TWO-STEP KINETICS ON INHOMOGENEOUS SURFACES

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The mechanism of a number of reactions that take place on the surfaces of solids fits into a simple two-step scheme [1-3]:

$$\begin{array}{l} 1)\ A_1 + A_2 + \cdots + (\ ) \rightleftarrows X_1 + X_2 + \cdots + (I) \\ 2)\ B_1 + B_2 + \cdots + (I) \rightleftarrows Y_1 + Y_2 + \cdots + (\ ) \\ \hline A_1 + A_2 + \cdots + B_1 + B_2 + \cdots = X_1 + X_2 + \cdots + Y_1 + Y_2 + \cdots \end{array} \qquad (1)$$

Here $A_1, A_2, \ldots, B_1, B_2, \ldots$ and $X_1, X_2, \ldots, Y_1, Y_2, \ldots$ are the molecules of the starting materials and reaction products, existing in the gas phase; ( ) is an empty space on the surface; (I) is a chemosorbed particle I. The kinetic equations corresponding to an equilibrium reaction according to scheme (1) have been obtained [1] for the cases when the surface is homogeneous or is uniformly inhomogeneous. Here we shall consider the kinetics under more general assumptions of inhomogeneity of the surface.

In the model of the surface used, each place on the surface capable of bonding one I particle is characterized by some value of the "desorption pressure" b, independent of whether the surrounding places are free or occupied. If b is the same for all places on the surface, i. e., the surface is homogeneous, then at equilibrium with a gas of free particles I, the pressure of which is equal to p_I, the degree of surface coverage

$$\theta = \frac{p_I}{p_I + b} \qquad (2)$$

(the Langmuir isotherm). The desorption pressure may be considered as the constant of the equilibrium

$$(I) = I + (\ ). \qquad (3)$$

Actually, expressing the concentrations of free and occupied places on a homogeneous surface by the quantities $1-\theta$ and θ, we obtain, according to the Law of Mass Action, $p_I(1-\theta)/\theta = b$, which is equivalent to Eq. (2).

The treatment of the kinetics on inhomogeneous surfaces developed [4, 5, 1] is based on the rule of transmission of changes in equilibrium to the rate. According to this rule, the rate constants of the steps at different places on the surfaces $\varkappa_s$ and the corresponding equilibrium constants of the steps K_s are related by functions of the type

$$\varkappa_s = g_{|s|} K_s^{a_s}, \qquad (4)$$

where $g_{|s|}$ and a_s are constants, $0 < a_s < 1$. The subscript s, which shows the number of the step, will be assigned a minus sign if it accompanies a quantity pertaining to the occurrence of a step in the reverse direction; the constant $g_{|s|}$ is the same for the forward and reverse directions of the step; hence, its subscript is written as $|s|$. The transmission coefficient a_s (also called the symmetry coefficient) will be denoted, according to A. N. Frumkin [6], as $\alpha_{|s|}$ when the space on the surface is occupied ($s = 1$ or $s = -2$) and $\beta_{|s|}$ when the space is free ($s = -1$ or $s = 2$); then $\alpha_{|s|} + \beta_{|s|} = 1$. For simplication, let us assume just as before [1] that $\alpha_1 = \alpha_2 = \alpha$, and, consequently, $\beta_1 = \beta_2 = \beta$.

Combining equilibrium (3) with the equilibrium of the first step of scheme (1) we find

$$K_1 = K_1' b^{-1}, \tag{5}$$

where K_1' is the equilibrium constant of

$$A_1 + A_2 + \ldots = X_1 + X_2 + \ldots + I. \tag{6}$$

Similarly

$$K_2 = K_2' b, \tag{7}$$

where K_2' is the equilibrium constant of

$$B_1 + B_2 + \ldots + I = Y_1 + Y_2 + \ldots \tag{8}$$

The quantities K_1' and K_2' are common to all places on the surface. Considering that $K_{-s} = K_s^{-1}$, on the basis of (4), (5), and (7), we obtain expressions for $\varkappa_s$ in the form of the function b:

$$\varkappa_1 = g_1 (K_1')^{\alpha} b^{-\alpha}; \quad \varkappa_{-1} = g_1 (K_1')^{-\beta} b^{\beta}; \quad \varkappa_2 = g_2 (K_2')^{\beta} b^{\beta}; \quad \varkappa_{-2} = g_2 (K_2')^{-\alpha} b^{-\alpha}. \tag{9}$$

Let us introduce the "index of desorbability" of the particles I, $\xi = \ln b$, and the differential function of the distribution of places on the surface with respect to the index of desorbability $\varphi(\xi)$ [7]. The latter is determined by the fact that the number of places with values of the index of desorbability in the range from ξ to $\xi + d\xi$ on a unit surface area is equal to $\varphi(\xi)d\xi$. For simplication of the calculations, let us use the concept of the reaction rate in the forward direction ω_+ and in the reverse direction ω_- [8, 9]. The observed reaction rate $\omega = \omega_+ - \omega_-$. On an inhomogeneous surface

$$\omega_+ = \int_{-\infty}^{\infty} \rho_+ (\xi)\, \varphi(\xi)\, d\xi, \tag{10}$$

where $\rho_+(\xi)$ is the contribution to ω_+ of one place on the surface with a given value of ξ. For the expression for ω_+, corresponding to scheme (1) for a homogeneous surface [1], it follows that

$$\rho_+ (\xi) = \frac{1}{L} \frac{\varkappa_1 p_A \varkappa_2 p_B}{\varkappa_1 p_A + \varkappa_{-1} p_X + \varkappa_2 p_B + \varkappa_{-2} p_Y}, \tag{11}$$

where L is the number of places on a unit surface area, $p_A = p_{A_1} p_{A_2} \ldots$, $p_B = p_{B_1} p_{B_2} \ldots$, etc. Equation (11) agrees with the general definition of ω_+ [8, 9].

Let us assume the following form of the distribution functions [5, 7]:

$$\begin{aligned} &\varphi(\xi) = 0 && \text{when } \xi < \xi_0, \\ &\varphi(\xi) = Ae^{\gamma\xi} && \text{when } \xi_0 < \xi < \xi_1, \\ &\varphi(\xi) = 0 && \text{when } \xi > \xi_1. \end{aligned} \tag{12}$$

Here A and γ are constants; $-1 < \gamma < 1$.

Since $\int_{\xi_0}^{\xi_1} \varphi(\xi)\, d\xi = L$, then

$$\begin{aligned} &A = \frac{\gamma L}{e^{\gamma\xi_1} - e^{\gamma\xi_0}} \quad \text{when} \quad \gamma \neq 0, \\ &A = \frac{L}{\xi_1 - \xi_0} \quad \text{when} \quad \gamma = 0. \end{aligned} \tag{13}$$

The second equation can be considered a particular case of the first, since it was obtained from it by approaching the limit when $\gamma \to 0$.

If $\gamma = 0$, the surface is uniformly inhomogeneous. Within the region of average degrees of coverage, adsorption equilibrium is approximately described by the following isotherms: when $\gamma = 0$—logarithmic [4]; when $\gamma > 0$—the Freundlich exponential isotherm with exponent equal to γ [10]; when $\gamma < 0$—a negative exponential isotherm, according to which the free surface is inversely proportional to the pressure to the power $|\gamma|$ [5].

It is convenient to use the quantity $\lambda = \xi - \xi_0$. Its greatest value $f = \xi_1 - \xi_0$ corresponds to the interval of variation of the desorbability index.

From Eq. (9), we find that

$$\varkappa_1 = \varkappa_1^0 e^{-\alpha\lambda}; \quad \varkappa_{-1} = \varkappa_{-1}^0 e^{\beta\lambda}; \quad \varkappa_2 = \varkappa_2^0 e^{\beta\lambda}; \quad \varkappa_{-2} = \varkappa_{-2}^0 e^{-\alpha\lambda}, \tag{14}$$

where $\varkappa_S^0$ is the value of $\varkappa_S$ at $\lambda = 0$, i. e., at places where the I particles are most firmly adsorbed. According to Eqs.(10)-(14)

$$\omega_+ = \frac{\gamma}{e^{\gamma f} - 1} \int_0^f \frac{\varkappa_1^0 p_A \varkappa_2^0 p_B e^{(n-m)\lambda} \alpha\lambda}{(\varkappa_1^0 p_A + \varkappa_{-2}^0 p_Y) e^{-m\lambda} + (\varkappa_{-1}^0 p_X + \varkappa_2^0 p_B) e^{n\lambda}}. \tag{15}$$

Here the following notations were introduced [5]:

$$\alpha - \gamma = m, \quad \beta + \gamma = n. \tag{16}$$

Let us mention that

$$m + n = 1. \tag{17}$$

Let us convert to the variable

$$u = \frac{\varkappa_{-1} p_X + \varkappa_2 p_B}{\varkappa_1 p_A + \varkappa_{-2} p_Y}, \tag{18}$$

which possesses a simple physical meaning: u is equal to the ratio of the probability that a given space is free to the probability that it is occupied [1]. From Eqs. (18) and (14), it follows that

$$\lambda = \frac{\varkappa_1^0 p_A + \varkappa_{-2}^0 p_Y}{\varkappa_{-1}^0 p_X + \varkappa_2^0 p_B} \ln u. \tag{19}$$

Dividing the numerator and denominator in the expression under the integral sign of Eq. (15) by $(\varkappa_1^0 p_A + \varkappa_{-2}^0 p_Y) e^{-m\lambda}$ and using the equality (19), we find that

$$\omega_+ = \frac{\gamma}{e^{\gamma f} - 1} \frac{\varkappa_1^0 p_A \varkappa_2^0 p_B}{(\varkappa_1^0 p_A + \varkappa_{-2}^0 p_Y)^m (\varkappa_{-1}^0 p_X + \varkappa_2^0 p_B)^n} \int_{u_0}^{u_1} \frac{u^{n-1}}{1+u} du, \tag{20}$$

where u_0 and u_1 are the values of u at $\lambda = 0$ and $\lambda = f$. Within the region of medium degrees of coverage $u_0 \cong 0$, $u_1 \cong \infty$. As is well known

$$\int_0^\infty \frac{u^{n-1}}{1+u} du = \frac{\pi}{\sin n\pi} \quad (0 < n < 1). \tag{21}$$

Hence, in the region of medium degrees of coverage, we find approximately (considering that $\sin n\pi = \sin m\pi$)

$$\omega_+ = \frac{\gamma}{e^{\gamma f} - 1} \frac{\pi}{\sin m\pi} \frac{\varkappa_1^0 p_A \varkappa_2^0 p_B}{(\varkappa_1^0 p_A + \varkappa_{-2}^0 p_Y)^m (\varkappa_{-1}^0 p_X + \varkappa_2^0 p_B)^{1-m}}. \tag{22}$$

Since the stoichiometric numbers of both steps of scheme (1) are equal to one, then according to the theory of steady-state reactions [8, 9],

$$\frac{\omega_+}{\omega_-} = K\frac{p_A p_B}{p_X p_Y}, \tag{23}$$

where K is the equilibrium constant.

It is easy to see that

$$K = K_1 K_2 = \frac{\varkappa_1^0 \varkappa_2^0}{\varkappa_{-1}^0 \varkappa_{-2}^0}. \tag{24}$$

Hence

$$\omega_- = \frac{\gamma}{e^{\gamma f} - 1}\frac{\pi}{\sin m\pi}\frac{\varkappa_{-1}^0 p_X \varkappa_{-2}^0 p_Y}{(\varkappa_1^0 p_A + \varkappa_{-2}^0 p_Y)^n (\varkappa_{-1}^0 p_X + \varkappa_2^0 p_B)^{1-m}}. \tag{25}$$

At $\gamma = 0$, Eqs. (22) and (25) are converted to those obtained earlier [1] for a uniformly inhomogeneous surface. The latter differ from (22) and (25) only in that the numerical factor $\gamma/(e^{\gamma f}-1)$ is replaced by $1/f$, and the exponent m by α. As a result of this coincidence of the form of the equations, the kinetic functions interpreted with the assumption of uniform inhomogeneity, in particular, the kinetics of isotopic exchange [2, 3]

$$HDO + H_2 = HD + H_2O \tag{26}$$

and the kinetics of ammonia synthesis far from equilibrium [11] permit a more general interpretation on the basis of exponential inhomogeneity (12). The exponent m varies depending on the nature of the catalyst; for example, for reaction (26) we obtained the values m = 0.5 on Ni, m = 0.3 on Cu, and m = 0.8 on Ag. Such results are compatible with the assumption that the transmission factor α is the same for all catalysts, while the differences in m are due to a difference in the nature of the inhomogeneity. For example, in the case of reaction (26), it is possible that $\alpha = 0.5$, $\gamma = 0$ for Ni, $\gamma = 0.2$ for Cu, and $\gamma = -0.3$ for Ag.

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