

STUDY OF ADSORPTION
ON UNIFORMLY INHOMOGENEOUS SURFACE

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An equation is derived describing the kinetics of adsorption on a uniformly inhomogeneous surface with an arbitrary coefficient of inhomogeneity. The deviations of this equation from the Roginský-Zeldovič equation for various values of the inhomogeneity coefficient are discussed. A kinetic isotherm for simultaneous adsorption of two substances on a uniformly inhomogeneous surface is derived from their individual kinetic isotherms. The theoretical conclusions regarding simultaneous adsorption of two substances were verified on adsorption of methyl alcohol and formic acid in 1N-H₂SO₄ on a smooth platinum electrode.

In studying the kinetics of adsorption from liquid and gaseous phase on to the surface of a solid phase, the following equation is often used to evaluate the experimental data:

$$\theta = A + (1/\alpha f) \ln t, \quad (1)$$

where θ denotes surface coverage with adsorbed substance, α transfer coefficient, f factor of surface inhomogeneity, A constant depending on experimental conditions and t time. Eq. (1) is called the Roginský-Zeldovič (or in western literature Jelovič or Elovich) equation¹. It was derived for a uniformly inhomogeneous surface under the assumption of a sufficiently large f value and applies in the above-mentioned form only for moderate θ values, i.e. for $0.2 < \theta < 0.8$ (assuming a negligible rate of desorption). For practical purposes, Eq. (1) is used so that the slope of the medium linear portion of the $\theta - \ln t$ plot is set equal to $1/\alpha f$. This, however, implies an error increasing with decreasing coefficient of inhomogeneity f .

The present paper deals with the derivation of a more general equation for the rate of adsorption on a uniformly inhomogeneous surface under the assumption that desorption is negligible. The equation applies for any factor of inhomogeneity and enables to determine the error involved in using Eq. (1) when the inhomogeneity factor is not large enough.

However, under typical experimental conditions it is often not possible to determine the surface coverage with the adsorbed substance exactly, since a solution

free of impurities is not always available. These are adsorbed together with the substance under study. In case where the fraction of the total surface coverage Θ due to impurities cannot be distinguished experimentally from that due to the studied substance the results are of course distorted.

The problem of adsorption of impurities is in the present paper dealt with by considering the simultaneous adsorption of two substances on a uniformly inhomogeneous surface. Our theoretical conclusions were verified experimentally on adsorption of methyl alcohol and formic acid from the medium of 1N-H₂SO₄ on to the surface of a smooth platinum electrode by the voltammetric method.

THEORETICAL

General Equation for Adsorption Kinetics

A more general equation for the rate of adsorption on a uniformly inhomogeneous surface can be derived in a similar manner as by Temkin^{2,3}, Brunauer, Love and Keenan⁴. The inhomogeneous surface can be divided into surface elements ds which are so small that they can be considered as homogeneous, *i.e.* every surface element is characterized by a single value of the activation energy of adsorption, E_a^s . This value varies from one surface element to another within the limits $E_a^0 < E_a^1$. The uniformly inhomogeneous surface is characterized by the relationship

$$E_a^s = E_a^0 + (E_a^1 - E_a^0) s, \quad (2)$$

where s varies from 0 to 1. We assume that the adsorption proceeds on the surface element ds in an ideal adsorbed layer, *i.e.* a) there is a finite and during adsorption constant number of adsorption sites, each of which can adsorb one particle, b) all adsorption sites are energetically equivalent and equally accessible for the adsorbing molecules, c) the adsorbed molecules do not interact with one another. If no dissociation of molecules occurs during adsorption then the rate of adsorption v_s on the individual surface elements is governed by the Langmuir equation:

$$v_s = k'c(1 - \Theta_s) \exp(-E_a^s/RT). \quad (3)$$

Here k' is a constant of adsorption which is the same for all surface elements, c concentration of the substance the adsorption of which is measured and Θ_s coverage of the surface element with the adsorbed substance. (In the case of gas adsorption, the concentration c is replaced by pressure p .) The concentration c is defined just at the surface on which adsorption proceeds, but it can be set equal to the bulk concentration if the rate of transport of the adsorbing substance is greater than the rate of adsorption.

On integrating Eq. (3) with the initial condition $t = 0$, $\Theta_s = 0$ and introducing (2) we obtain

$$\Theta_s = 1 - \exp[-k_0 ct \exp(-\alpha fs)], \quad (4)$$

where

$$k_0 = k' \exp(-E_a^0/RT), \quad \alpha f = (E_a^1 - E_a^0)/RT. \quad (5), (6)$$

(The symbols in Eq. (6) are the same as used in Temkin's derivation² of the kinetic adsorption isotherm (1).) On integrating Eq. (4) with respect to s from 0 to 1, i.e. over all surface elements, we obtain the surface coverage with the adsorbed substance on the whole surface as a function of time:

$$\Theta = \int_0^1 \Theta_s ds = 1 + (\alpha f)^{-1} [\text{Ei}(-\beta e^{-\alpha f}) - \text{Ei}(-\beta)], \quad (7)$$

where the exponential integral $\text{Ei}(-x)$ is defined by

$$\text{Ei}(-x) = - \int_x^\infty y^{-1} e^{-y} dy \quad (8)$$

and

$$\beta = k_0 ct. \quad (9)$$

Eq. (7) is valid for adsorption on a uniformly inhomogeneous surface with an arbitrary coefficient of inhomogeneity $f \neq 0$, the rate of desorption being equal to zero. It is represented graphically in Fig. 1 for various αf values, where Θ is plotted as function of $\ln \beta$. The medium portion of the curves is approximately linear, its slope depending on αf .

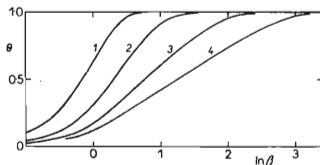


FIG. 1

Course of Adsorption on a Uniformly Inhomogeneous Surface for Various αf Values
 Values of αf : 1 0; 2 2-303; 3 4-605; 4 6-908.

For large αf values the term $\text{Ei}(-\beta)$ in Eq. (7) can be neglected against $\text{Ei}(-\beta e^{-\alpha f})$ except for the case where β is very small. If we use the approximate relation

$$\text{Ei}(-x) = \ln(1.781x) \quad (10)$$

for $x \ll 1$, Eq. (7) takes the form of (1). The greater the αf value the greater is the range of β values for which Eq. (7) can be approximated by (1).

The slope of the tangent in the inflexion point of the $\Theta - \ln \beta$ curves can be derived from Eq. (7) as

$$(d\Theta/d \ln \beta)_i = (1/\alpha f) F(\alpha f), \quad (11)$$

where

$$F(\alpha f) = \exp[-\beta_i \exp(-\alpha f)] - \exp \beta_i, \quad (12)$$

and β_i is the value of β in the inflexion point. According to the simple isotherm (1), $d\Theta/d \ln \beta = 1/\alpha f$. The function $F(\alpha f)$ in Eq. (11) (Fig. 2) represents a correction

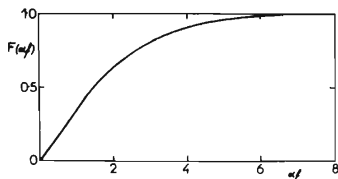


FIG. 2

Course of Function $F(\alpha f)$

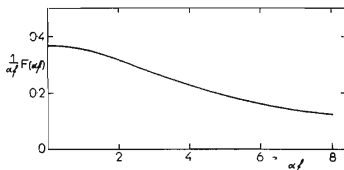


FIG. 3

Course of Function $F(\alpha f)/\alpha f$

factor by which the slope of the medium portion of the kinetic isotherm calculated from the more general Eq. (7) differs from that calculated from the simple Eq. (1). For $\alpha f > 10$ the $F(\alpha f)$ value approaches unity, and Eq. (1) applies for calculation of αf . For smaller αf values (smaller surface inhomogeneity), $F(\alpha f)$ is smaller than 1; for example, the slope according to Eq. (11) for $\alpha f = 4$ is by 10% smaller than according to (1).

To determine the value of αf experimentally, the dependence of Θ on $\ln t$ is plotted and the slope $d\Theta/d \ln t$ in the inflexion point is found graphically; this is equal to $F(\alpha f)/\alpha f$ according to Eq. (11). The αf value can then be found from Fig. 3.

Simultaneous Adsorption of Two Substances

We shall assume that two substances, A and B, that are adsorbed at the same time without dissociation do not interact with each other, they are adsorbed both on the same adsorption sites and can occupy the whole surface area. The rate of adsorption on a surface element ds will be given by

$$d\Theta_{A,s}/dt = k_A c_A (1 - \Theta_A - \Theta_B), \quad (13)$$

$$d\Theta_{B,s}/dt = k_B c_B (1 - \Theta_A - \Theta_B), \quad (14)$$

where $\Theta_{A,s}$ and $\Theta_{B,s}$ denote the coverage of the surface element with the substances A and B, c_A and c_B their concentrations, k_A and k_B the corresponding rate constants. In the case where $\Theta_A = \Theta_B = 0$ for $t = 0$, we have

$$\Theta_{A,s} = [k_A c_A / (k_A c_A + k_B c_B)] \{1 - \exp[-(k_A c_A + k_B c_B) t]\}, \quad (15)$$

$$\Theta_{B,s} = [k_B c_B / (k_A c_A + k_B c_B)] \{1 - \exp[-(k_A c_A + k_B c_B) t]\}. \quad (16)$$

If the surface is quasihomogeneous, analogous equations hold as for adsorption of a single substance on a uniformly inhomogeneous surface:

$$k_A = k_A^0 \exp(-\alpha fs), \quad k_B = k_B^0 \exp(-\alpha fs). \quad (17)$$

On integrating Eqs (15) and (16) over the whole surface we obtain analogously to Eq. (7)

$$\Theta_A = [k_A^0 c_A / (k_A^0 c_A + k_B^0 c_B)] \{1 + (1/\alpha f) [\text{Ei}(-\beta_1 e^{-\alpha f}) - \text{Ei}(-\beta_1)]\}, \quad (18)$$

$$\Theta_B = [k_B^0 c_B / (k_A^0 c_A + k_B^0 c_B)] \{1 + (1/\alpha f) [\text{Ei}(-\beta_1 e^{-\alpha f}) - \text{Ei}(-\beta_1)]\}. \quad (19)$$

The total surface coverage Θ is given by

$$\Theta = \Theta_A + \Theta_B = 1 + (1/\alpha f) [\text{Ei}(-\beta_1 e^{-\alpha t}) - \text{Ei}(-\beta_1)], \quad (20)$$

where

$$\beta_1 = (k_A^0 c_A + k_B^0 c_B) t. \quad (21)$$

On introducing the simplified expression (10) into (18)–(20) we get

$$\Theta_A = [k_A^0 c_A / (k_A^0 c_A + k_B^0 c_B) \alpha f] \ln(1.781 \beta_1), \quad (22)$$

$$\Theta_B = [k_B^0 c_B / (k_A^0 c_A + k_B^0 c_B) \alpha f] \ln(1.781 \beta_1), \quad (23)$$

$$\Theta = (1/\alpha f) \ln(1.781 \beta_1). \quad (24)$$

These simplified kinetic isotherms apply only for moderate coverages. From Eqs (22) and (23) or from (18) and (19) it follows that $\Theta_B/\Theta_A = k_B^0 c_B/k_A^0 c_A$, *i.e.* in simultaneous adsorption of two substances the ratio of the corresponding surface coverages is independent of time.

By comparing Eq. (22) or (23) with the kinetic isotherm corresponding to adsorption of a single substance we obtain

$$\Theta_A/\Theta = k_A^0 c_A / (k_A^0 c_A + k_B^0 c_B) = \exp(\alpha f \Theta'_A) / \exp(\alpha f \Theta), \quad (25)$$

where Θ'_A denotes surface coverage in the case where only substance A (in absence of B) is adsorbed, and is defined for the same time of adsorption and the same concentration c_A as Θ .

When both substances, A and B, are adsorbed individually, their adsorptivities are expressed by the products $k_A^0 c_A$ and $k_B^0 c_B$; if these are equal to each other then

$$\Theta = \Theta'_A + (1/\alpha f) \ln 2. \quad (26)$$

For $\alpha f = 6$ (found in adsorption of organic substances from the medium of 1N-H₂SO₄ on to platinum electrodes⁵) the surface coverage $\Theta = \Theta_A + \Theta_B$ in simultaneous adsorption of two substances A and B of equal adsorptivities is by 0.1155 higher than in adsorption of substance A only, as shown in Fig. 4. Owing to equal adsorptivities of both substances A and B their individual adsorption isotherms are also the same. When they are adsorbed simultaneously, the isotherm calculated from Eq. (25) or (26) is depicted by curve 1. For moderate Θ values a linear relationship between Θ and logarithm of time holds. It is seen from Fig. 4 that in this case of strong competition between two adsorbing substances the slope of the adsorption

isotherm is the same as with the individual adsorption isotherms; the isotherm is only shifted along the axis of ordinates. We denote the magnitude of this shift as ξ .

The calculated ξ values are plotted as function of the ratio of adsorptivities $\psi = k_B^0 c_B / k_A^0 c_A$ in Fig. 5. For $\psi = 1$ (equal adsorptivities) is $\xi = 0.1155$, whereas for

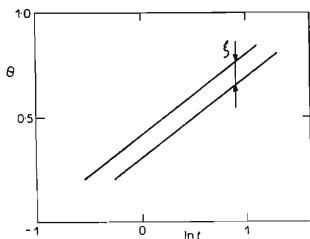


FIG. 4

Adsorption of Two Substances of Equal Adsorptivities

Upper line: Adsorption isotherm corresponding to simultaneous adsorption; lower line: kinetic adsorption isotherm of either substance adsorbed individually (both isotherms fuse to a single one).

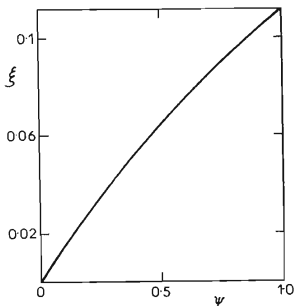


FIG. 5

Dependence of Shift of Linear Portion of Kinetic Adsorption Isotherm (ξ) on Ratio of Adsorptivities of Both Substances (ψ)

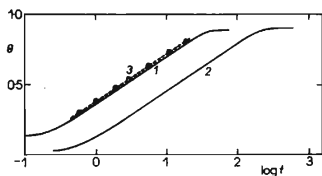


FIG. 6

Experimental Verification of Simultaneous Adsorption of Two Substances

1 Kinetic adsorption isotherm for methyl alcohol; 2 same for formic acid; 3 experimental kinetic isotherm of both substances. Points were calculated from Eq. (25) and curves 1 and 2.

$\psi = 0.1$ (adsorptivity of A greater by the factor of 10 than that of B) is $\xi = 0.0145$. This calculation applies also in the case where the substances dissociate during adsorption. In the range of moderate surface coverages the logarithmic isotherms (22)–(26) have the same form regardless of whether dissociation occurs or not.

EXPERIMENTAL

Our theory was verified on adsorption of formic acid and methyl alcohol on a smooth platinum electrode in the medium of 0.5M- H_2SO_4 . The surface coverage was determined at 0.4 V against hydrogen electrode in the same medium by a pulse method⁶ from the decrease of charge consumed in adsorption of hydrogen. The temperature of measurement was 20°C.

RESULTS AND DISCUSSION

The kinetic isotherms for 0.5M- CH_3OH and for 0.01M- $HCOOH$ are shown in Fig. 6 (curves 1 and 2). The αf value is for both the same, hence the assumption of a quasi-homogeneous surface underlying our theory is justified. Curve 3 in Fig. 6 corresponds to a mixture of 0.5M- CH_3OH + 0.01M- $HCOOH$.

The theoretical course of simultaneous adsorption of both studied substances was calculated from Eq. (25) and curves 1 and 2 in Fig. 6 and denoted by points which lie close to curve 3 found experimentally. Thus, the equation for simultaneous adsorption of two substances appears justified. This statement is of significance mainly in studying adsorption of two substances of widely differing adsorptivities. This is for example the case of adsorption from a solution of an organic substance containing a surface active impurity that cannot be easily removed. Our theory shows that when the adsorptivity of the impurity is at least by an order of magnitude lower than that of the substance under study, the adsorption of the impurity can be neglected. This applies naturally only if the rate of desorption of the substance under study is practically zero so that the latter cannot be desorbed during adsorption of the impurity. This necessary condition is fulfilled with adsorption of a number of organic compounds from acidic solutions on to a platinum electrode.

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