| Title | A MODEL FOR THE ZERO ORDER DESORPTION KINETICS |
|---|---|
| Author(s) | ASADA, Hiromu |
| Citation | JOURNAL OF THE RESEARCH INSTITUTE FOR CATALYSIS HOKKAIDO UNIVERSITY, 30(2), 55-59 |
| Issue Date | 1983-02 |
| Doc URL | http://hdl.handle.net/2115/25128 |
| Type | bulletin (article) |
| File Information | 30(2)_P55-59.pdf |

Instructions for use

# A MODEL FOR THE ZERO ORDER
# DESORPTION KINETICS

By

Hiromu ASADA[*]

(Received September 9, 1982)

**Abstract**

A model for the zero order desorption kinetics is presented. Adatoms are assumed to desorb via a unimolecular process from dilute adlayers which are effectively in phase-equilibrium with a dense adlayer. The dilute phase is allowed to exist in the next upper layer of the dense phase as well as in the same layer as the latter. A lower potential energy of an adatom results in a higher areal atomic density of a dilute adlayer and a higher activation energy of desorption. These two are compensated each other in the desorption rate, leading to the zero order kinetics.

In several adsorption systems of monatomic molecules on solid surfaces[1] the desorption kinetics has been found to be zero order with respect to the areal density of adatoms. These systems also showed an evidence that adatoms aggregated into *islands* with a high areal density or were separated into a dense phase and a dilute one. Recently, Opila and Gomer[2] found that Xe desorbed layer by layer from the (110) plane of W and that the desorption kinetics was zero order until the fractional coverage of Xe for each layer decreased down to $0.25 \sim 0.30$ where a sharp transition to first order kinetics occurred.

These experimental results strongly suggest that the zero order desorption takes place when two phases of adsorbed layers (dense and dilute, 2 D (two-dimensional) gas and 2 D solid, or *islands* and *sea*) coexist on the surface. In fact, many models have been proposed to explain the zero order desorption from the viewpoint of phase-equilibrium, but none of them was successful as discussed in detail in ref. 2.

We present here a model for the zero order desorption kinetics, which is based on phase-equilibrium in adsorbed layers in a similar manner as previous models;[1,2] adatoms are assumed to desorb from a dilute phase via a unimolecular process and so slowly that the dilute phase is effectively in

---

\*) Research Institute for Catalysis, Hokkaido University, Sapporo, 060 Japan.

equilibrium with a dense phase. The only one difference with the previous models is that there may exist a dilute adlayer in the next upper layer of an incomplete dense adlayer as well as in the same layer of the latter: In general a dense layer, whether it is complete or incomplete, may adsorb foreign atoms as far as it provides adsorption potential wells for them. However, we assume that the mutual attractive interaction between adatoms, which results in condensation of adatoms into a dense phase, is not so strong as to give rise to formation of an incomplete dense adlayer piled up on another incomplete dense adlayer, *i. e.*, three-dimensional nucleation. The dilute phase is assumed to be like a 2 D gas where each adatom moves independently on a surface as a 2 D free particle. Furthermore, we suppose that a substrate and a dense adlayer serve only as a potential field to bind foreign atoms onto their surfaces with respect to the motion perpendicular to their surfaces.

Our argument starts with a system where adatoms adsorb and desorb *layer by layer*. Let us denote an adsorbed phase in the $i$-th layer with a higher atomic density by $H_i$ and that with a lower atomic density by $L_i$. We write the areal atomic densities of $H_i$ and $L_i$ as $\rho_0$ independent of $i$ and $\rho_0\theta_i$, respectively. Figure 1 shows schematically a situation where the dense phase $H_i$ and the dilute phase $L_i+L_{i+1}$ are in equilibrium with the gas phase on a surface of a complete layer of $H_{i-1}$ ($H_0$ being the substrate). It will be helpful to see the corresponding adsorption isotherm illustrated in Fig. 2. As the pressure of the gas phase rises up, the areal density $\theta_i$ of $L_i$ increases up to $\theta_{i,h}$ where adatoms begin to condense into a dense phase $H_i$ with a
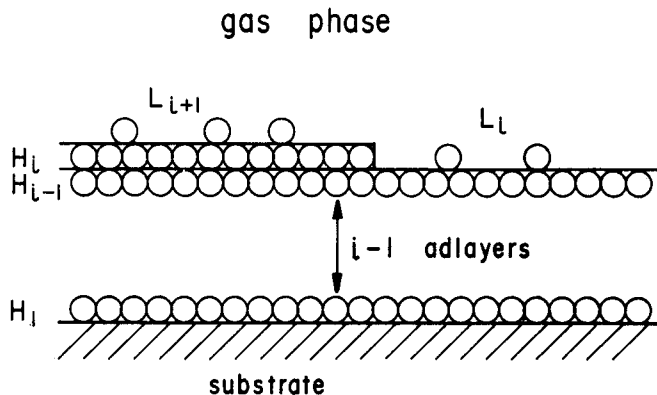


**Fig. 1.** Schematic drawing of the layer-by-layer adsorption. A dilute layer may exist upon an incomplete dense layer as well as in the same layer as the latter.
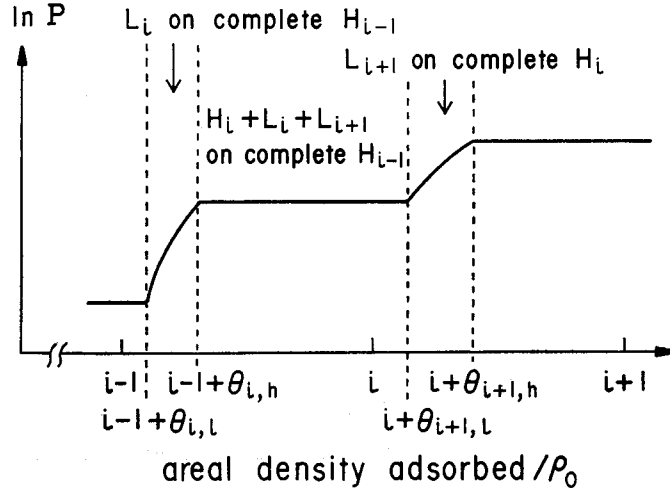
**Fig. 2.** Layer-by-layer adsorption isotherm in the range of adsorbed amount from $i-1$ to $i+1$ monolayers. $P$ the pressure of the gas phase.

dilute layer $L_{i+1}$ lying upon its surface. During the course of condensation, the fractional coverages $\theta_i$ and $\theta_{i+1}$ are held constant at $\theta_{i,h}$ and $\theta_{i+1,l}$, respectively. Since we suppose an *ideal* 2 D gas for the dilute phase, there should be a relation between $\theta_{i,h}$ and $\theta_{i+1,l}$, *i.e.*,

$$\theta_{i+1,l}/\theta_{i,h} = \exp\left[-(V_{i+1}-V_i)/k_B T\right], \tag{1}$$

where $V_i$ represents a potential energy of an atom adsorbed in the $L_i$ layer, $T$ the temperature of the system, and $k_B$ the Boltzmann constant. When the $H_i$ layer covers the whole surface of $H_{i-1}$ layer, the total areal density adsorbed is $i+\theta_{i+1,l}$ in units of $\rho_0$. The system may be regarded as in a single phase of $L_{i+1}$ until $\theta_{i+1}$ increases up to $\theta_{i+1,h}$ with increasing pressure, where the next condensation starts.

When there coexist a dense phase $H_i$ and a dilute phase $L_i+L_{i+1}$ on a complete layer of $H_{i-1}$, the desorption rate $R$ per unit area of the substrate is given by a sum of first order desorption rates from the $L_i$ and $L_{i+1}$ layer, *i.e.*,

$$R = \alpha k_{i+1}\theta_{i+1,l}+(1-\alpha)\,k_i\theta_{i,h}, \tag{2}$$

where $\alpha$ represents a fraction of the surface of $H_{i-1}$ covered by the $H_i$ layer. As usual the rate constant $k_i$ for the $i$-th dilute adlayer is written as

$$k_i = \rho_0\nu_1 \exp\left(-E_i/k_B T\right). \tag{3}$$

In our model, the first order frequency factor $\nu_1$ does not depend on $i$, while

the activation energy $E_l$ should involve a term of the potential energy $V_l$. Then we have

$$k_{l+1}/k_l = \exp\left[-(E_{l+1}-E_l)/k_B T\right] = \exp\left[(V_{l+1}-V_l)/k_B T\right]. \qquad (4)$$

Substituting eqs. (1) and (4) into eq. (2) leads to

$$R = k_l \theta_{l,h} = \rho_0 \nu_1 \theta_{l,h} \exp\left(-E_l/k_B T\right), \qquad (5)$$

showing the zero order desorption. This result means that the desorption rate per unit area from the $L_l$ layer and that from the $L_{l+1}$ layer are equal to each other. This is because an advantage of higher areal density of adatoms due to a deeper potential field is just canceled out by a disadvantage of higher activation energy.

When the dense phase $H_l$ vanishes entirely as the desorption proceeds, the desorption kinetics is switched over to first order in the $L_l$ phase, *i. e.*,

$$R = k_l \theta_l = \rho_0 \nu_1 \theta_l \exp\left(-E_l/k_B T\right). \qquad (6)$$

The first order process continues until $\theta_l$ decreases down to $\theta_{l,1}$ where the underlying complete layer of $H_{l-1}$ (if it exists) begins to shrink. Figure 3 shows schematically the time-dependence of the desorption rate $R$.

Since the coverage $\theta_{l,h}$ may be expected to be much less dependent on temperature than the exponential activation factor, except near the critical temperature, it follows from eq. (5) that the activation energy in the zero
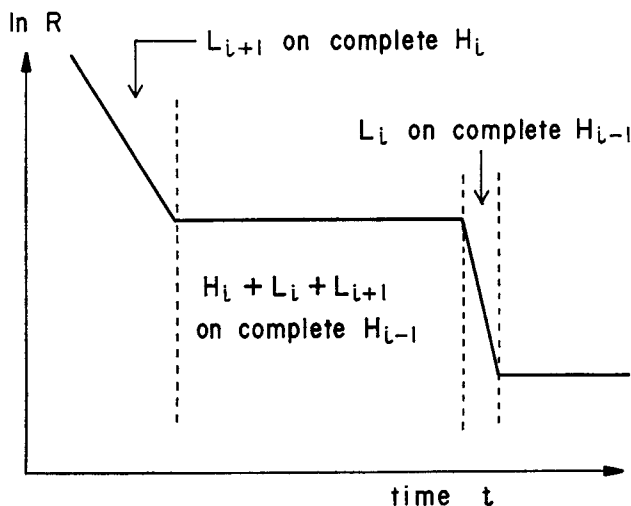


**Fig. 3.** Isothermal desorption rate $R$ shown schematically, indicating a zero order kinetics regime where $\ln R$ is independent of $t$ and a first order regime where $\ln R$ is linear with $t$.

order desorption is nearly equal to $E_i$, the activation energy in the first order desorption on the same surface of a complete dense layer. This result is confirmed by experiments of Opila and Gomer[2]. Denoting the zero order frequency factor $\rho_0 \nu_1 \theta_{i,h}$ by $\nu_{0i}$, we have

$$\nu_{0i}/\nu_1 = \rho_0 \theta_{i,h} . \tag{7}$$

When this relation is applied to experimental data on Xe/W (110)[2], we obtain values of $\theta_{i,h}$ as given in Table 1. Their order of magnitude seems to be reasonable. However, values of $\theta_{i,h}$ which were experimentally determined from the transition from a zero order to a first order desorption are $0.25 \sim 0.30$ for $i = 1$, 2, and 3, inconsistent with the results in table 1. One possible explanation for the discrepancy might be that a dilute layer lying upon an incomplete dense layer was removed before the underlying dense layer was depleted entirely: The dilute layer might be unstable upon too small dense layer.

TABLE 1.  Experimental data[2] on frequency factors $\nu_{0i}$ and $\nu_1$ and calculated values of $\theta_{i,h}$ via eq. (7).  $\rho_0 = 6.6 \times 10^{14}$ atoms/cm$^2$ [2]

|  | $i$ | $\nu_{0i}(s^{-1})$ | $\nu_1(s^{-1})$ | $\theta_{i,h}$ |
|---|---|---|---|---|
| First layer | 1 | $3 \times 10^{25}$ | $1 \times 10^{12}$ | 0.05 |
| Second layer | 2 | $5 \times 10^{26}$ | $6 \times 10^{12}$ | 0.13 |

Sharp transitions between desorption kinetics may provide a tool for investigating phase transitions in adsorbed layers which are now attracting great attention.

## References

1 ) See literatures cited in ref. 2.
2 ) R. Opila and R. Gomer, Surface Sci., **112**, 1 (1981).