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Title	MULTILAYER LATTICE GAS MODEL FOR THE ZERO ORDER DESORPTION KINETICS
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Citation	JOURNAL OF THE RESEARCH INSTITUTE FOR CATALYSIS HOKKAIDO UNIVERSITY, 31(1), 1-5
Issue Date	1983-11
Doc URL	<a href="https://hdl.handle.net/2115/25142">https://hdl.handle.net/2115/25142</a>
Type	departmental bulletin paper
File Information	31(1)_P1-5.pdf



## MULTILAYER LATTICE GAS MODEL FOR THE ZERO ORDER DESORPTION KINETICS

By

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(Received May 9, 1983)

### Abstract

A multilayer lattice gas model is presented to explain the zero order kinetics of the unimolecular desorption of adatoms from solid surfaces. The desorption is assumed to occur layer by layer, but a dilute adlayer in the next upper layer and sparse vacancies in the just under layer are taken into account. When the system is in the two-phase coexisting regime, it is demonstrated that the desorption obeys zero order kinetics provided that adatoms desorb unimolecularly from the lower-density phase.

There has been a puzzling problem concerning the zero order kinetics in unimolecular desorption from solid surfaces.<sup>1)</sup> For this desorption kinetics the author has recently proposed a bilayer model<sup>2)</sup> where unimolecular desorption takes place in the dilute phase coexisting with the dense phase in the same layer and also in the next upper layer of the latter. His essential idea is that: The adsorption energy of an atom in the lower dilute adlayer is in general greater than in the upper dilute adlayer, which results in a higher areal density of atoms and a higher activation energy of desorption for the lower dilute adlayer. These two are compensated each other, leading to the equal desorption rate per unit surface area for the lower and upper dilute adlayers, *i. e.*, the zero order desorption kinetics.

This paper is essentially statistical mechanical justification of the previous idea based on a more elementary statistical mechanical model, *viz.*, a multilayer lattice gas where the mutual interaction between adatoms is treated in the Bragg-Williams approximation.

Consider a stacking of 2D hexagonal lattices on a substrate surface. The resultant structure of the 3D lattice may be either f. c. c. or h. c. p. Every hexagonal layer is composed of  $N_0$  lattice points, each of which serves as an adsorption site to be occupied exclusively by a single atom. We pre-

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sume that an atom can occupy a site whose three nearest neighbor sites in the underlayer (if they exist) are all occupied and that it interacts with an energy  $\epsilon_m$  ( $<0$ ) only with first nearest neighboring atoms. Let us denote by  $N_j$  the number of atoms in the  $j$ -th layer and define  $\theta_j \equiv N_j/N_0$  and  $b_j \equiv 1 - \theta_j$ . We restrict our adsorption system within a regime where adsorption occurs layer by layer. (A safe condition for this restriction would be  $\epsilon_{i+1} - \epsilon_i > k_B T$  if we say in connection with eq. (10).) When adsorption and desorption take place mainly in the  $i$ -th layer, we may put  $N_j = N_0$  for  $j \leq i-2$  and  $N_j = 0$  for  $j \geq i+2$  and also

$$\theta_{i+1} \ll 1 \quad \text{and} \quad b_{i-1} \ll 1. \quad (1)$$

Then we have a canonical partition function  $Q_i(T)$  for our system in the Bragg-Williams approximation for mutual adatom interaction<sup>9</sup>:

$$\begin{aligned} Q_i(T) = & \frac{N_0!}{N_i! (N_0 - N_i)!} \cdot \frac{(N_i \theta_i^2)!}{N_{i+1}! (N_i \theta_i^2 - N_{i+1})!} \\ & \cdot \frac{\{(N_0 - N_i)(1 - \theta_i)^2\}!}{(N_0 - N_{i-1})! \{(N_0 - N_i)(1 - \theta_i)^2 - N_0 + N_{i-1}\}!} \\ & \times \exp \left[ - \sum_{j=1}^{i+1} (\epsilon_j + 3\theta_j \epsilon_m) N_j / k_B T \right], \quad (2) \end{aligned}$$

where  $T$  is the temperature and  $\epsilon_j$  the potential energy of a  $j$ -th layer adatom due to both the substrate and first nearest neighboring adatoms in the underlayer (if  $j \geq 2$ ). The first factor of eq. (2) represents the number of different distributions of  $N_i$  adatoms over  $N_0$  sites of the  $i$ -th layer. The mean number of triangles constituted by three nearest neighboring adatoms in the  $i$ -th layer is  $2N_i \theta_i^2$ . Therefore, the number of  $i+1$ -th layer sites available for occupation is half of that value (because we must take either f. c. c. or h. c. p. positions for adsorption sites), and the number of different ways of distribution of  $N_{i+1}$  atoms over those available sites forms the second factor of eq. (2). Similarly,  $N_0 - N_{i-1}$  vacant sites in the  $i-1$ -th layer must be distributed over  $(N_0 - N_i)(1 - \theta_i)^2$  available positions, half of the mean number of triangles constituted by three nearest neighboring vacant sites in the  $i$ -th layer, because three nearest neighbor sites in the upper layer of a particular site should be vacant if the particular site is unoccupied. Then we have the third factor in eq. (2) for the number of possible distributions of  $N_0 - N_{i-1}$  vacant sites in the  $i-1$ -th layer under the mean configuration of the  $i$ -th layer. As a consequence the first three factors of eq. (2) represent the number of configurations of  $N_j$ 's adatoms in our multilayer lattice.

The free energy  $F_i(T)$  per site of a single layer is given by

*Lattice Gas Model for Desorption Kinetics*

$$\begin{aligned}
F_i(T) &= -k_B T \ln Q_i(T)/N_0 \\
&= k_B T \left\{ \theta_i \ln \theta_i + (1-\theta_i) \ln (1-\theta_i) \right\} + (\varepsilon_i + 3\varepsilon_m \theta_i) \theta_i \\
&\quad + b_{i-1} \left[ k_B T \left\{ \ln b_{i-1} - 3 \ln (1-\theta_i) - 1 \right\} - \varepsilon_{i-1} - 6\varepsilon_m \right] \\
&\quad + \theta_{i+1} \left[ k_B T \left\{ \ln \theta_{i+1} - 3 \ln \theta_i - 1 \right\} + \varepsilon_{i+1} \right] + \text{const.}, \quad (3)
\end{aligned}$$

expanding to the first order of  $b_{i-1}$  and  $\theta_{i+1}$ . The values of  $\theta_j$ 's should be determined from the relation,  $\partial F_i / \partial \theta_j = \mu$ , the chemical potential of adatoms:

$$\frac{\theta_i}{1-\theta_i} = \exp \left[ -\frac{\varepsilon_i + 6\varepsilon_m \theta_i - \mu}{k_B T} - \frac{3b_{i-1}}{1-\theta_i} + \frac{3\theta_{i+1}}{\theta_i} \right], \quad (4)$$

$$b_{i-1} = (1-\theta_i)^3 \exp \left[ -(\mu - \varepsilon_{i-1} - 6\varepsilon_m) / k_B T \right], \quad (5)$$

$$\theta_{i+1} = \theta_i^3 \exp \left[ -(\varepsilon_{i+1} - \mu) / k_B T \right]. \quad (6)$$

If we put  $b_{i-1} = \theta_{i+1} = 0$  in eq. (4), we have the well-known ideal 2D isotherm<sup>4</sup> in the  $i$ -th layer, whose critical temperature  $T_c$  is  $k_B T_c = -3\varepsilon_m/2$ . When the ideal 2D system is in the two-phase coexisting regime below  $T_c$ ,

$$\mu = \varepsilon_i + 3\varepsilon_m. \quad (7)$$

Since the fractional density  $\theta_g$  of the dilute phase well below  $T_c$  may be regarded as much less than unity, expansion of eq. (4) with respect to  $\theta_i$  with  $b_{i-1} = \theta_{i+1} = 0$  and with  $\mu$  given by eq. (7) yields

$$\theta_g = \exp (3\varepsilon_m / k_B T). \quad (8)$$

The fractional density  $\theta_s$  of the dense phase is then given by

$$\theta_s = 1 - \theta_g = 1 - \exp (3\varepsilon_m / k_B T), \quad (9)$$

owing to the symmetry of the  $\mu - \theta_i$  curve.

In the case of our multilayer system, the non-zero  $b_{i-1}$  and  $\theta_{i+1}$  result in a deviation from the ideal two-dimensionality of the  $i$ -th layer phase transition, but it can be easily seen that they give rise to only higher order infinitesimal corrections in  $\theta_g$  and  $\theta_s$ . Hence we may be permitted to use eqs. (8) and (9) also for the multilayer system. The fractional density  $\theta_{i+1}$  of the dilute adlayer on the dense phase of the  $i$ -th layer is then given by substituting eqs. (7) and (9) for  $\mu$  and  $\theta_i$ , respectively, in eq. (6):

$$\theta_{i+1} = \exp \left[ -(\varepsilon_{i+1} - \varepsilon_i - 3\varepsilon_m) / k_B T \right]. \quad (10)$$

Incidentally, the fractional density  $b_{i-1}$  of vacancies under the dilute phase of the  $i$ -th layer is derived from eqs. (5), (7), and (8) as

$$b_{i-1} = \exp \left[ -(\varepsilon_i - \varepsilon_{i-1} - 3\varepsilon_m) / k_B T \right]. \quad (11)$$

We see from eqs. (8)–(11) that the ratio  $\theta_{i+1}/\theta_g$  of atomic densities is equal to the Boltzmann factor of the difference between their potential energies  $\varepsilon_i$ 's and that the ratio  $b_{i-1}/(1-\theta_g)$  of the densities of vacancies is equal to the Boltzmann factor of the difference between their excitation energies  $-\varepsilon_i$ 's.

As in the previous paper,<sup>2)</sup> desorption of adatoms is postulated to occur unimolecularly in the dilute phase and not so fast to destroy the phase-equilibrium in the adlayers. The activation energy of desorption from the  $i$ -th layer is equated with the adsorption energy  $-\varepsilon_i$ . Let  $\nu_1$  be the frequency factor of desorption and  $\alpha_i$  be the fraction of the surface covered with the dense phase of the  $i$ -th layer. We have for the desorption rate  $R_i$  per unit surface area

$$R_i = \alpha_i \rho_0 \nu_1 \theta_{i+1} \exp(\varepsilon_{i+1}/k_B T) + (1 - \alpha_i) \rho_0 \nu_1 \theta_g \exp(\varepsilon_i/k_B T), \quad (12)$$

where  $\rho_0$  represents the areal density of adsorption sites in a single layer. Substituting eqs. (8) and (10), we get a zero order desorption formula:

$$R_i = \rho_0 \nu_1 \exp \left[ (\varepsilon_i + 3\varepsilon_m) / k_B T \right]. \quad (13)$$

When the dense adlayer vanishes entirely as the desorption proceeds and only the dilute adlayer remains on the surface, the kinetics is switched over to first order, *i. e.*,

$$R_i = \rho_0 \nu_1 \theta_i \exp(\varepsilon_i/k_B T). \quad (14)$$

It is interesting to note that there is a difference of  $3|\varepsilon_m|$  in the activation energy between two kinetics, which is in conflict with the previous assertion.<sup>2)</sup> The conflict arises from the neglect of  $T$ -dependence of  $\theta_g$  in the previous paper. The difference of  $3|\varepsilon_m|$  is estimated as  $3|\varepsilon_m| = 2k_B T_c \simeq 0.5 \text{ kcal/mole}^{\text{b}}$  in the case of Xe adsorption, which would be as large as detectable in experiments. Unfortunately, experimental results on Xe/W(110)<sup>1)</sup> are not necessarily favorable for our expectation. Equations (13) and (14) imply that the frequency factors of the two kinetics should be independent of the layer number, which seems at first sight inconsistent with available experimental data.<sup>1)</sup> The author feels that the crudity of our theoretical model should share the responsibility for the inconsistency.

*Lattice Gas Model for Desorption Kinetics***References**

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