)\theta(1-\theta)]^{1/2}. \tag{13}$$

Hence, the chemical potential of the adlayer is defined by the equation

$$\exp\left(\frac{\mu_s}{kT}\right) = \left(\frac{\theta}{1-\theta}\right)\left[\frac{\gamma_1 - 1 + 2\theta}{\gamma_1 + 1 - 2\theta}\left(\frac{1-\theta}{\theta}\right)\right]^{Z/2} \times \left(f_A\eta_1^{Z/2}\right)^{-1}. \tag{14}$$

From the equilibrium conditions of adparticles and ideal-gas particles with pressure P above the surface, $\mu_s = \mu_g$, where $\mu_g = kT\,\ln(P/kTf_g) + E_g$, one can obtain the equation of state $P(\theta)$ (i.e., the adsorption isotherm).

Eqs. (13) and (14) have the same form as in Refs. [1–9], however, the quantities γ_1 and η_1 in these equations depend not only on the interaction energy u, as in Refs. [1–9], but also on the entropy factor α_0, the physical meaning of which will be discussed in more details at the end of the paper.

3. First-order phase transition

It follows from Eqs. (13) that

$$\lambda(\theta) = \lambda(1-\theta) = \lambda(1/2). \tag{15}$$

This relation means that, under some conditions, the coexistence of two phases with coverages θ_1 and $\theta_2 = 1 - \theta_1$ is possible on the surface, i.e. two-dimensional phase transition of the condensation type is possible from nearly vanishing coverage θ_1 to coverage θ_2 which is close to unity [1,4,9]. The condition of its existence, as well as the T-dependence of the coverage θ_1, is determined by Eq. (15).

Substituting Eq. (14) into Eq. (15), we obtain

$$\eta_1^{-1/2}(T) = \Psi(\theta_1), \tag{16}$$

or

$$kT = -u/\left(2\ln\Psi^{-1}(\theta_1) - \ln\alpha_0\right), \tag{17}$$

where

$$\Psi(\theta) = \left(\frac{\theta}{1-\theta}\right)^{1/Z}\left(\frac{1-\theta}{1-2\theta}\right) \times \left[1 - \left(\frac{\theta}{1-\theta}\right)^{(Z-2)/Z}\right]. \tag{18}$$

It can be shown that $\Psi(\theta) \le (Z-2)/Z$. Taking this result into account, with the aid of Eqs. (16) and (17) one can easily derive the condition of the phase transition

$$\eta_1^{1/2} \ge Z/(Z-2) \tag{19}$$

and the critical temperature

$$T_c = -\frac{u}{k}\left(2\ln\frac{Z}{Z-2} - \ln\alpha_0\right)^{-1}, \tag{20}$$

below which this phase transition is possible. It follows from Eq. (20) that the introduction of the additional factor α_0 into the theory leads to the appearance of the additional term $(-\ln\alpha_0)$ in the square brackets in Eq. (20). As a result, new conditions for a condensation-type phase transition will be written as follows:

$$\sqrt{\alpha_0} < Z/(Z-2) \quad \text{at} \quad u < 0,$$

$$\sqrt{\alpha_0} > Z/(Z-2) \quad \text{at} \quad u > 0. \tag{21}$$

The latter condition means that, α_0 being not unity, the phase transition is possible in the case of repulsion between adatoms also.

As already mentioned, the lattice-gas theory is widely used for calculation of phase diagrams in adsorbed layers. Phase diagrams $T(\theta)$, calculated

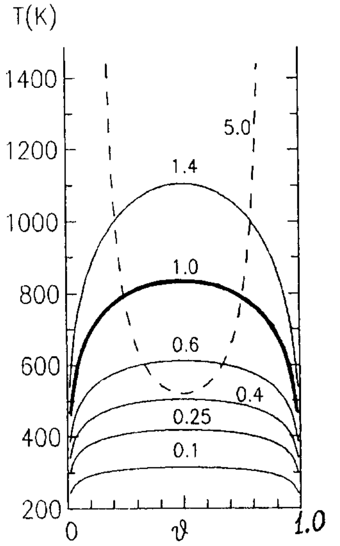

Fig. 1. Phase diagrams determining the temperatures T_1 and coverages θ at which two-dimensional gas and condensed phase coexist on the surface. The case of lateral attraction: $u = -0.1$ eV, various α_0 values shown by figures at the lines. The case of lateral repulsion: $u = +0.1$ eV, $\alpha_0 = 5$ (dashed line).

with the aid of formulae (17) and (18) for various α_0 values, are presented in Fig. 1. Apparently, the allowance for $\alpha_0 \neq 1$ strongly affects the region of phase coexistence: in the case of attraction between adatoms ($u < 0$) the critical temperature of the phase transition decreases at $\alpha_0 < 1$ and increases at $\alpha_0 > 1$. Accordingly, the range of the phase coexistence decreases or increases also, which is of great importance for studying absorption–desorption equilibrium. Similar diagrams for $u < 0$ were obtained by Asada [24c]. The phase diagram in the case of repulsion ($u > 0$, dashed line in Fig. 1) shows that the phase transition here is theoretically allowed only in the high-temperature region $T > T_c$.

4. Influence of $\alpha_0 \neq 1$ on desorption rates

An adatom can be desorbed from any ith configuration of nearest neighbors in the adlayer. Therefore, on the ground of the theory of absolute reaction rates we write the desorption rate as the sum

$$-\frac{d\theta}{dt} = \frac{kT}{h}\sum_i \frac{Q^{\neq}_{Ai}}{Q_{Ai}}\mathscr{P}_{Ai}(1, n_1, \dots, n_Z), \tag{22}$$

where $\mathscr{P}_{Ai}$ is the probability that an adatom has the given surrounding $i = (n_1, \dots, n_Z)$, and h is the Planck constant. We find the $\mathscr{P}_{Ai}$ value by the use of Eqs. (10)–(12):

$$\mathscr{P}_{Ai}(1, n_1, \dots, n_Z) = \theta(\eta_1\mathscr{E}_1)^{n_1+\dots+n_Z}(1+\mathscr{E}_1\eta_1)^{-Z}. \tag{23}$$

The quantities $Q^{\neq}_{Ai}$ and Q_{Ai} are the partition functions of activated and ground states of an adatom in the ith surrounding. The $Q^{\neq}_{Ai}$ does not include the freedom degree which corresponds to the motion along the desorption coordinate. Taking into account Eq. (2), one may write

$$\frac{Q^{\neq}_{Ai}}{Q_{Ai}} = \frac{F^{\neq}(1, n_1, \dots, n_Z)}{F(1, n_1, \dots, n_Z)} \times \exp\left[-\left(\frac{u^* - u}{kT}\right)\sum_{i=1}^{Z} n_i\right]. \tag{24}$$

We shall express the quantity $F^{\neq}(1, n_1, \dots, n_Z)$ by analogy with Eq. (6) in terms of the partition functions of particles constituting a given cluster,

$$F^{\neq}(1, n_1, \dots, n_Z) \approx f_A^{\neq} f_A^{n_1+\dots+n_Z}(\alpha^*)^{n_1+\dots+n_Z}. \tag{25}$$

Substituting Eqs. (23)–(25) into Eq. (22), we obtain an equation for the monomolecular desorption rate in the usual form [1–9]

$$-\frac{d\theta}{dt} = k_d(\theta)\theta;$$

$$k_d(\theta) = \frac{kT}{h}\frac{f^{\neq}_{1s}}{f_{1s}}e^{-E_1/kT}\left(\frac{1+\eta_1^*\mathscr{E}_1}{1+\eta_1\mathscr{E}_1}\right)^Z, \tag{26}$$

where $\eta_1^* = \alpha^* \exp(-u^*/kT)$, and $E_1 = E^*_{1S} - E_{1S}$ is the desorption activation energy of a monomer at $\theta \to 0$.

The desorption rate constant $k_d(\theta)$ can be represented in the form of the Arrhenius law

$$k_d(\theta) = C(\theta)\exp(-E(\theta)/kT), \tag{27}$$

where $E(\theta)$ is the desorption activation energy, and $C(\theta)$ is the pre-exponential factor. Then, using Eqs. (13), (26) and (27), the following expressions for $E(\theta)$ and $C(\theta)$ can be obtained under the assumption that $\eta_1^* = 1$:

$$E(\theta) = E_1 - \frac{Zu}{2}\left(\frac{2\theta - 1 + \gamma_1}{\gamma_1}\right), \tag{28}$$

$$\ln(C(\theta)/C_0) = Z \ln\left(\frac{2\theta - 1 + \gamma_1}{2\eta_1\theta}\right) - \frac{Zu}{2kT}\left(\frac{2\theta - 1 + \gamma_1}{\gamma_1}\right), \tag{29}$$

where E_1 and C_0 are the $E(\theta)$ and $C(\theta)$ values at $\theta = 0$. Figs. 2 and 3 present $E(\theta)$ and $C(\theta)$ dependences for various α_0 values and $|u| = 0.1$ eV. The parts (a) of these figures correspond to the case of attraction between adatoms ($u < 0$), while the parts (b) correspond to the repulsion ($u > 0$). These dependences qualitatively change their behavior by the inclusion of the entropy factor α_0 in the theory. So, in the case of attraction between adatoms (Fig. 1a) and $\alpha_0 = 1$ (this case corresponds to the conventional treatment developed in the above-mentioned Refs. [1–9]) the desorption activation energy $E(\theta)$ varies faster with increasing θ at small and large coverages. Changes of E are still small in the region about $\theta = 1/2$. However, at such values of $\alpha_0 < 1$ that $\eta_1 < 1$ (e.g., $\alpha_0 = 0.1$ in Fig. 2) the $E(\theta)$ dependence acquires another form: now the main changes of E take place at the coverages close to $\theta = 1/2$.

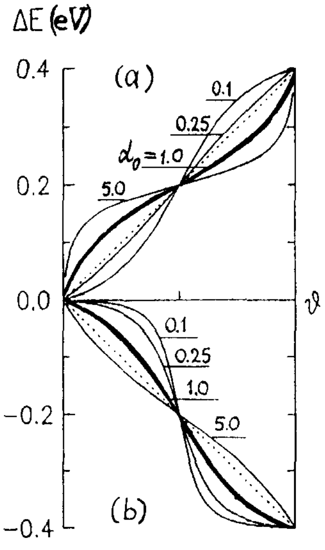

Fig. 2. Dependence of the desorption heat on the coverage for various α_0 values (shown by figures at the lines). The full-width line ($\alpha_0 = 1$) corresponds to the traditional approach. The dotted lines correspond to the Bragg–Williams approximation (Eq. (30)).

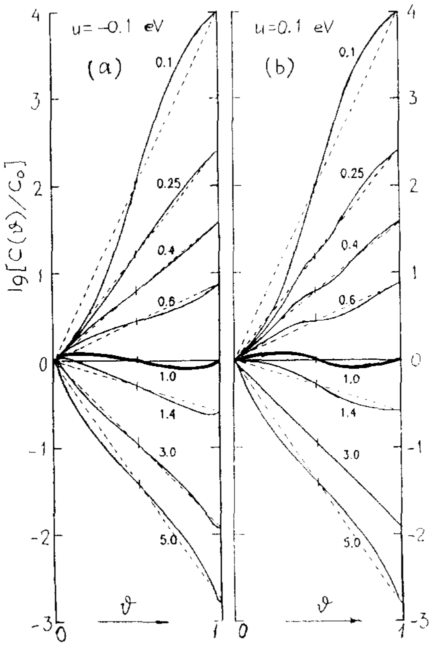

Fig. 3. Dependence of the pre-exponential desorption factor on the coverage θ for various α_0 values (shown by figures at the lines) in the cases of (a) lateral attraction with $u = -0.1$ eV and (b) lateral repulsion with $u = +0.1$ eV. Dashed lines show the functions (31). The full-width line shows the traditional approach ($\alpha_0 = 1$).

Including the factor $\alpha_0 \neq 1$ in the theory gives an even more significant influence of the quantity C on the concentration dependences. At $\alpha_0 = 1$ (full line in Fig. 3), the $C(\theta)$ dependences are antisymmetric with respect to the θ axis with the antisymmetry center $\theta = 1/2$, and variations of C are insignificant in the entire interval $0 < \theta < 1$, whereas at $\alpha_0 \neq 1$ the situation radically changes. First, the function $C(\theta)$ becomes monotonic at sufficiently small $\alpha_0 < 1$ in the case of $u < 0$, and at sufficiently large $\alpha_0 > 1$ in the case of $u > 0$ ($\alpha_0 < 0.4$ at $u = -0.1$ eV in Fig. 3a and $\alpha_0 > 2$ at $u = +0.1$ eV in Fig. 3b), while the range of the variation of $C(\theta)$ with coverage varying from $\theta = 0$

to $\theta = 1$ may reach many orders of magnitude. Second, at approximately the same values of u and α_0 the compensation effect arises, that is, $E(\theta)$ and $C(\theta)$ vary symbatically. Third, in limiting cases, when $\alpha_0 < \exp(u/kT)$ at $u < 0$ or $\alpha_0 > \exp(u/kT)$ at $u > 0$, the variation of the pre-exponential factor in Eq. (27) exceeds the $\exp(-E(\theta)/kT)$ variation. As a result, the adsorbed film densifying is accompanied by an increasing desorption rate in the case of attraction, and by its decreasing in the case of repulsion, in sharp contrast with the traditional lattice-gas theory. The possibility of realization of such limiting cases in real adsorption systems will be discussed below.

The functions (28) and (29) are shown in Figs. 2 and 3 compared to the linear dependences

$$\mathscr{E}(\theta) = E_0 - Zu\theta, \tag{30}$$

$$f(\theta) = -Z\theta \ln \alpha_0, \tag{31}$$

which are plotted by dashed lines. Eq. (30) corresponds to the Bragg–Williams approximation.

The dependences of $C(\theta)$ are antisymmetric with respect to the straight lines (Eq. (31)). The latter ones meet the lines $C(\theta)$ at $\theta = 0$, 1/2 and 1. According to Eqs. (28) and (29), at $\theta = 1$ one has

$$E(1) = E_1 - Zu, \quad \log(C(1)/C_0) = -Z \log \alpha_0. \tag{32}$$

The dependences of $C(\theta)$ become more complicated in those α_0 and u regions where the anticompensation effect occurs ($\alpha_0 > 1$ for $u < 0$ and $\alpha_0 < 1$ for $u > 0$). Additional points of their intersections with the straight lines $f(\theta)$ appear. However, they remain antisymmetric with respect to these lines.

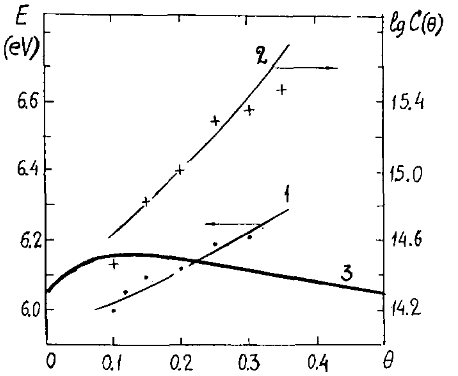

Fig. 4. Comparison of experimental dependences $E(\theta)$ (dots) and $C(\theta)$ (crosses) [13,14] for the adsorption system Nd–W(100) with theoretical dependences (solid lines) calculated for $u = -0.28$ eV at $kT = 0.17$ eV: (1) dependence $E(\theta)$, calculated according to Eq. (28) for $\alpha_0 = 0.11$; (2) dependence $C(\theta)$, calculated according to Eq. (29) for $\alpha_0 = 0.11$; (3) dependence $C(\theta)$, calculated according to the conventional quasi-chemical approximation (with $\alpha_0 = 1$ in Eq. (29)).

In order to elucidate the capabilities of the approach ($\alpha_0 \neq 1$) developed in the present work, the theoretical results were compared with experimental ones. Fig. 4 shows such results for the adsorption system Nd–W(100) [13,14]. We performed calculations both in the frame of the traditional quasi-chemical approximation ($\alpha_0 = 1$) and with the aid of the approximation developed in the present work. For the concentration dependence of the heat of adsorption $E(\theta)$ in the coverage range $0 < \theta \leq 0.35$ both approaches yield similar results, being in a satisfactory agreement with the experimental data (in Fig. 4 the dependence $E(\theta)$ (line 1) is given, which is obtained with the use of the modified quasi-chemical approximation). However, the capabilities of the two approaches are sharply different when describing the dependence of the pre-exponential factor $C(\theta)$ on coverage θ. It follows from Fig. 4 that, the traditional approach ($\alpha_0 = 1$) being incapable to give a satisfactory agreement with the experimental data, the modified approximation yields such an agreement, reached at $u = -0.28$ eV and $\alpha_0 = 0.11$.

A substantial difference between the traditional and modified quasi-chemical approximations, when applied to the system Nd–W(100), is revealed also in estimates of the critical temperature T_c for the first-order phase transition. So, according to the traditional approximation, $T_c = 2430$ K at $u = -0.28$ eV. It follows from this estimate that the adsorption isobars registered in Ref. [14] lie in the region of temperatures lower than T_c. This means that a coverage range ($\theta_1 < \theta < \theta_2$) must exist in which an equilibrium between an adsorbed layer and a gaseous phase is impossible. This conclusion, however, contradicts to experimental data for the Nd–W(100) system. Indeed, the adsorption isobars given in Ref. [14] reveal no vertical sections which would indicate a phase transition from θ_1 to θ_2. In contrast, according to the modified quasi-chemical approximation, the critical temperature for $u = -0.28$ eV and $\alpha_0 = 0.11$ is equal to $T_c = 904$ K. This result testifies that all adsorption heats of Nd atoms on W(100) were measured, in Refs. [13,14], at temperatures above the critical one and, therefore, there should not be any singularities (breaks or vertical pieces) on the adsorption isobars, in agreement with the experiment.

In the Sm–W(100) system [15] at coverages $0.5 \leq \theta \leq 0.95$ four-fold sites are occupied in a sublattice of c(2 × 2) Sm adatoms on the W(100) surface. Here the increase of both the heat and the pre-exponential factor of desorption is also observed with θ increasing (as in the system Nd–W(100)). Using the formulae (28) and (29), we find parameters $u = -0.09$ eV and $\alpha_0 = 0.25$. If α_0 were equal to unity, the pre-exponential factor would be nearly constant. Possible reasons for the small α_0 values for the Nd–W(100) and Sm–W(100) adsorption systems will be discussed below.

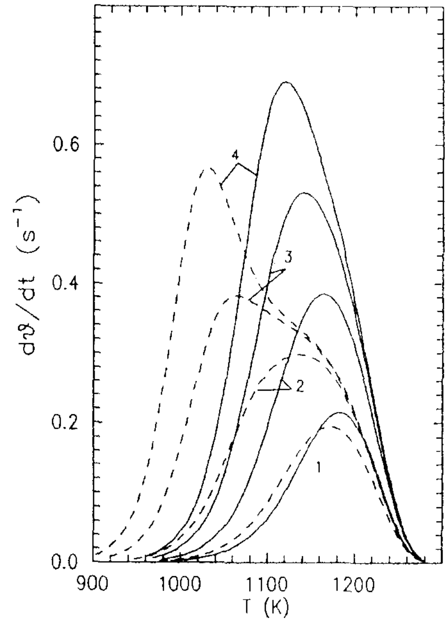

Fig. 5. Influence of the initial coverage θ_0 on TD spectra in the case of lateral attraction with $u = -0.1$ eV, $E_1 = 3$ eV, $C_0 = 10^{13}$ s^{-1}, $\beta = 100$ K s^{-1}; $\alpha_0 = 0.2$ (solid lines) and 0.1 (dashed lines); $\theta_0 = 0.25$ (1), 0.50 (2), 0.75 (3), 1.0 (4).

5. Influence of $\alpha_0 \neq 1$ on thermal desorption spectra

The temperature-programmed desorption process is described by the equations

$$-\frac{d\theta}{dt} = k_{d,x}(\theta)\theta^x, \quad T = T_0 + \beta t, \tag{33}$$

where x is the desorption order, t is the time and β is a constant. For monomolecular ($x = 1$) desorption, the function $k_d(\theta)$ is defined by Eq. (26) and depends upon the combination $\eta_1 = \alpha_0 \exp(-u/kT)$, but not upon α_0 and u separately. In spite of this, the allowance for $\alpha_0 \neq 1$ significantly affects the dependence of thermal desorption (TD) spectra on the initial coverage θ_0. In the conventional theory (with $\alpha_0 = 1$) an increase of the initial coverage θ_0 causes a shift of TD-spectra peaks towards lower temperatures in the case of repulsion between adatoms and towards higher temperatures in the case of attraction. However, these predictions do not always agree with experimental data. So, it was found in Refs. [18–20] that, even in the case of lateral attraction in the adlayer, the TD spectra are shifting with θ_0 increasing towards lower, rather than higher, temperatures.

One can account for these results by allowance for the entropy factor $\alpha_0 \neq 1$. Indeed, it is seen from Fig. 5 that at small $\alpha_0 < \exp(u/kT)$ the TD spectra may shift leftwards with θ_0 increasing, rather than rightwards, as it would be at $\alpha_0 = 1$. This may be accompanied by spectra splitting, like it would be in the case of the repulsion [5–9].

Fig. 6 demonstrates the influence of α_0 on the TD-spectra type when the repulsive forces act between adatoms. The values $\alpha_0 < 1$ enhance the spectra splitting and their shift towards lower temperatures, while at $\alpha_0 > 1$ the opposite occurs. The first case corresponds to the anticompensation between $C(\theta)$ and $E(\theta)$, and the second one corresponds to the compensation.

Fig. 7 presents experimental [19] and our numerical TD spectra of the Eu–W(211) adsorption system. For this system, in the coverage range $0 < \theta_0 \leq 0.5$, a growth of both the heat and the pre-exponential factor of the desorption was observed. In the same θ_0 interval, the densifying of the adsorbed film is accompanied by a shift of TD spectra towards lower temperatures. From a comparison of data [19] on the $C(\theta)$ growth with the formula (29) at $\theta = 1/2$ it follows that the α_0 value is close to 1/4 for the considered system. We have performed calculations of the TD spectra for this system having chosen the values $E_1 =$ 3.8 eV and $C_0 = 5 \times 10^{13}$ s^{-1}, at which the experimental TD peaks for the initial coverage $\theta_0 =$ 0.09 coincide with the numerical ones. Fig. 7 shows that the spectra are shifting towards lower temperatures, in spite of increasing the heat of adsorption. However, the theoretical shift is less than the experimental one. Besides, a more smooth transition to the maximum is seen for the experimental spectra. Probably here, apart from the entropy factors, a θ-dependence of the interaction energy (u decreasing with the θ growth) plays also a role.

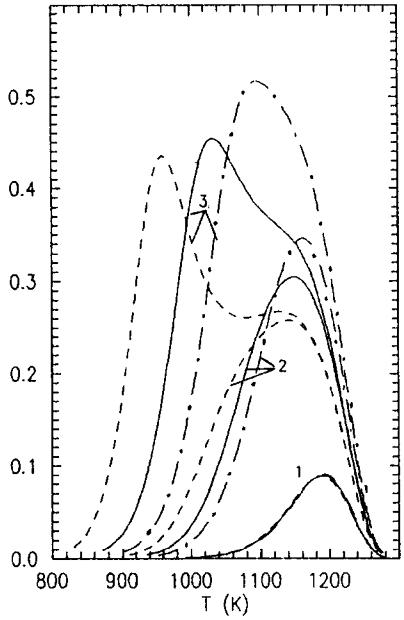

Fig. 6. Influence of α_0 and θ_0 on TD spectra in the case of lateral repulsion with $u = +0.1$ eV, E_1, C_0 and β same as in Fig. 5; $\alpha_0 = 1.0$ (solid lines), 0.6 (dashed lines), 1.4 (dash-dotted lines); $\theta_0 = 0.1$ (1), 0.50 (2), 1.0 (3).

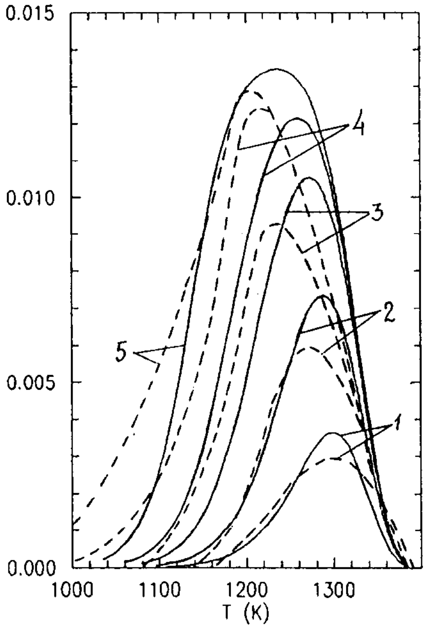

Fig. 7. Comparison of experimental TD spectra [19] for the Eu–W(211) system (dashed lines) with theoretically calculated ones (solid lines) at $u = -0.03$ eV, $E_1 = 3.8$ eV, $C_0 = 5 \times 10^{13}$ s^{-1}, $\beta = 4.3$ K s^{-1}, $\alpha_0 = 0.2$; $\theta_0 = 0.09$ (1), 0.2 (2), 0.33 (3), 0.435 (4), 0.595 (5).

6. On the physical meaning of the entropy parameter $\alpha_0 \neq 1$

Let us consider some causes of the α_0 deviations from unity, and estimate a possible range of such deviations. Introduction of the additional factor $F(T, n, i)$ into Eqs. (2) and (4) is equivalent to treating the chemical equilibrium $A + A \rightleftharpoons A_2$ in an adlayer by the use of a new equation for the probability $\mathcal{P}_{AA}$ that two neighbor cells are occupied by adatoms. This new equation is more similar to the chemical equilibrium equation than the formerly used one [4–9]. Indeed, using Eq. (5) for Ξ, one can obtain the equilibrium constant of this reaction in the lattice gas (assuming that $F(0, 0,\ldots,0) = 1$):

$$\frac{\mathcal{P}_{AA}\mathcal{P}_{00}}{\mathcal{P}_{A0}^2} = \frac{1}{4}\,\frac{F(1, 1, 0,\ldots,0)}{f_A^2}\exp\left(-\frac{u}{kT}\right). \qquad (34)$$

Here $\mathscr{P}_{A0}$ and $\mathscr{P}_{00}$ are the probabilities that one or neither of the two neighbor cells is occupied. In contrast to Refs. [1–9], in Eq. (34) the factor

$$\alpha_0 = F(1, 1, 0, \dots, 0)/f_A^2 = f_{11}/f_{1S}^2 \tag{35}$$

is taken into account. This factor is the ratio of the internal partition functions of the quasi-molecule A_2 (f_{11}) and two single particles A (f_{1S}) on the surface. The energies in f_{11} and f_{1S} are measured from the ground levels of these configurations, the difference between them being equal to u. This difference is taken into account by the exponent in Eq. (34). In the case of attraction between adatoms, the factor f_{11} may be closer to the partition function f_{2S} of the diatomic molecule than to the product $(f_{1S})^2$. In order to estimate the possible range of the α_0 values, let us consider a hypothetical example of a diatomic molecule and its constituting atoms, assuming that they are weakly bound with the surface. Let us restrict to a localized adsorption and assume that electronic and vibrational freedom degrees are separated. Then the partition function of an adatom and that of a pair of bound adatoms may be presented in the form of the products

$$f_{1S} \approx G_1 \prod_{i=1}^{3} f_1(\nu_i); \quad f_{2S} \approx G_2 \prod_{i=1}^{6} f_2(\nu_i), \tag{36}$$

where $G_{1,2} = g_{1,2}^{(0)} + \Sigma_j g_{1,2}^{(j)} \exp[-(E_{1,2}^{(j)} - E_{1,2}^{(0)})/kT]$ is the electronic partition function, and $g_{1,2}^{(j)}$ is the statistical weight of the jth state; subscripts 1 and 2 indicate the atom and the molecule, respectively; $f(\nu_i) \approx (kT/h\nu_i)[1 - \exp(-D_i/kT)]$ is the partition function of one vibrational freedom degree with the frequency ν_i; D_i is the energy of the disconnection of the ith bond. Substituting f_{2S} for f_{11} in Eq. (35), we come to the estimate

$$\alpha_0 \approx \frac{G_2}{G_1^2} \left[\prod_{i=1}^{6} f_2(\nu_i) \left(\prod_{i=1}^{3} f_1(\nu_i) \right)^{-2} \right]. \tag{37}$$

Vibrations of a pair of bound atoms differ from vibrations of isolated atoms on the surface, therefore the second multiplier in Eq. (37) deviates from 1. One may expect that it is less than unity in the case of attraction, because bond strengthening results in increasing longitudinal frequencies and decreasing related partition functions.

Table 1
Terms of the lowest states of atoms (A) and molecules (A_2), the values of the electronic partition functions G_1, G_2, and the ratio G_2/G_1^2 at $T = 1700$ K

Atom A	Term A	G_1	Term A_2	G_2	G_2/G_1^2
Li	$^2S_{1/2}$	2	$^1\Sigma_g^+$	1	0.25
B	$^2P_{1/2,3/2}$	6	$^3\Sigma_g^-$	3	0.08
C	$^3P_{0,1,2}$	9	$^1\Sigma_g^+$ $^3\Pi_u$	4.3	0.05
N	$^4S_{3/2}$	4	$^1\Sigma_g^+$	1	0.06
O	$^3P_{0,1,2}$	8.5	$^3\Sigma_g^-$	3	0.04
S	$^3P_{2,0,1}$	9	$^3\Sigma_g^+$	3	0.04
Cl	$^3P_{3/2}$ $^2P_{1/2}$	4.95	$^1\Sigma_g^+$	1	0.04
Au	$^2S_{1/2}$	2	$^1\Sigma_g^+$	1	0.25
Mg	^1So	1	$^1\Sigma_g^+$	1	1

As for the ratio G_2/G_1^2, it is also most likely less than unity. To clarify this, let us consider this ratio for some homeopolar molecule, which is a model for dimer formation under the effect of attractive forces. This is illustrated by Table 1 which presents the G_2/G_1^2 values for some homeopolar molecules. The atomic and molecular terms are taken from Refs. [28,29]. It follows from the table that the G_2/G_1^2 ratio may be much smaller than 1. The only exclusion are the atoms with closed shells, for which this ratio is equal to 1.

It should be noted that the formation of direct bonds between adatoms is not the unique reason for their electronic state changing when a cluster is formed. Apart from this, the association process is accompanied by the depolarization of bonds between atoms and the substrate, and by the related rearrangement of electronic shells. Hence, the deviation of G_2/G_1^2 from unity is possible even for a noble gas on a surface.

One may conclude from the above estimates that in the case of attraction between adatoms the α_0 value is most likely less than 1. This conclusion is confirmed by the results of the MD simulation for Xe adsorption on the Pt(111) surface [30] and also by the calculation of the free energy of adsorbed Ar as a function of the number of nearest neighbors [24c]. Attractive forces between Xe adatoms cause such changes of the vibrational spectrum of the adlayer, which increase the pre-exponential factor in the desorption rate constant, partially compensating the increase of the desorption activation energy.

There are also other reasons for the deviation of α_0 from unity, aside from the already considered ones [13,14]. They are the decrease of the adatom mobility with θ increasing; the small value of the numerator in the vibrational partition function $f(\nu_i)$ at small binding energy D_i in a quasi-molecule on the surface; a perturbation of that surface site at which an association of adatoms is formed; etc. We have considered in more details the variation of the electronic part of the partition function, since almost no attention was paid to this factor in literature. It was taken into account only in quantum-mechanical calculations analogous to Ref. [31]. This is probably why such calculations describe most properly the observed desorption-rate tendencies [16].

7. Summary

The quasi-chemical approximation in the two-dimensional lattice-gas theory has been successfully used to describe the kinetics of processes in adsorbed layers. The single parameter of the theory was the energy of lateral interaction u. The simplicity and clearness of the theoretical model help one to understand and to predict the character of physical processes in adlayers. However, this approximation in its conventional form failed to describe some experimental results. In the present paper one of several possible ways to improve this model is considered.

The proposed modification of the quasi-chemical approximation consists in including into the conventional theory an entropy parameter, α_0, allowing for changes of the internal partition functions of adatoms caused by their mutual interactions. This parameter is equal to the ratio of the internal partition function of a dimer to that of two isolated monomers on the surface, and in principle it should be always different from unity. The greater is a perturbation of an electronic configuration of adatoms and a substrate by neighboring adatoms, the larger is the difference of α_0 from unity. Thus, introduction of the new parameter has principal physical justification.

The modified quasi-chemical approximation essentially extends the capabilities of the theory in describing experimental results. The clear physical meaning of the introduced parameter α_0 makes it possible to obtain not only a description, but also a physical explanation of a number of phenomena, which could not be grasped in frames of the traditional approach, for example: (i) the compensation effect; (ii) the wide-range monotonic variation (either increasing or decreasing) of the pre-exponential factor in the desorption rate constant with increasing coverage; (iii) the growth of the desorption rate constant with densifying an adsorbed film in the case when attractive forces act between adatoms; (iv) the shift of some maxima of thermal-desorption spectra towards lower temperatures with increasing initial coverage of adsorbed atoms in the case when attractive forces act between them.

The theoretical conclusions are compared quantitatively with experimental data for some real adsorption systems.

In the present paper we have considered in detail the case of a quadratic lattice. It can be shown that the same modification is possible also in the case of a hexagonal lattice, where all interactions in a cluster are equivalent. Now the work on the modified quasi-chemical approximation applied to the case of a hexagonal lattice is in progress.

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