Kinetics and Dynamics of Gas and Vapour Adsorption on Solid Sorbents. III.
Adsorption Dynamics in Fixed Bed at Variable Value of the Overall Mass-Transfer Coefficient and at Negligible Influence of Longitudinal Diffusion

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Some general relationships expressing the shape of adsorption isoplane and the height of adsorption zone have been deduced under supposition that the mass-transfer coefficient in solid phase is not constant during saturation.

An analytical expression giving the dependence of mass-transfer coefficient in solid phase on concentration of adsorbate in adsorbent has been presented. This expression is valid on condition that the adsorption equilibria in a system may be described by the Langmuir equation of adsorption isotherm.

On this basis the equations of adsorption isoplanes have been expressed for the validity region of the Langmuir equation of adsorption isotherm.

In the preceding papers [1, 2] we have expressed the material balance of gas and vapour adsorption on solid sorbents. We have also deduced the equations describing the shape of adsorption isoplanes provided that the overall mass-transfer coefficient is constant, the longitudinal diffusion is negligible, and the adsorption equilibria may be expressed by the Freundlich or Langmuir equation of adsorption isotherm. Comparing these equations with experimental data, we have found that they do not express with sufficient accuracy the adsorption dynamics in fixed bed [3]. On the basis of the analysis of mass transfer in adsorber we have come to the conclusion that one of the causes of this disagreement is the assumption that the overall mass-transfer coefficient is constant.

The assumption of constancy of the mass-transfer coefficient in gaseous phase is satisfactorily physically founded on the basis of film theory and is, therefore, generally accepted. On the other hand, the mass-transfer coefficient in solid phase depends on the parameters of system in an intricate way and the assumption of its constancy cannot be physically justified. It is, therefore, necessary to assume its variability during the process.

A similar conclusion has been drawn by *Dubinin* and *Lezin* [4] on the basis of the measurement of adsorption kinetics in differential bed as well as by Afanasiev [5] on the basis of the measurement of adsorption dynamics. In contrast to these authors who have given the dependence of mass-transfer coefficient in solid phase on concentration of adsorbate on sorbent only in graphic form, this dependence is described by an analytical expression in this paper. The dependence of the overall mass-

-transfer coefficient on mass-transfer coefficients in gaseous and solid phase is expressed by the equation

$$\frac{1}{k} = \frac{1}{k_g} + \frac{1}{k_s}. \qquad (1)$$

It is convenient to define some characteristic value of the mass-transfer coefficient in solid phase k_{s0} to which all calculations should relate. The best choice of the characteristic value is governed by the nature of relevant concrete problem. On the basis of the characteristic value of mass-transfer coefficient in solid phase the characteristic value of the overall mass-transfer coefficient is defined by the relation

$$\frac{1}{k_0} = \frac{1}{k_g} + \frac{1}{k_{s0}}. \qquad (2)$$

From the equations (*1*, *2*) it follows

$$\frac{k_0}{k} = 1 - \frac{k_0}{k_{s0}} + \frac{k_0}{k_{s0}} \cdot \frac{k_{s0}}{k_s}. \qquad (3)$$

The ratios k/k_0 and k_s/k_{s0} express the ratio of the local value of relevant mass-transfer coefficient to its characteristic value for the given experiment and are denoted by symbols Φ and Φ_s. Equation (*3*) thus assumes the form

$$\frac{1}{\Phi} = 1 - K + \frac{K}{\Phi_s}. \qquad (4)$$

Equation (*4*) in a dimensionless form expresses the dependence of the overall mass-transfer coefficient on coefficients in gaseous and solid phase. The simplex $K = k_0/k_{s0}$ represents that part of the overall resistance to mass transfer for which the resistance in solid phase is responsible. Accordingly, it varies from 0 to 1. At $K = 0$, the rate of process is governed only by external diffusion whereas it is the internal diffusion which controls the process at $K = 1$. It means, the more the resistance in solid phase exerts influence upon the overall rate of process, the greater the value of K. It is obvious that this value depends not only on the structure of adsorbent but also on the parameters of the process itself because they have bearing on the value of the overall mass-transfer coefficient in addition to the resistance in solid phase.

If a variability of the mass-transfer coefficient in solid phase and a constancy of the mass-transfer coefficient in gaseous phase during saturation is assumed according to the above analysis, the equation of break-through curve at stable sorption front may be derived in the same manner as in paper [2] provided the longitudinal diffusion is negligible

$$Z = \int \frac{dQ}{\Phi(Q - Q^*)} - \int_0^1 dQ \int \frac{dQ}{\Phi(Q - Q^*)}. \qquad (5)$$

The validity of the relationship $q = Q$ is observed [2]. The dimensionless transformed time Z is defined like in paper [2], the difference being in the fact that, instead of the constant value of the overall mass-transfer coefficient, its characteristic value for the given experiment defined by equation (*2*) is substituted.

With respect to (*4*), the equation (*5*) may be written in the form

$$Z = (1 - K)\left[\int \frac{\mathrm{d}Q}{Q - Q^*} - \int_0^1 \mathrm{d}Q \int \frac{\mathrm{d}Q}{Q - Q^*}\right] + K\left[\frac{\mathrm{d}Q}{\Phi_{\mathrm{s}}(Q - Q^*)} - \right.$$

$$\left. - \int_0^1 \mathrm{d}Q \int \frac{\mathrm{d}Q}{\Phi_{\mathrm{s}}(Q - Q^*)}\right]. \qquad (6)$$

In view of the physical sense of the simplex K which has been discussed before, the first and second terms in the sum in equation (*6*) represent the contribution of external and internal diffusion and accordingly the corresponding terms in square brackets are denoted Z_{g} and Z_{s}. Then equation (*6*) has the form

$$Z = (1 - K) Z_{\mathrm{g}} + K Z_{\mathrm{s}}. \qquad (7)$$

Equations (*5—7*) may also be used for the calculation of adsorption isochrones and thus they enable us to determine the height of adsorption zone in operation.

In practice the height of adsorption zone Δh is often expressed as the height of a bed in which the relative concentration changes within the limits from Q to $(1 - Q)$ (see [6]). On the basis of the equations of dynamics for stable adsorption front, the quantity ΔH may be expressed by the equation

$$\Delta H = \int_Q^{1-Q} \frac{\mathrm{d}Q}{\Phi(Q - Q^*)}, \qquad (8)$$

where

$$\Delta H = \frac{k_{0\mathrm{v}}}{w} \Delta h. \qquad (9)$$

By substituting the relationship (*4*) into equation (*8*), it is possible to express the height of adsorption zone ΔH analogously to the transformed time Z in equation (*7*) as a sum of the contributions of external and internal diffusion

$$\Delta H = (1 - K)\, \Delta H_{\mathrm{g}} + K\, \Delta H_{\mathrm{s}}, \qquad (10)$$

while

$$\Delta H_{\mathrm{g}} = \int_Q^{1-Q} \frac{\mathrm{d}Q}{Q - Q^*}, \qquad (11)$$

and

$$\Delta H_{\mathrm{s}} = \int_Q^{1-Q} \frac{\mathrm{d}Q}{\Phi_{\mathrm{s}}(Q - Q^*)}. \qquad (12)$$

From equations (*10—12*) it is also possible to calculate the time Δt within the relative concentration in a given height of bed changes from Q to $(1 - Q)$ at stable sorption front. Since $\varepsilon_{\mathrm{v}} \ll \Gamma_{0\mathrm{v}}$, the relationship between Δt and Δh may be expressed by the equation [2]

$$\Delta t = \frac{\Gamma_{0\mathrm{v}}}{w} \Delta h, \qquad (13)$$

and in dimensionless notation

$$\Delta Z \doteq \Delta H\,. \tag{14}$$

In equation (*14*) the symbol ΔZ is used; since at constant h the difference between z and t is a constant (see equation (*12*) in paper [2]), $\Delta z \equiv \Delta t$ and thus also $\Delta Z \equiv \Delta \tau$.

Relationships (*5—12*) are a general expression of relevant quantities within the scope of the mathematical model defined in paper [1]. For practical calculations it is necessary to express the changes of the resistance to the mass transfer during saturation by concrete mathematical relationships what is possible at present only in a semiempirical way.

From the analysis of experimental data the conclusion has been drawn that provided the Langmuir equation describes the adsorption equilibria in the system in question, under kinetic as well as dynamic conditions the value of the mass-transfer coefficient in solid phase decreases during the saturation and its variability may be expressed by the following equation [3]

$$k_{\mathrm{s}} = \frac{k_{\mathrm{s}}(\Theta = 0)}{1 + \dfrac{\Theta_0}{1 - \Theta_0}\, q} \tag{15}$$

where $k_{\mathrm{s}}(\Theta = 0)$ is the limiting value of mass-transfer coefficient for $\Theta = 0$. Eventually, the dependence of the resistance in solid phase on concentration of adsorbate in adsorbent may be expressed under these conditions by the relationship

$$\frac{1}{k_{\mathrm{s}}} = \frac{1}{k_{\mathrm{s}}(\Theta = 0)} \left(1 + \frac{\Theta_0}{1 - \Theta_0}\, q\right). \tag{16}$$

It follows from this consideration that the resistance in solid phase linearly increases with progressive saturation of adsorbent and the greater the curvature of equilibrium curve the more rapid this increase.

Provided the characteristic value of mass-transfer coefficient in solid phase is defined as its limiting value at the saturation close to equilibrium

$$k_{\mathrm{s}0} = \lim_{q \to 1} k_{\mathrm{s}}\,, \tag{17}$$

Φ_{s} may be expressed by the equation

$$\frac{1}{\Phi_{\mathrm{s}}} = 1 - \Theta_0 + \Theta_0\, q\,. \tag{18}$$

For the analysis of adsorption dynamics it is convenient to refer all relevant quantities to Q. For this reason it is necessary to express Φ_{s} as a function of Q. With respect to the supposition $q = Q$ which has been used for the derivation of equations (*5—12*), the equation (*18*) is transformed into the form suitable for adsorption dynamics

$$\frac{1}{\Phi_{\mathrm{s}}} = 1 - \Theta_0 + \Theta_0\, Q\,. \tag{19}$$

After substituting for Φ_s from equation (*19*) into equation (*4*), it follows

$$\frac{1}{\Phi} = 1 - K\,\Theta_0(1 - Q). \tag{20}$$

By substituting the expression of equation (*20*) for Φ in equation (*5*) and using the equations of operating line and equilibrium curve within the validity region of the Langmuir equation of adsorption isotherm [1, 2], the quantity Q^* can be expressed as a function of Q. Integration of the relationship (*5*) thus formed affords the resulting equation of adsorption isoplane

$$Z = \frac{1 - \Theta_0 K}{\Theta} \ln \frac{Q}{1 - Q} + (1 - K)[1 + \ln(1 - Q)] + \Theta_0 K\left(Q - \frac{1}{2}\right). \tag{21}$$

If this equation expresses the rate of process, the values $k_{0\mathrm{v}}$ and K must be constant in the whole range of the Q values. For $K = 0$ equation (*21*) changes into equation (see [2])

$$Z_g = \frac{1}{\Theta_0} \ln \frac{Q}{1 - Q} + \ln(1 - Q) + 1. \tag{22}$$

For $K = 1$ it assumes the form

$$Z_s = \frac{1 - \Theta_0}{\Theta_0} \ln \frac{Q}{1 - Q} + \Theta_0\left(Q - \frac{1}{2}\right). \tag{23}$$

Analogously to the above procedure, a relationship for the calculation of the height of adsorption zone can be obtained

$$\Delta H = \left(\frac{2}{\Theta_0} - K - 1\right) \ln \frac{1 - Q}{Q} + K\,\Theta_0(1 - 2Q). \tag{24}$$

For $K = 0$ this relationship is transformed into the form

$$\Delta H_g = \frac{2 - \Theta_0}{\Theta_0} \ln \left(1 - \frac{1 - Q}{Q}\right), \tag{25}$$

while for $K = 1$ it holds

$$\Delta H_s = \frac{2(1 - \Theta_0)}{\Theta_0} \ln \frac{1 - Q}{Q} + \Theta_0(1 - 2Q). \tag{26}$$

In conclusion, it is necessary to state that in view of the heterogeneity of the system an exact mathematical description of adsorption kinetics and dynamics is out of the question at present and only a semiempirical treatment enables us to reach a satisfactory accuracy. The insufficiency in the present state of the simulation of adsorption processes consists firstly in the fact that only very simplified models can be mastered mathematically. The conclusions drawn by many authors on the basis of such models are of importance only for theoretical research but their practical usage is in the best case limited only to narrow regions of operating conditions. If the internal diffusion has been expressed in terms of mass-transfer coefficient in solid phase in these papers, the variability of this coefficient has not been taken into consideration. For this reason, we consider that in spite of its semiempirical character the treatment presented in this paper is suited for the calculation as well as the optimalization of adsorption processes. That is confirmed by a great accuracy with which this treatment has enabled us to express the adsorption dynamics in bed as well as the adsorption kinetics what will be presented in a subsequent paper.

Symbols

a^*_{0v}	equilibrium concentration of adsorbate in adsorbent corresponding to C_0 and referred to a volume unit of bed
C_0	concentration of adsorbate in gas entering the column
k	overall mass-transfer coefficient
k_g	gas-film mass-transfer coefficient
k_0	the characteristic value of the overall mass-transfer coefficient
k_s	mass-transfer coefficient in solid phase
k_{s0}	the characteristic value of the mass-transfer coefficient in solid phase
k_{0v}	the characteristic value of the mass-transfer coefficient referred to a volume unit of bed
K	coefficient characterizing the contribution of the resistance in solid phase to the overall resistance to mass transfer
q	relative concentration of adsorbate in adsorbent
Q	relative concentration of adsorbate in gas
Q^*	relative equilibrium concentration of adsorbate in gas
w	linear gas velocity based on empty column cross-section
Z	dimensionless transformed time
Z_g	dimensionless transformed time for $K = 0$
Z_s	dimensionless transformed time for $K = 1$
Γ_{0v}	ratio a^*_{0v}/C_0
Δh	height of adsorption zone in which the relative concentration of adsorbate changes from Q to $(1 - Q)$
ΔH	dimensionless height of adsorption zone ranging from Q to $(1 - Q)$
ΔH_g	dimensionless height of adsorption zone ranging from Q to $(1 - Q)$ for $K = 0$
ΔH_s	dimensionless height of adsorption zone ranging from Q to $(1 - Q)$ for $K = 1$
Δt	period of time in the course of which the relative concentration in bed changes from Q to $(1 - Q)$ at stable sorption front
ΔZ	dimensionless time within the range between Q and $(1 - Q)$
ε_v	porosity of bed
Θ	degree of covering of active surface
Θ_0	equilibrium degree of covering of active surface at the concentration C_0
Φ	ratio of the local value of overall mass-transfer coefficient to its characteristic value
Φ_s	ratio of the local value of mass-transfer coefficient in solid phase to its characteristic value

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