Kinetics and dynamics of gas and vapour adsorption on solid sorbents. IV. Generalization of the definition of similitude criteria

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The definitions of dimensionless concentration of the adsorbate in gaseous as well as solid phase presented in paper [1] have been so generalized that the same system of partial differential equations in dimensionless form with unchanged initial and boundary conditions describes both the dynamics of adsorption on fully and non-fully recovered sorbent and the desorption. A general procedure for the derivation of the equation of equilibrium curves in dimensionless coordinates in presented and the equations of equilibrium curves corresponding to the linear, Freundlich, and Langmuir adsorption isotherm have been deduced. The definitions of other dimensionless quantities necessary for the description of the dynamics of adsorption have been generalized in such a way that it is possible to derive their form convenient for arbitrary mathematical model of the mass-transfer rate.

In the first publication of this series [1] a system of partial differential equations was presented. This system describes the dynamics of adsorption in a fixed as well as continuous bed with a piston flow of both phases

$$\varepsilon_{\mathrm{v}} \frac{\partial C}{\partial t} + \frac{\partial C}{\partial h} + \frac{\partial a_{\mathrm{v}}}{\partial t} - v \frac{\partial a_{\mathrm{v}}}{\partial h} = D_1 \frac{\partial^2 C}{\partial h^2} \tag{1}$$

$$\frac{\partial a_{\mathrm{v}}}{\partial t} - v \frac{\partial a_{\mathrm{v}}}{\partial h} = r_{\mathrm{v}} \tag{2}$$

$$r_{\mathrm{v}} = k_{\mathrm{gv}}(C - C_{\mathrm{F}}) \tag{3}$$

$$r_{\mathrm{v}} = k_{\mathrm{v}}(C - C^*). \tag{4}$$

The boundary and initial conditions are

$$C(0,t) = C_0 = \mathrm{const},$$

$$a(h_{\mathrm{k}},t) = a_1 = \mathrm{const} \tag{5}$$

for $t > 0$ and

$$C(h,0) = 0$$

$$a(h,0) = 0 \tag{6}$$

for $0 \leq h \leq h_{\mathrm{k}}$.

In relationships $(1-6)$ ε_v denotes the porosity of bed, w and v are the rates of the gas flow and the movement of the particles of sorbent, h is the distance from the bottom of column, t is time, C is the concentration of adsorbate in gas, a is the concentration of the adsorbate in adsorbent expressed in arbitrary units, a_v is the concentration of the adsorbate in adsorbent referred to a volume unit of bed, D_l is the coefficient of longitudinal diffusion, r_v is the mass-transfer rate referred to a volume unit of bed, k_{gv} is the gas-film mass-transfer coefficient referred to a volume unit of bed, k_v is the overall mass-transfer coefficient referred to a volume unit of bed, C_F is the concentration of adsorbate in the interface, C^* is the equilibrium concentration corresponding to the given value of a, and h_k is the height of column.

On the basis of relationships $(1-6)$ a set of dimensionless quantities convenient for the description of the adsorption in fixed as well as continuous beds has been derived. The definitions of dimensionless quantities given in [1] may be generalized from two points of view.

A generalized formulation of initial conditions

The initial conditions (6) correspond to the assumption that at the beginning of the process the column is filled with fully recovered adsorbent. This assumption is not always fulfilled and for this reason it is convenient to formulate the initial conditions in a more general manner. Let us assume that at $t = 0$ the adsorbent in the whole bed is uniformly saturated to the value a_i which is in the case of a continuous counter-current column equal to the concentration of adsorbate at inlet to column

$$a(h,0) = a(h_k,t) = a_i = \text{const} \qquad (7)$$

and that at $t = 0$ the gas in the whole column is in equilibrium with adsorbent

$$C(h,0) = C_i = C^*(a_i) \qquad (8)$$

for $0 \leq h \leq h_k$.

In order that the dimensionless concentration in both phases may change in the interval $\langle 0,1 \rangle$ at the formulation of initial conditions thus generalized, they are defined by the following expressions

$$Q = \frac{C - C_i}{C_0 - C_i} \qquad (9)$$

$$q = \frac{a - a_i}{a_0^{\bullet} - a_i}, \qquad (10)$$

where $a_0^{\bullet}$ is the equilibrium concentration of adsorbate in adsorbent corresponding to the concentration in gas C_0. Then the dimensionless expression of boundary and initial conditions [5, 7, 8] will be

$$Q(0,\tau) = 1$$
$$q(H_k,\tau) = q(H,0) = 0 \qquad (11)$$
$$Q(H,0) = 0,$$

H, H_k, and τ being dimensionless coordinate, dimensionless height of column, and dimensionless time, respectively. The definitions of these quantities will be given later.

The generalized definitions of q and Q enable us to use the same system of partial differential equations with unchanged boundary and initial conditions [11] for the description of adsorption on a fully ($a_i = 0$) and non-fully ($a_i > 0$) recovered adsorbent as well as for the description of desorption ($C_i > C_0$). The shape of equilibrium curve in dimensionless coordinates $q - Q$ and the values of dimensionless parameters derived from the equation of adsorption isotherm will depend on the values of C_0 and a_i.

By using the equation of adsorption isotherm it is possible to express the equilibrium concentration in gas as a function of the concentration in sorbent

$$C^* = f(a) . \tag{12}$$

Simultaneously it holds

$$C_i = f(a_i) \tag{13}$$

and

$$a_0^{\bullet} = f^{-1}(C_0) , \tag{14}$$

where f^{-1} is a function inverse with respect to f. By substituting for a in expression (12) in agreement with (10) and inserting the expression thus obtained in (9) we get a dimensionless formulation of the equation of equilibrium curve

$$Q^* = \frac{f[a_i + q(a_0^{\bullet} - a_i)] - f(a_i)}{f(a_0^{\bullet}) - f(a_i)} . \tag{15}$$

On substituting the pertinent mathematical expressions for the function f we obtain an equation which contains, in general, further dimensionless parameters in addition to q and Q^*. These parameters are the similitude criteria searched for.

For the simplest linear adsorption isotherm C^* is expressed as follows

$$C^* = \frac{a}{\Gamma} . \tag{16}$$

After substituting in (15) and rearranging we obtain

$$Q^* = q \tag{17}$$

Therefore the shape of equilibrium curve does not depend on boundary and initial conditions in the case of linear adsorption isotherm.

The subsequent expression of C^* ensues from the Freundlich equation of adsorption isotherm

$$C^* = \left(\frac{a}{K}\right)^{\frac{1}{n}} , \tag{18}$$

where K and n are the constants of the Freundlich equation. After substitution in (15) and rearrangement we obtain the equation of equilibrium curve

$$Q^* = \frac{|q + b_F|^{\frac{1}{n}} - |b_F|^{\frac{1}{n}}}{|1 + b_F|^{\frac{1}{n}} - |b_F|^{\frac{-1}{n}}} , \tag{19}$$

where the parameter b_F is defined by the fraction

$$b_F = \frac{a_i}{a_0^{\bullet} - a_i} . \tag{20}$$

For adsorption it holds $a_0^* > a_i$ and $b_F \in \langle 0, +\infty)$ whereas for desorption $a_0^* < a_i$. Since $(a_0^* - a_i) < a_i$, it holds $b_F \in (-\infty, -1\rangle$ and $(q + b_F) < 0$. That is why absolute values appear in equation (19). For adsorption on pure sorbent it holds $a_i = 0$ and $b_F = 0$ so that relationship (19) turns into the relation derived in [1]

$$Q^* = q^{\frac{1}{n}}. \qquad (21)$$

For desorption in a flow of inert gas $C_0 = 0$ and $b_F = -1$ and equation (19) assumes the form

$$Q^* = 1 - (1 - q)^{\frac{1}{n}}. \qquad (22)$$

From the Langmuir equation of adsorption isotherm it follows

$$C^* = C_{1/2} \frac{a}{a_M - a} \qquad (23)$$

and the equation of equilibrium curve in dimensionless coordinates is

$$Q^* = \frac{(1 - b_L)q}{1 - b_L q}, \qquad (24)$$

where b_L is defined as the fraction

$$b_L = \frac{a_0^* - a_i}{a_M - a_i} = \frac{\Theta_0^* - \Theta_i}{1 - \Theta_i}. \qquad (25)$$

The symbols Θ_i and Θ_0^* denote the degree of covering of active surface at $t = 0$ and the equilibrium degree of covering corresponding to concentration C_0. For adsorption it is valid $a_i < a_0^* \leq a_M$ and $b_L \in (0,1\rangle$ whereas for desorption $a_0^* < a_i \leq a_M$ and $b_L \in (-\infty, 0\rangle$. For adsorption on pure sorbent $b_L = \Theta_0^*$ while for desorption with pure inert gas $b_L = \dfrac{\Theta_i}{1 - \Theta_i}$.

Generalization of the definitions of other dimensionless variables

The definitions of dimensionless variables introduced in paper [1] were derived from one of mathematical models of mass transfer, namely equation (4). To express the mass-transfer rate during adsorption, a number of different mathematical models [2—7] are used. For this reason it is convenient to put forward such definition of dimensionless variables which would be generally valid and enable us to use an arbitrary mathematical description of the mass transfer. Therefore the system of equations (1—3) is to be transformed into a dimensionless form

$$\lambda_v \frac{\partial Q}{\partial \tau} + \frac{w}{w^\circ} \frac{\partial Q}{\partial H} + \frac{\partial q}{\partial \tau} - \frac{1}{K_m} \frac{\partial q}{\partial H} = \Omega_0 \frac{\partial^2 Q}{\partial H^2} \qquad (26)$$

$$\frac{\partial q}{\partial \tau} - \frac{1}{K_m} \frac{\partial q}{\partial H} = \frac{r_v}{\overset{\circ}{r_v}} \qquad (27)$$

$$\frac{r_v}{\overset{\circ}{r_v}} = K_g (Q - Q_F). \qquad (28)$$

In order that the system of equations $(26-28)$ might be a correct transformation of system $(1-3)$ into a dimensionless form the following relations among the units must be fulfilled

$$\frac{\overset{\circ}{\varepsilon_v} C^\circ}{t^\circ \overset{\circ}{r_v}} = \frac{C^\circ w^\circ}{\overset{\circ}{r_v} h^\circ} = \frac{a_v^\circ}{t^\circ \overset{\circ}{r_v}} = \frac{v^\circ a_v^\circ}{h^\circ \overset{\circ}{r_v}} = \frac{D_l^\circ C^\circ}{h^{\circ 2} \overset{\circ}{r_v}} = \frac{k_v^\circ C^\circ}{\overset{\circ}{r_v}} = 1 \qquad (29)$$

Expression (29) represents six relationships among ten quantities. Then four quantities may be thought of as the basic units, their values being characteristic of a given system and working conditions. Two of the basic units are determined by relations (9) and (10)

$$C = C_0 - C_i \qquad (30)$$

$$a_v = \overset{\bullet}{a_{0v}} - a_{iv}. \qquad (31)$$

Another characteristic quantity is the flow velocity of gaseous mixture w. We shall take it for the third basic unit and define

$$w^\circ = w. \qquad (32)$$

Since the substantial factor having effect on the course of adsorption is the mass transfer, it is convenient to choose the mass-transfer rate as the fourth basic quantity. We shall denote the respective unit with the symbol $\overset{\circ}{r_v}$. The definitions of dimensionless quantities will then be with respect to relations $(29-31)$.

$$\lambda_v = \frac{\varepsilon_v}{\overset{\circ}{\Gamma_v}} \qquad K_m = \frac{w}{\overset{\circ}{\Gamma_v} v} \qquad H = \frac{\overset{\circ}{r_v}}{(C_0 - C_i) w} h \qquad \Omega_0 = \frac{\overset{\circ}{r_v} D_l}{(C_0 - C_i) w^2}$$

$$H_k = \frac{\overset{\circ}{r_v}}{(C_0 - C_i) w} h_k \qquad K_g = \frac{k_{gv}(C_0 - C_i)}{\overset{\circ}{} } \qquad \tau = \frac{\overset{\circ}{r_v}}{\overset{\bullet}{a_{0v}} - a_{iv}} t, \qquad (33)$$

where

$$\overset{\circ}{\Gamma_v} = \frac{\overset{\bullet}{a_{0v}} - a_{iv}}{C_0 - C_i}. \qquad (34)$$

Relationships (33) represent symbolic definitions of dimensionless quantities. Particular definitions can be obtained from them by replacing the symbolic unit $\overset{\circ}{r_v}$ by an expression representing the characteristic mass-transfer rate for the corresponding mathematical model, given system, and working conditions. Some examples will be given in part VI of this series of papers.

List of symbols

a — concentration of adsorbate in adsorbent (in arbitrary units)

a_1 — concentration of adsorbate in adsorbent at inlet to column (in arbitrary units)

a_i — concentration of adsorbate in adsorbent in column at $t = 0$ (in arbitrary units)

a_M — capacity of monomolecular layer (in arbitrary units)

a_v — concentration of adsorbate in adsorbent referred to the volume of bed (kg m^{-3})

a_v° — unit for the concentration of adsorbate in adsorbent (kg m^{-3})

b_F — dimensionless parameter defined by expression (20)

b_L — dimensionless parameter defined by expression (25)

C — concentration of adsorbate in gas (kg m^{-3})

C_0 — concentration of adsorbate in gas at inlet to column (kg m^{-3})

$C_{1/2}$ — concentration of adsorbate corresponding to half-covering of active surface (kg m^{-3})

C_F — concentration of adsorbate in interface (kg m^{-3})

C_i — concentration of adsorbate in gas at $t = 0$ (kg m^{-3})

C^* — equilibrium concentration of adsorbate in gas (kg m^{-3})

C° — unit for the concentration of adsorbate (kg m^{-3})

D_l — coefficient of longitudinal diffusion (m^2 s^{-1})

D_l° — unit for the coefficient of longitudinal diffusion (m^2 s^{-1})

H — dimensionless coordinate

H_k — dimensionless height of column

h — coordinate (m)

h_k — height of column (m)

h° — unit for height (m)

K — coefficient in the Freundlich equation of adsorption isotherm

K_g — dimensionless mass-transfer coefficient in gaseous phase

K_m — slope of the operating line for the process in $Q - q$ coordinates

k_{gv} — gas-film mass-transfer coefficient referred to a volume unit of bed (s^{-1})

k_v — overall mass-transfer coefficient referred to a volume unit of bed (s^{-1})

k_v° — unit for the mass-transfer coefficient (s^{-1})

n — exponent in the Freundlich equation of adsorption isotherm

Q — dimensionless concentration of adsorbate in gas

Q_F — dimensionless concentration of adsorbate in interface

Q^* — dimensionless equilibrium concentration of adsorbate in gas

q — dimensionless concentration of adsorbate in adsorbent

r_v — mass-transfer rate referred to a volume unit of bed (kg m^{-3} s^{-1})

r_v° — unit for mass-transfer rate (kg m^{-3} s^{-1})

t — time (s)

t° — unit for time (s)

v — transport velocity of bed through adsorber (m s^{-1})

v° — unit for the transport velocity of bed (m s^{-1})

w — linear gas velocity based on empty column cross section (m s^{-1})

w° — unit for linear gas velocity (m s^{-1})

Γ — Henry coefficient (in arbitrary units)

Γ_v° — fraction defined by expression (34)

ε_v — porosity of bed

ε_v° — unit for the porosity of bed

Θ_i — degree of the covering of active surface at $t = 0$

$\Theta_0^{\bullet}$ — equilibrium degree of the covering of active surface at C_0
λ_v — dimensionless parameter defined by expression (33)
τ — dimensionless time
Ω_0 — dimensionless coefficient of longitudinal diffusion

References

1. Kachaňák, Š., Moncmanová, A., and Valtýni, J., *Chem. Zvesti* **24**, 182 (1970).
2. Timofeev, D. P., *Kinetika adsorbcii.* (Kinetics of Adsorption.) Izd. Akad. nauk SSSR. (Publishing House of the Academy of Sciences of USSR.) Moscow, 1962.
3. Zabezhinskii, J. L., Zhukhovitskii, A. A., and Tikhonov, A. N., *Zh. Fïz. Khim.* **23**, 192 (1949).
4. Hiester, N. K. and Vermeulen, T., *Chem. Eng. Progr.* **48**, 505 (1952).
5. Rosen, J. B., *J. Chem. Phys.* **20**, 387 (1952).
6. Rosen, J. B., *Ind. Eng. Chem.* **46**, 1590 (1954).
7. Chi Tien and Thodos, G., *A. I. Ch. E. Journal* **5**, 373 (1959).

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