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Abstract

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TWO-STAGE KINETICS ON INHOMOGENEOUS SURFACES

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The mechanism of a number of reactions occurring on the surfaces of solids fits into a simple two-stage scheme ($^{1-3}$):

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

Here $A_1, A_2, \ldots, B_1, B_2, \ldots$ and $X_1, X_2, \ldots, Y_1, Y_2, \ldots$ are molecules of the initial substances and reaction products in the gas phase, $(\,)$ is a free surface site; (I) is a chemisorbed particle I. The kinetic equations corresponding to the stationary course of the reaction according to scheme (1) were obtained (^{1}) for the cases in which the surface is homogeneous or uniformly inhomogeneous. Here the kinetics will be considered under more general assumptions about the inhomogeneity of the surface.

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

$$\theta = \frac{p_I}{p_I + b} \tag{2}$$

(the Langmuir isotherm). The desorption elasticity may be regarded as the equilibrium constant

$$(I) = I + (\,). \tag{3}$$

Indeed, expressing the concentrations of free and occupied sites 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 equality (2).

The interpretation of kinetics on inhomogeneous surfaces developed here (^{4,5,1}) is based on the rule of transferring changes in equilibrium to rates. According to this rule, the rate constants of the stages at different surface sites $\varkappa_s$ and the corresponding equilibrium constants of the stages K_s are related by dependences of the form

$$\varkappa_s = g_{|s|} K_s^{a_s}, \tag{4}$$

where $g_{|s|}$ and a_s are constants, $0 < a_s < 1$. A minus sign is assigned to the index s, which indicates the number of the stage, if the quantity bearing it refers to the course of the stage in the reverse direction; the constant $g_{|s|}$ is the same for the forward and reverse directions of a stage, and therefore its index is written as $|s|$. The transfer coefficient a_s (also called the symmetry coefficient) will be denoted, following A. N. Frumkin (^{6}), by

$\alpha_{|s|}$ when a surface site is occupied ($s = 1$ or $s = -2$) and by $\beta_{|s|}$ when a site is vacated ($s = -1$ or $s = 2$); then $\alpha_{|s|} + \beta_{|s|} = 1$. For simplicity we assume, 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 stage of scheme (1), we find

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

where K_1' is the equilibrium constant

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

Similarly,

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

where K_2' is the equilibrium constant

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

The quantities K_1' and K_2' are common to all surface sites. Taking into account that $K_{-s} = K_s^{-1}$, on the basis of (4), (5), and (7) we obtain expressions for $\varkappa_s$ as functions of b:

$$\varkappa_1 = g_1 (K_1')^{\alpha} b^{-\alpha}; \qquad \varkappa_{-1} = g_1 (K_1')^{-\beta} b^{\beta}; \qquad \varkappa_2 = g_2 (K_2')^{\beta} b^{\beta};$$

$$\varkappa_{-2} = g_2 (K_2')^{-\alpha} b^{-\alpha}. \tag{9}$$

Let us introduce the "desorbability index" of particles I, $\xi = \ln b$, and the differential distribution function of surface sites with respect to the desorbability index $\varphi(\xi)$ (^{7}). The latter is defined by the fact that, on a surface of unit area, the number of sites with desorbability-index values in the interval from ξ to $\xi + d\xi$ is equal to $\varphi(\xi)d\xi$. To simplify the calculations we use the concepts of the reaction rate in the forward direction, ω_+, and in the reverse direction, ω_- (^{8,9}). The observed reaction rate is $\omega = \omega_+ - \omega_-$. 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 surface site with the given value ξ. From 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 sites on a surface of unit 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}).

We adopt the following form of the distribution function (^{5,7}):

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

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

Since

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

we have

$$A = \frac{\gamma L}{e^{\gamma\xi_1} - e^{\gamma\xi_0}} \quad \text{for } \gamma \neq 0,$$

$$A = \frac{L}{\xi_1 - \xi_0} \quad \text{for } \gamma = 0. \tag{13}$$

The second equation may be regarded as a special case of the first, since it is obtained from it by passage to the limit as $\gamma \to 0$.

If $\gamma = 0$, the surface is uniformly heterogeneous. In the region of intermediate coverages the adsorption equilibrium is approximately described by the following isotherms: for $\gamma = 0$, by the logarithmic isotherm (^{4}); for $\gamma > 0$, by the Freundlich power-law isotherm with exponent equal to γ (^{10}); for $\gamma < 0$, by a negative-power 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 largest value $f = \xi_1 - \xi_0$ corresponds to the interval of variation of the desorbability exponent.

From equations (9) we obtain

$$\chi_1 = \chi_1^0 e^{-\alpha\lambda}; \qquad \chi_{-1} = \chi_{-1}^0 e^{\beta\lambda}; \qquad \chi_2 = \chi_2^0 e^{\beta\lambda}; \qquad \chi_{-2} = \chi_{-2}^0 e^{-\alpha\lambda}, \tag{14}$$

where χ_s^0 is the value of χ_s at $\lambda = 0$, i.e., at the sites that most strongly adsorb particles I. According to equations (10)–(14),

$$\omega_+ = \frac{\gamma}{e^{\gamma f} - 1} \int_0^f \frac{\chi_1^0 p_A \chi_2^0 p_B e^{(n-m)\lambda}\, d\lambda}{(\chi_1^0 p_A + \chi_{-2}^0 p_Y) e^{-m\lambda} + (\chi_{-1}^0 p_X + \chi_2^0 p_B) e^{n\lambda}}. \tag{15}$$

Here the notations (^{5}) have been introduced

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

We note that

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

We pass to the variable

$$u = \frac{\chi_{-1} p_X + \chi_2 p_B}{\chi_1 p_A + \chi_{-2} p_Y}, \tag{18}$$

which has a simple physical meaning: u is equal to the ratio of the probability that a given site is free to the probability that it is occupied (^{1}). From equations (18) and (14) it follows that

$$\lambda = \frac{\chi_1^0 p_A + \chi_{-2}^0 p_Y}{\chi_{-1}^0 p_X + \chi_2^0 p_B} \ln u. \tag{19}$$

Dividing the numerator and denominator in the integrand of equation (15) by $(\chi_1^0 p_A + \chi_{-2}^0 p_Y) e^{-m\lambda}$ and using equality (19), we obtain

$$\omega_+ = \frac{\gamma}{e^{\gamma f} - 1} \frac{\chi_1^0 p_A \chi_2^0 p_B}{(\chi_1^0 p_A + \chi_{-2}^0 p_Y)^m (\chi_{-1}^0 p_X + \chi_2^0 p_B)^n} \int_{u_0}^{u_1} \frac{u^{n-1}}{1+u} \, du, \tag{20}$$

where u_0 and u_1 are the values of u at $\lambda = 0$ and $\lambda = f$. In the region of intermediate coverages $u_0 \cong 0$, $u_1 \cong \infty$. As is known,

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

Therefore, in the region of intermediate coverages, approximately (taking into account that $\sin n\pi = \sin m\pi$),

$$\omega_+ = \frac{\gamma}{e^{\gamma f} - 1} \frac{\pi}{\sin m\pi} \frac{\chi_1^0 p_A \chi_2^0 p_B}{(\chi_1^0 p_A + \chi_{-2}^0 p_Y)^m (\chi_{-1}^0 p_X + \chi_2^0 p_B)^{1-m}}. \tag{22}$$

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

$$\frac{\omega_+}{\omega_-} = K \frac{p_{Ap}B}{p_{Xp}Y}, \tag{23}$$

where K is the equilibrium constant.

It is easy to see that

$$K = K_1 K_2 = \frac{\chi_1^0 \chi_2^0}{\chi_{-1}^0 \chi_{-2}^0}. \tag{24}$$

Hence

$$\omega_- = -\frac{\gamma}{e^{\gamma f} - 1} \frac{\pi}{\sin m\pi} \frac{\chi_{-1}^0 p_X - \chi_{-2}^0 p_Y}{\left(\chi_1^0 p_A + \chi_{-2}^0 p_Y\right)^m \left(\chi_{-1}^0 p_X + \chi_2^0 p_B\right)^{1-m}}. \tag{25}$$

For $\gamma = 0$, equations (22) and (25) reduce to the previously obtained equations (1) for a uniformly heterogeneous 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. Owing to this coincidence in the form of the equations, kinetic dependences interpreted with the aid of the assumption of uniform heterogeneity, in particular the kinetics of isotope exchange ([2,3])

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

and the kinetics of ammonia synthesis upon displacement from equilibrium (11), admit a more general interpretation on the basis of exponential heterogeneity (12). The exponent m varies depending on the nature of the catalyst; for example, for reaction (26) the values $m = 0.5$ on Ni, $m = 0.3$ on Cu, and $m = 0.8$ on Ag were obtained. Such results are compatible with the assumption that the transfer coefficient α is the same for all catalysts, while the differences in m are caused by differences in the character of the heterogeneity. 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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named after L. Ya. Karpov

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