Kinetics and Dynamics of Gas and Vapour Adsorption on Solid Sorbents. I.
Material Balances and Similitude Criteria

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Material balances of a countercurrent adsorption column are given. Their transformation into a dimensionless form yields a set of dimensionless parameters which are suitable for a description of adsorption dynamics in both continuous and fixed beds. The necessity to introduce further dimensionless parameters characterizing the shape of equilibrium curve in dimensionless coordinates is proved. A general method is introduced which enables us to deduce these parameters from the equation of adsorption isotherm. The equations of equilibrium curves corresponding to the adsorption isotherms of Freundlich, Dubinin for the first and second structural type of sorbent, Langmuir, and B.E.T are presented.

In spite of a rather ample and steadily growing use of adsorption in various fields of chemical technology, the state of the theory of adsorption processes is not satisfactory yet. Thus the necessity appears to work intensively in this field in both theoretical and experimental way. This paper opens a serial of publications which cover the results achieved in both laboratory and pilot plant research of gas and vapour adsorption on charcoal. A mathematical model for the adsorption in bed is presented on the basis of which the equations of adsorption isoplanes and isochrones have been deduced. These equations agree with experimental data better than the equations hitherto published by other authors. The scope of their validity is tested by means of the experimental material which has been obtained either from the authors' measurements or from other publications.

Material balance of a countercurrent column

Owing to the intricacy of the process an exact mathematical description of the course of adsorption in bed is not feasible at the present state of theory. Some basic simplifications are to be asserted for the formulation of a mathematical model suitable for practical use. Even simplified models are mathematically so complicated that they can be solved only by approximative methods. In designing a mathematical model for the rather usual application of adsorption to the removal of small amounts of admixtures from gaseous and liquid substances, the following assumptions are proposed [1, 2]:

a) A single substance is adsorbed from the inert carrier fluid.
b) The process is steady from the hydrodynamic point of view.
c) The porosity of bed is constant in the whole volume.

d) The density change of fluid phase in column is negligible.

e) The concentration of adsorbate in a mixture entering the column is so low that the partial volume of adsorbate is negligible in comparison to that of inert medium.

f) The process is isothermal.

g) The process takes place in a column with a constant cross-section while the concentration of adsorbate in both solid and fluid phase vary in the direction of the column axis only.

On the basis of assumptions a) to f), the material balances of a volume element of the bed have been derived and expressed vectorially in the paper [2]. By simplifying these balances for a one-dimensional case according to assumption g), the following equations could be obtained

$$\varepsilon_v \frac{\partial C}{\partial t} + w \frac{\partial C}{\partial h} + \frac{\partial a_v}{\partial t} - v \frac{\partial a_v}{\partial h} = D_1 \frac{\partial^2 C}{\partial h^2},$$ (1)

$$\frac{\partial a_v}{\partial t} - v \frac{\partial a_v}{\partial h} = r_v.$$ (2)

An unambiguous formulation of the problem demands a statement of the initial and boundary conditions. With respect to the cases which often occur in practical applications, the boundary conditions are formulated as follows

$$C(0,t) = C_0 = \text{const},$$
$$a(h_k,t) = a_1 = \text{const}$$ (3)

for $t \geqslant 0$, while the initial conditions are

$$C(h,0) = 0,$$
$$a(h,0) = 0$$ (4)

for $0 \leqslant h \leqslant h_k$.

The rate of proper adsorption on the active surface is much higher than the rate of transfer of the adsorbed substance to this surface. The resulting rate is therefore controlled by the external as well as internal diffusion of adsorbate from the gaseous mixture among the particles of adsorbent to the active surface.

The rate of external diffusion is expressed by subsequent equation

$$r = k_g(C - C_F),$$ (5)

which is often used in practice because of its simplicity [1—4].

An exact expression of the rate of internal diffusion on the charcoal is out of the question because of the heterogeneity of its structure. A solution is feasible only in case of some sorbent models which are homogeneous with respect to the shape and structure. For instance, Wicke [4] admits some simplifications in deducing the equations of internal diffusion which fundamentally disagree with a real process. He assumes spherical particles of the sorbent, the pores of which are cylindrical having equal diameter. The diffusion coefficient is constant at all places of pores and it does not depend on the direction in which the diffusion proceeds. Moreover, he assumes a linear shape of isotherm and an isothermal character of the process. Even for this simplified model, the solution is feasible only by the use of infinite series.

By using the equations of Wicke, we have evaluated our experimental data obtained from the kinetic measurements of vapour adsorption on charcoal [5]. It has been pro-

ved that these equations do not express the rate of process. This disagreement is due to the above simplifications which are not fulfilled in case of charcoal. Likewise, an analytical solution of the material balance equations $(1, 2)$ is also not possible for the simplified model of Wicke even in case $D_1 = 0$.

For above reasons, a practical application of adsorption demands to express the rate of internal diffusion by some empirical equations which enable us to solve the equation system $(1, 2)$ for the adsorption in bed. The rate of internal diffusion is most frequently expressed by a relationship which is formally analogous with the expression for the rate of external diffusion

$$r = k_s(C_F - C^*). \tag{6}$$

Since the transport rate of adsorbate vapour to the external surface equals to the transport rate from the external surface into the particle, the mass-transfer rate of the substance r_v in the equation (2) can be expressed regarding the equations $(5, 6)$ by the relationship

$$r_v = k_v(C - C^*). \tag{7}$$

Transformation of the material balances into a dimensionless form

Though an accurate physical simulation of adsorption processes is rather limited owing to the intricacy and variety of adsorption systems, their description by means of dimensionless variables still permits a reduction of variables and generalization of results in both theoretical and experimental study.

On substituting (7) for r_v in the equation (2) and introducing the dimensionless quantities

$$
\begin{aligned}
q &= \frac{a}{a_0^\bullet} & H &= \frac{k_{0v}}{w}h, \\
Q &= \frac{C}{C_0} & \tau &= \frac{k_{0v}}{\Gamma_{0v}}t, \\
Q^* &= \frac{C^*}{C_0} & K_m &= \frac{w}{v\,\Gamma_{0v}}, \\
\Phi &= \frac{k_v}{k_{0v}} & \Omega_0 &= \frac{k_{0v}\,D_1}{w^2},
\end{aligned}
\tag{8}
$$

the equations $(1, 2)$ are transformed into

$$\frac{\varepsilon_v}{\Gamma_{0v}} \cdot \frac{\partial Q}{\partial \tau} + \frac{\partial Q}{\partial H} + \frac{\partial q}{\partial \tau} - \frac{1}{K_m} \cdot \frac{\partial q}{\partial H} = \Omega_0 \frac{\partial^2 Q}{\partial H^2}, \tag{9}$$

$$\frac{\partial q}{\partial \tau} - \frac{1}{K_m} \cdot \frac{\partial q}{\partial H} = \Phi(Q - Q^*). \tag{10}$$

The initial and boundary conditions $(3, 4)$ being

$$Q(0,\tau) = 1,$$
$$q(H_k,\tau) = q_1 = \text{const} \quad \text{for } \tau \geqslant 0; \tag{11}$$
$$Q(H,0) = 0,$$
$$q(H,0) = 0 \quad \text{for } 0 \leqslant H \leqslant H_k. \tag{12}$$

The physical significance of the simplexes q, Q and Q^* is obvious from their definitions. Φ denotes the ratio of the local value of the overall mass-transfer coefficient to its characteristic value. The choice of the characteristic value depends on the kind of relevant individual problem. The groups τ and H represent the dimensionless time and dimensionless coordinate, respectively, and H_k denotes the dimensionless height of the column. The symbol K_m means the slope of the operating line in $Q-q$ coordinates and Ω_0 characterizes the contribution of a longitudinal diffusion to the material balance of a volume element.

Expression of the equation of equilibrium curve in dimensionless form

In the papers hitherto published by other authors [6—8] no attention has been paid to the problem of the effect of the shape of adsorption isotherm on the course of process. A linear shape of adsorption isotherm which is usually supposed is not real even approximately in most practical applications. The shape of adsorption isotherm in an actual concentration interval is, however, a very important factor because it is one of the parameters determining the space and time distribution of driving forces during the process. In terms of the similitude theory, the significance of this factor may be expressed by means of a postulate that one of the necessary conditions for similarity of two adsorption processes is an identical shape of corresponding equilibrium curves in $q-Q$ coordinates. It is, therefore, necessary to complete the set of dimensionless quantities (8) by the parameters which characterize the shape of equilibrium curve. These parameters can be derived by following procedure.

Using the equation of the adsorption isotherm, C^* can be expressed as a function of a

$$C^* = \mathrm{f}(a). \tag{13}$$

At the same time

$$C_0 = \mathrm{f}(a_0^*), \tag{14}$$

or

$$a_0^* = \mathrm{f}^{-1}(C_0), \tag{15}$$

where f^{-1} is an inverse function with respect to f.

On dividing the equation (13) by the equation (14) and substituting for a in accordance with (8), eventually on further substituting for a_0^* using expression (15), two equivalent equations may be obtained

$$Q^* = \frac{\mathrm{f}(q\,a_0^*)}{\mathrm{f}(a_0^*)}, \tag{16a}$$

$$Q^* = \frac{\mathrm{f}[q\,\mathrm{f}^{-1}(C_0)]}{C_0}. \tag{16b}$$

If the mathematical form of the equation of adsorption isotherm does not allow an explicit expressing $C^* = \mathrm{f}(a)$, the equation of equilibrium curve can be obtained in an inverse form

$$q = \frac{\mathrm{f}^{-1}(Q^*\,C_0)}{\mathrm{f}^{-1}(C_0)}. \tag{16c}$$

The parameters to be found are represented by the mutually independent dimensionless groups (except q and $Q*$) which can be obtained on substituting suitable mathematical expressions for the functions f, f^{-1} in the equations ($16a-c$) and making corresponding arrangements or by the mutually independent combinations of these groups.

The Freundlich equation of adsorption isotherm which is widely used in the practice can be transformed according to ($16a$) into the form

$$Q* = q^{\frac{1}{n}}.$$ (17)

The shape of the equilibrium curve is thus characterized by a single parameter n which is independent of C_0.

The authors have proved in the paper [9] that the Dubinin adsorption isotherm for the second structural type may be transformed into a form which is identical with the Freundlich equation of adsorption isotherm. The equilibrium curve shall thus be expressed by the relationship (17) in which n is defined by the expression

$$n = \frac{AT}{\beta \ln 10}.$$ (18)

According to ($16b$), the Dubinin adsorption isotherm for the first structural type gives

$$Q* = \frac{1}{x_0} \exp\left[- \sqrt{\ln^2 x_0 - \frac{\ln q}{Du}} \right]$$ (19)

where

$$x_0 = \frac{p_0}{p_s},$$ (20)

$$Du = B\left(\frac{T}{\beta \ln 10}\right)^2.$$

p_0 denotes the partial pressure of adsorbate vapour corresponding to the concentration C_0, while p_s is the pressure of saturated vapour of adsorbate. The dimensionless complex Du has been called the Dubinin criterion. The shape of equilibrium curve is defined by two parameters, namely Du and x_0.

The equation of equilibrium curve corresponding to the Langmuir adsorption isotherm has the form

$$Q* = \frac{(1 - \Theta_0) q}{1 - \Theta_0 q}.$$ (21)

Θ_0 being the equilibrium degree of covering of the surface corresponding to the concentration C_0.

The equilibrium curve for the adsorption isotherm of Brunauer, Emmett and Teller is expressed in accordance with ($16b$) by the equation

$$Q* = \frac{2q}{m_1 - m_2 q + \sqrt{(m_1 - m_2 q)^2 + 4(1 - m_1 + m_2) q^2}},$$ (22)

where

$$m_1 = (1 - x_0)[1 + (c - 1) x_0],$$

$$m_2 = (c - 2) x_0. \tag{23}$$

Similarly as in case of the Dubinin equation for the first structural type, the characterization of the shape of equilibrium curve requires two parameters: c and x_0 or m_1 and m_2.

By means of the above equations of equilibrium curves, the equation system ($9, 10$) can be solved for some adsorption isotherms provided the necessary simplification has been made.

The equations ($9, 10$) express in a convenient dimensionless form the material balance for the process of adsorption regeneration of gases and vapours from industrial exhalates in static and continuous adsorbers. In subsequent papers, these equations as well as the equations of equilibrium curves will be used to express dynamics of these processes. At the same time, the change of resistance of the solid phase during saturation of bed will be taken into account.

Symbols

A constant for the second structural type of sorbent

a concentration of adsorbate in adsorbent

a_v concentration of adsorbate in adsorbent referred to a volume unit of bed

a_0^* equilibrium concentration of adsorbate in adsorbent corresponding to C_0

a_{0v}^* equilibrium concentration of adsorbate in adsorbent corresponding to C_0 and referred to a volume unit of bed

a_1 concentration of adsorbate in adsorbent at the top of column

B constant for the first structural type of sorbent

C concentration of adsorbate in gas

C_F concentration of adsorbate at the interphase

C^* equilibrium concentration of adsorbate

C_0 concentration of adsorbate in the gas entering the column

c constant in the B.E.T. adsorption isotherm

D_1 coefficient of quasidiffusion

Du Dubinin criterion defined by the expression (20)

H dimensionless coordinate

H_k dimensionless height of column

h coordinate

h_k height of column

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

k_g gas-film mass-transfer coefficient

k_s mass-transfer coefficient in solid phase

k_v overall mass-transfer coefficient referred to a volume unit of bed

k_{0v} the characteristic value of the overall mass-transfer coefficient referred to a volume unit of bed

m_1, m_2 dimensionless parameters, defined by expression (23)

n exponent in the Freundlich equation of adsorption isotherm

p_0 vapour pressure of adsorbate corresponding to the concentration C_0

p_s pressure of saturated vapour of adsorbate

Q	relative concentration of adsorbate
$Q*$	relative equilibrium concentration of adsorbate
q	relative concentration of adsorbate in adsorbent
q_1	relative concentration of adsorbate in adsorbent at the top of column
r	mass-transfer rate
r_v	mass-transfer rate referred to a volume unit of bed
T	absolute temperature
t	time
v	transport rate of bed through adsorber
w	linear gas velocity based on empty column cross-section
x_0	ratio p_0/p_s
β	affinity coefficient
Γ_{0v}	ratio $a^\bullet_{0v}/C_0$
ε_v	porosity of bed
Θ_0	equilibrium degree of covering of active surface at the concentration C_0
τ	dimensionless time
Φ	ratio k_v/k_{0v}
Ω_0	criterion defined by the expression (8)

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