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Sorption mechanism and prediction of sorbents' behaviour in physicochemical systems

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Abstract. The possibility of quantitative and semiquantitative prediction of sorbents' behaviour in various physicochemical systems is discussed. The attention is primarily devoted to the investigation of elementary processes at different surface areas of a sorbent grain. It is noted that the achieved level of the description of sorption processes based on semiquantitative estimations provides sufficient information to predict sorption kinetics and equilibrium *a posteriori*. The possibility of sorption by both a separate sorbent grain and grain agglomerates is analysed. The peculiarities of sorption processes on biosorbents are considered. Steps in the search for an optimum sorbent for a given system are described. The bibliography includes 242 references.

I. Introduction

In the present review, sorption implies the transfer of a substance onto the surface or into the bulk of solids or liquids from the environment without formation of a separate phase of the substance. Such a viewpoint corresponds to a common sorption definition (see Ref. 1, for instance), though it is much broader than the interpretation of the process as the uptake of a substance from the medium by a specially prepared sorbent only. In real systems, any solid or liquid phase of a substance is a sorbent for the other substances being present in the environment. The character of such a sorption differs from that on a specially prepared sorbent in terms of quantity only.

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The sorption accompanies any processes occurring in heterogeneous systems, and so researchers from almost all laboratories over the world deal with it to a greater or lesser extent. Information about sorption is mainly an incidental result of laboratories' work, although a vast number of studies specially cover the study of sorption and sorbents every year. The scope of sorption phenomena under investigation has significantly been extended [2–11] during the last decade. Methods for the detailed and express analysis of sorbents' and sorbates' state have gained ground, efficient methods for the mathematical simulation of sorption processes have become available. Yet the main thing is that the possibility of observing the behaviour of separate adsorbed atoms and molecules *in situ* has arisen. The first observations of adsorbed atoms were made as early as 1958.[12] However, such observations became widespread as late as the present time. As a result, a transition to a new stage of sorption investigation is possible, which can be called the stage of visualisation of sorbed molecules.

A change in direction of many sorption investigations can be considered as the first indication of the advent of the new stage. If previously one aimed to create a macrokinetic model of sorption first and then make conclusions about molecules' motion, at present, one aims to obtain experimental data about behaviour of separate molecules first and, based on this, interpret macrokinetic sorption characteristics.[13]

The second indication is the introduction of a new research methodology avoiding application of *a priori* conceptions of the character of elementary processes. This methodology includes successive alternate implementation of laboratory, computing and, further, pilot experiments, based on the data obtained from observations *in situ* on connection of molecular motion with sorption macrokinetics.[14]

The fact that there is a tendency to predict the behaviour of sorbing bodies quantitatively by solution of kinetic equations describing the state change of these bodies and the medium during sorption can be considered as the third indication. The prediction can be incorrect if the kinetic equations employed ignore a number of necessary factors. However, methods for composing and solving kinetic equations of sorption are presently being improved rapidly.

This review considers only new studies giving an idea of the recent achievements in the investigation of elementary processes

with an emphasis on the data obtained by visualisation of molecular motion. The matter of the synthesis and usage of sorbents to solve applied problems is not concerned here.

II. General pattern of sorption

Consider a system which consists of sorbing bodies and a liquid or gaseous environment containing a sorbate. The 'bodies' can be represented by single crystals; microcrystals' agglomerates accreted so that the medium can penetrate into pores remaining between them; aggregates of particles of the amorphous substance; globules of polymeric molecules; pieces of tissue from sorbing fibres, *etc*. The bodies can form dense layers, localise in certain parts of the system or move freely in its bulk.

The sorbate molecules (ions) migrate from the bulk of the medium to the surface of each body and transfer into its adsorption layer during sorption. The adsorbed molecules migrate in this layer, diffuse into the bulk of the body or desorb. Molecules in the adsorption layer interact with each other and with the sorbent atoms located in the near-surface monoatomic layer of the bodies (Fig. 1). If the interaction of sorbate molecules with each other is sufficiently strong, they assemble into two-dimensional clusters that can grow over the surface until they contact neighbouring clusters. The two-dimensional clusters do not form on weak interaction of absorbed molecules with each other, while the influence of surface atomic relief on adsorption increases.

Migrating over the surface, molecules stay on an adsorption centre for some time, then jump to an adjacent centre. Molecule's dwell times on vertices, edges or steps of single crystal faces can differ by factor of tens in this process. This difference is the case for molecules' dwell times on adsorption centres located at different crystal faces with different atomic relief. Therefore, faces with an unequal number of steps have different sorbing abilities. Each face is characterised by its own local adsorption factor and sorptive capacity.[15]

The difference in sorbing properties of different faces is levelled if a body represents an agglomerate of microcrystals with pores between them. In that case, the sorbate first gets into pores between the microcrystals and subsequently adsorbs on their surfaces and diffuses into the bulk. Microcrystals have usually various habits and differ in composition, defectiveness, faces' relief and mutual arrangement. Hence, agglomerate properties can vary significantly.[16] Considerable distinctions in properties are observed for aggregates of amorphous particles, globules of polymeric molecules, *etc*.[17, 18]

Taking into consideration the discussion above, one should operate with a distribution function of sorbing bodies (sorbent particles) over properties (state parameters) to describe sorption

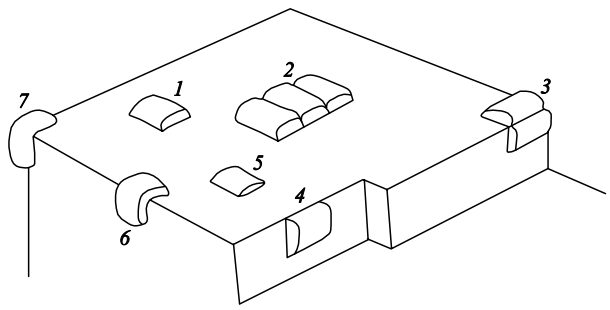


Figure 1. Scheme of the arrangement of adsorbed molecules on the surface of the sorbent crystal.
(*1*) Single molecule, (*2*) two-dimensional cluster on a face, (*3*) cluster at the vertex, (*4*) molecule at the adsorption site on the step end, (*5*) molecule that passed to the near-surface monolayer, (*6*) molecule at the edge, (*7*) single molecule at the vertex.

$$\varphi(\{x_i\},t)=\frac{\partial^p N}{\partial x_1\cdots\partial x_i\cdots\partial x_p},$$

where x_i (i = 1, 2, ..., p) is one of the state parameters of the particles at the moment t, p is the number of the state parameters considered, N is the number of particles in a volume unit of the system, which have values of state parameters not exceeding $\{x_i\}$.

The state of each body is being changed during sorption: they undergo Ostwald curing and structural ordering,[19–21] the bodies dissolve partly and sorb extraneous agents.[21,22] If bodies are in a stirred medium, they are partly destroyed upon collisions with each other and with walls of the system (vessel) and decompose at high temperature.[23] Bearing this in mind, one should define the state of each body with external parameters, among which are the spatial coordinates of its centre of gravity $\{X_i\}$, the velocity of movement relative to the walls ($\vec{v}_k$) and the mass m_k, and with internal parameters, the habit, characteristics of surface relief, and the phase and elemental composition. Each sorbing body can be presented as an aggregate of several species of structural elements. The structural element implies an aggregate of similar sorbing centres, and the sorbing centre is a group of atoms in the bulk or on the surface of a body, which can hold one molecule of the sorbate. Hence,

$$\{x_i\}=X_i,\vec{v}_k,m_k,\{n_j\},\{\theta_j\},$$

where n_j is the number of adsorbing centres in the same state, which is determined by the centre's location in the body, the composition and configuration of molecules forming it, θ_j is the fraction of centres of a given sort occupied by the sorbate.

A conservation condition for the number of sorbent particles and all species of adsorbing centres can be written in the form[24–26] (taking into account the continuous change of their states)

$$-\frac{\partial\varphi}{\partial t}=\sum_{i=1}^{p}\frac{\partial}{\partial x_i}\left[G_i\varphi-\sum_{j=1}^{p}\frac{\partial}{\partial x_j}(D_{ij}\varphi)\right]+Q(x_i,\varphi), \tag{1}$$

where

$$G_i=\lim_{\Delta t\to 0}\frac{\langle\Delta x_i\rangle}{\Delta t}, \tag{2}$$

$$D_{ij}=\frac{1}{2}\lim_{\Delta t\to 0}\frac{\langle\Delta x_i\Delta x_j\rangle}{\Delta t}.$$

In these equations, G_i is the rate of the change of parameter x_i for particles with approximately the same properties, D_{ij} is the fluctuation factor of the rate G_i upon the influence of random changes of the parameter x_j; $Q(x_i,\varphi)$ is the frequency of particles' dissociation upon collisions with each other, thermal decomposition or phase transitions in the particles' bulk; Δx_i is the increment of x_i over the interval Δt; averaging is performed for an ensemble of particles.

Equation (1) reflects the concept that every particle can with a certain probability move from one state to another, which is consistent with the conservation laws. The probability of some transitions is negligibly small, but they must be taken into account within the framework of a general pattern of sorption.

Another conservation condition has the form

$$-\frac{\partial(\varepsilon c)}{\partial t}=\mathrm{div}[\varepsilon(\vec{v}_{\mathrm{L}}c-D\mathrm{grad}c)]+\frac{\mathrm{d}M}{\mathrm{d}t}, \tag{3}$$

where M is the number of moles of a substance extracted by the sorbent from a volume unit of the medium,

$$M=\int_{-\infty}^{+\infty}q\varphi\mathrm{d}x_i,$$

$$\varepsilon = 1 - \int_{-\infty}^{+\infty} V_k \varphi \mathrm{d}x_i ,$$

ε, c and $\vec{v}_\mathrm{L}$ stand correspondingly for the local porosity, the concentration of the sorbate, and the velocity of medium movement in the interval where particles have distribution $\varphi(x_i, t)$, D is the molecular diffusion constant for the sorbate in the medium, q is the sorbate quantity in a particle with parameters $\{x_i\}$, V_k is the volume of the particle, integration is performed over all parameters x_i.

Variable q is usually represented as a sum of sorbate quantities in the near-surface layer of a body

$$q_\mathrm{s} = \sum_j q_{\mathrm{s}j}$$

and in its bulk

$$q_\mathrm{v} = \sum_j q_{\mathrm{v}j} ,$$

where index j belongs to the adsorption centres of the jth species. If a body is a single crystal, then the layer of adsorbed molecules (sometimes along with one or two additional monolayers of crystal atoms) is regarded as a near-surface one.[27]

If a body is composed of accreted microcrystals, then one includes both those which have at least one facet contacting the medium and the pores between them in the near-surface layer.

For the near-surface layer which is homogeneous along a normal to the surface, we have

$$\frac{\mathrm{d}q_\mathrm{s}}{\mathrm{d}t} = \sum_j \left[\omega_j a S c - (\lambda_j + v_j) q_{\mathrm{s}j}\right] , \tag{4}$$

$$\frac{\mathrm{d}q_\mathrm{v}}{\mathrm{d}t} = \sum_j \lambda_j q_{\mathrm{s}j} ,$$

where ω_j, ν_j are correspondingly the probabilities of the sorbate intake from the medium into the near-surface monolayer through sorption centres of the jth species and its leaving from these centres for the medium in a time unit, a is the normalising factor (effective width of the layer, from which sorbate molecules can get into the near-surface layer as a result of unit translation), S is the surface area, λ_j is the probability of a sorbate molecule transfer from the adsorption centre of the near-surface layer into the bulk of the body in a time unit.

Terms in the second member of Eqn (4) can differ in the order of magnitude, which will reveal itself in the stepwise character of sorption.[28]

If a body is homogeneous, a transition of a sorbate from the near-surface layer into the bulk can approximately be described as a convective transfer with the effective diffusion constant D_v upon ordered motion of sorbate particles relative gravity centre of the body with velocity $\vec{v}_\mathrm{v}$. The velocity $\vec{v}_\mathrm{v}$ rides on the shift of the near-surface boundary due to dissolution and swell (compression) of the body upon sorption. If a body is highly porous, $\vec{v}_\mathrm{v}$ is associated with the flow in pores caused by external pressure or phase transitions in the body.[29]

The change with time of the sorbate concentration c_v in each region of the body in which the position is fixed relative to the body's surface is described by the equation

$$-\frac{\partial c_\mathrm{v}}{\partial t} = \mathrm{div}(\vec{v}_\mathrm{v} c_\mathrm{v} - D_\mathrm{v} \mathrm{grad} c_\mathrm{v}) + W(t), \tag{5}$$

where $W(t)$ is the rate of a sorbate transition into a motionless state in the bulk of the body.

In terms of D_v, $\vec{v}_\mathrm{v}$, c_v quantities, we have

$$\sum_j \lambda_j q_{\mathrm{s}j} = \lim_{r \to 0} \oint_S \left(v_\mathrm{v} c_\mathrm{v} - D_\mathrm{v} \frac{\partial c_\mathrm{v}}{\partial r} \right) \mathrm{d}S, \tag{6}$$

where r stands for the distance from the near-surface layer to the point where the sorbate concentration is equal to c_v, v_v is the normal component for the velocity of a surface shift to the centre of the body over the area $\mathrm{d}S$.

Quantities included in Eqns (1)–(6) are functions of medium properties $\{y_i\}$, from which the following are usually defined:

$$\{y_i\} = T, c_i, \vec{v}_\mathrm{L}, H_i, \rho_\mathrm{L}, \mu_\mathrm{L} ,$$

where c_i is the concentration of the system components in the medium, $\vec{v}_\mathrm{L}$ is the medium velocity, H_i is the field strength for an external field, ρ_L and μ_L are the medium density and viscosity, respectively.

Equations (1)–(6) are applied in a simplified form. For example, one assumes that $D_{ij} = 0$ (considering sorption as a purely determinate process) and $\vec{v}_\mathrm{v} = 0$. If one takes into account the fluctuations of bodies' properties, then one assumes that $D_{ij} = \mathrm{const}$, and changes in state parameters $\{x_i\}$ are independent of each other.[30–32] This makes the solution easier, but excludes 'cross effects' reflecting the mutual influence of the body's state parameters and the medium's ones[33,34] from the consideration. The cross effects are indirectly taken into account by the introduction of functions $G_i(x_i, y_i)$ and $D_{ij}(x_i, y_i)$ reflecting all the elementary processes.

III. Sorption gas dynamics and hydrodynamics

Velocities $\vec{v}_k$ and $\vec{v}_\mathrm{L}$ determine the bodies' positions in the system. The sorption systems are heterogeneous as a rule, therefore, the position of a body is its most important state parameter.

1. Motion of an individual body in the flow of the medium

Any component of the instantaneous velocity of a body's movement can be represented as a sum of the velocities of the ordered motion $G_i = v_{ki}$ and the random fluctuations characterised by coefficient $D_{ij} = D_{ki}$, *i.e.*

$$\frac{\mathrm{d}Z_i}{\mathrm{d}t} = v_{ki} + D_{ki} \xi_{ki}(t), \tag{7}$$

where Z_i is the coordinate of the gravity centre of the body, $\xi_{ki}(t)$ is a random function of time,

$$D_{ki} = D_\mathrm{B} + v_{ki} p_{ki} ,$$

v_{ki} is a component of the velocity $\vec{v}_k$, averaged over time, D_B is the diffusion constant when $v_{ki} \to 0$, and p_{ki} is the characteristic scale for fluctuations of the body's position.

Velocity v_{ki} is formed from the velocities of the body sedimentation in the field of terrestrial gravity, the approach of the bodies under the action of molecular interaction forces, the bodies' shifts in electric and magnetic fields, the thermo- and diffusiophoresis, the drift caused by the flow of medium and the chemoreactive movement. These kinds of motion are investigated with regard the sorbing bodies of simple form with little internal porosity.[35–38] The movement of the bodies of complex forms has not been adequately studied.

Quantity D_B is determined by the Brownian motion. Functions $\xi_{ki}(t)$ and $p_{ki}(x_i, y_i)$ have different shapes. Theoretical approaches to their determination have been developed for the movement of particles in homogeneous suspensions.[38–41]

The experiment has repeatedly been confirming the propriety of using correlation (7). As a result of the observations of trajectories of particles with dimensions of 1–5 μm in a liquid medium, it was established in recent time that the motion of the particles is really the sum of the ordered sedimentation in the field of terrestrial gravity and the random fluctuations characterised by coefficient D_B invariable with time.[42,43]

2. Liquid flow near the surface of a body

The motion of a liquid near the surface of a solid determines in many respects the mass transfer to the surface of the solid.[35, 42–46] The motion of a liquid whose molecules' interaction with each other and with molecules of the body is described by the Lennard–Jones potential, has been calculated by the molecular dynamics method [47, 48]

$$v(r') = 4\varepsilon_i\left[\left(\frac{\sigma_i}{r'}\right)^{12} - \left(\frac{\sigma_i}{r'}\right)^{6} - \left(\frac{\sigma_i}{r'_{0i}}\right)^{12} + \left(\frac{\sigma_i}{r'_{0i}}\right)^{6}\right], \qquad (8)$$

where r' is the distance between the gravity centres of the molecules, ε_i, σ_i are correspondingly the energy parameter and the dimension parameters of the potential of the interaction of molecules of the liquid with each other ($i = 1$) and with molecules of the solid ($i = 2$), r'_{0i} is the boundary of the potential action area.

It was assumed in calculations that the body's surface is molecular smooth, and the molecules of the liquid move chaotically with a resulting shift along the direction of the stationary flow.

The calculations showed that in a broad interval of flow velocities, when $\varepsilon_2/\varepsilon_1 > 0.6$ and $\sigma_1 = \sigma_2$, the liquid moves along the surface so as the liquid's molecules in the layer of width σ practically do not move along the flow, and so this layer is motionless. The molecules which are more remote from the body surface move in accordance with the velocity gradient of the shear flow. Provided that $\varepsilon_2/\varepsilon_1 \leqslant 0.6$ and $\sigma_2 < \sigma_1$, a jump in the flow velocity takes place at a distance σ from the surface, in other words, the liquid 'slides' over the body's surface. This result means that numerous considerations of the near-surface motion of the liquid that do not take into account the slide motion and the existance of a 'motionless' layer need refinement.

When motion velocity increases, 'vortexs' are produced near the surface, which, multiplying, form wave structures disintegrating into chaotic vortexs in velocity flows *l*.[49] The most important peculiarity of the liquid's motion relative to a body is the anisotropy of motion velocity that leads to an unequal accessibility of different surface areas to the sorbate.[35, 50, 51] Figure 2 illustrates the results of the calculations of velocities of medium motion near a body of size d at different flow velocities $\vec{v}_L$.[52] In this case, there are several critical values of the Reynolds numbers

$$\mathrm{Re} = \frac{1.6d\,|\,\vec{v}_L\,|}{\mu_L},$$

changing the character of the velocity distribution of medium motion near them. If $\mathrm{Re} < 0.1$, the flux flows around a body without producing vortexes; a stationary 'rear' vortex is produced near each body in the interval of $0.1 < \mathrm{Re} < 100$; provided that $\mathrm{Re} > 100$, vortexes break periodically away from the body. [An analogous vortex forming occurs for a body being in an ascending current (the Karman track) and for other motion regimes.[53]]

Vortexes magnify anisotropy of the sorbate concentration field around the body and, therefore, increase unequal accessibility of its surface areas. If a body is fixed, its surface is unequally accessible at any Re values; if not, the difference in the area accessibility is substantial upon the laminar medium motion. In the latter case, the body orients in the flow in such a way that the medium makes a minimum resistance to the motion. The body retains such orientation (if we neglect re-orientation shifts caused by the rotary diffusion).[54] Thereby, the body retains unequal accessibility of its surface. It chaotically migrates and rotates in a turbulent flow so that its surface becomes equally accessible on average.

The concept of accessibility of different surface areas of bodies is fundamental to describe the external-diffusion regime of sorption. The consideration of this regime requires the determination of velocities of bodies' motion and medium flows around the bodies with high accuracy.

3. Chemoreactive movement

Chemoreactive movement is added to the common forms of the body's motion if the surface of a body is sorptively heterogeneous, in other words, if there are active sites distributed irregularly over the surface.[55–60] Such a movement was discovered, for example, for sorbing water vapour on Al_2O_3 grains. The bodies' movement was investigated in a release reactor of which a scheme is shown in Fig. 3. Sorbent grains are introduced into section *1* for sorbent preparation, then they are blown in pre-reactor *2*. A portion of the grains gets over channel *3* into adsorber *4*, where they fall freely down in a sorbate gas. Flying through the adsorber, the grains deflect from the vertical trajectory if their velocity has a horizontal component.

The bodies were of size $d = 30 \pm 5$ microns and represented agglomerates of microcrystals. They were one by one introduced into the reactor filled with a mixture of water vapour and air. The agglomerates fell freely down reaching the bottom in several seconds. After that, distribution functions of agglomerates were determined with respect to motion velocities in the horizontal direction over the falling time. The measurements demonstrated that the distribution of the bodies over the velocities was the same as in the case of a dry sorbent in dry air if the bodies were brought to an equilibrium with water vapour before introduction into the reactor. If the bodies contained a non-equilibrium amount of water and fell in a humid medium, the velocity of their motion was considerably higher (Fig. 4). There were areas with a high rate of adsorption of water on the bodies' surfaces, which was caused by the capillary condensation started to proceed there. These sites adsorbed water vapour at the same rate as the other sites did, but desorbed it to a lesser degree, since a portion of the adsorbed water

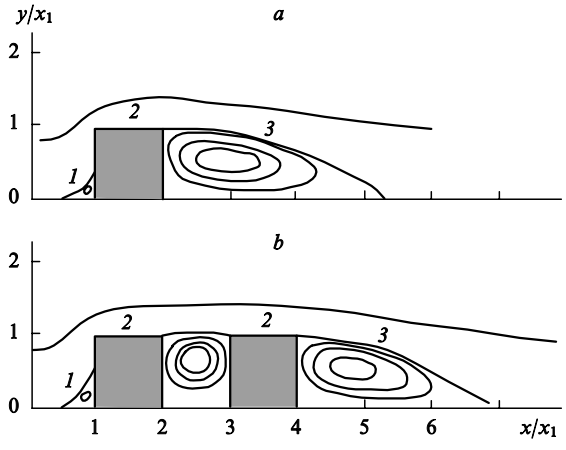


Figure 2. Results of calculations for solution streams flowing around a single grain of the sorbent (*a*) or a group of grains fixed on the support (*b*) by numerical solution of the Navier–Stokes equation for $\mathrm{Re} = 10$.[52] (*1*) Frontal vortex, (*2*) grain, (*3*) rear vortex; y and x are the spatial coordinates, x_1 is the size of the body.

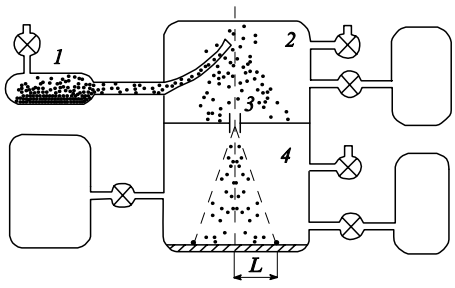


Figure 3. Scheme of the release reactor.[55]

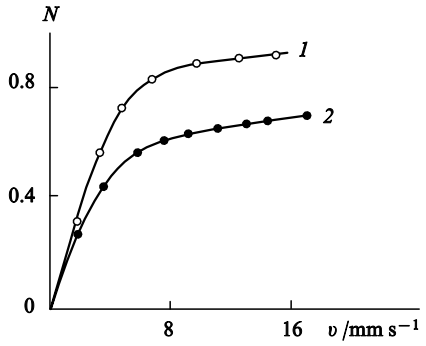


Figure 4. Distribution of Al_2O_3 grains according to the movement velocities in water vapour (from Refs 55 and 56).
N is the fraction of grains that move in the horizontal direction at a rate lower than υ. Partial vapour pressure, kPa: (*1*) 2.0, (*2*) 3.0.

was removed as a condensate. As a result, the momentum flux of recoil from desorbed water molecules over such sites was less than the momentum flux over the other areas, and this caused the bodies' movement.

4. Motion in an ensemble of sorbing bodies

The motion of bodies in an ensemble of them is affected by the superposition of fields of velocities in the environment around the bodies and by direct contacts of different bodies. Interaction in the vortex medium furthers the approach and coordinated movement of bodies. For instance, if a homogeneous suspension of glass balls of diameter ~ 50 μm in a water–glycerol medium ($\mu_L = 5 \times 10^{-2}$ Pa s, $\varepsilon = 0.5-0.9$) is poured into an empty vessel, the coordinated motion of aggregates of hundreds of balls will take place in different directions against a background of slow sedimentation after the cessation of the motion caused by pouring.[61,62] The bodies can stick together, undergo a plastic deformation and even be destroyed if the velocity of their approach is great.[63–65]

The dimensions and shapes of the aggregates produced in ensembles of moving bodies depend on the flow velocity, the medium composition, the sizes, shapes, and relief of the bodies' surfaces. Any suspension flow is characterised by its own distribution function of aggregates over dimension and shape parameters. This function shifts to smaller dimensions of the aggregates on increasing the flow velocity and decreasing the concentration of particles in the flow. In contrast, the function shifts to large aggregates on increasing the concentration of the particles, and the aggregates can change their shapes from fractal ones to colloid crystals depending on the movement regime. All these results follow from the observations of moving suspensions with an optical or atomic force microscope *in situ*, and also from the observations of 'preserved' suspensions with an electronic microscope (see Refs 66–69, for example).

The force of resistance to the flow changes upon aggregation of particles and, therefore, so does the regime of their motion. One can make conclusions about the scale of such changes from data on effective viscosities μ_{ef} of sorbent–medium suspensions. Thus, the effective viscosity of a suspension of polystyrene spherical particles with sizes of $d = 70$ nm in an aqueous solution of gelatin (1 mass %) with particles' concentration $q_0 = 2.7 \times 10^{20}$ m^{-3} and shearing strain $p_s = 0.1$ Pa in the shearing strain of the suspension is 500 times greater than in the absence of the particles.[67] The dependence $\mu_{ef}(p_s)$ shows that the suspension is a single 'loose' aggregate which moves as a whole at the indicated concentration q_0 and $p_s < 0.3$ Pa. This aggregate dissociates into smaller fragments upon increasing p_s, and most particles move at $p_s > 30$ Pa almost independently from each other. The value of μ_{ef} keeps at the level of 10^8 Pa s in the shearing flow of SiO_2 particles in an ester ($T = 300$ K, $d = 14$ nm, $q_0 = 1.7 \times 10^{20}$ m^{-3}) at $p_s < 10$ Pa, while at $p_s \to 10$ Pa it undergoes a jump until ~ 0.1 Pa s, at which it stays in the interval of $p_s = 10-100$ Pa (see Refs 67 and 68). This jump indicates a mechanically stimulated rearrangement of the suspension, resembling a first-order phase transition. The accessibility of the surface of bodies to a sorbate on such a rearrangement changes with a jump too.

The possibility of aggregation of bodies in an ensemble depends on the composition of the adsorption layer. The sorption can both accelerate and suppress the aggregation.[67,70] This dependence becomes of particular significance in the presence of a sorbate whose molecules can adsorb on two close particles at once, producing 'molecular bridges' between them.[70] Such sorbates are employed to control the aggregation.

These facts highlight the change in the velocity of a stationary flow of a suspension due to a change in its effective viscosity caused by the adsorption-induced acceleration or the deceleration of aggregation. It seems that such 'adsorption-dependent destabilisation' of a flow is more intensive for concentrated suspensions of small particles.

Dissipative structures reflecting cooperative interactions of bodies arise in moving suspensions.[71–73] For example, if a mixture of glass balls of diameter of ~ 0.27 mm and sucrose crystals of size ~ 0.80 mm is discharged to an empty vessel with the form of a rectangular parallelepiped with dimensions of $5 \times 200 \times 300$ mm along one of the long edges, a texture is formed of inclined layers of the glass balls alternating with layers of the sucrose crystals. The widths of the layers and their angles of inclination relative to the bottom of the vessel will depend on the form and subtle peculiarities of the surface relief of sucrose crystals.[73] Separation of the initial mixture of particles with the formation of a spatially dissipative structure occurs at a comparatively low input of mechanical energy in the system. The grounds of such separation could be explained after a considerable specification of conditions of particles' contacts in the flow.

The examples above indicate that the variety of hydrodynamic phenomena accompanying sorption increases nonlinearly with an increasing number of bodies in the system. Each of these phenomena can influence or depend on sorption under certain conditions as it takes place for the adsorption destabilisation of a suspension flow. The phenomena in question can be described by the motion equation of solids in the flow and by Navier–Stokes equation by detailed accounting of the forces affecting the sorbing bodies.

5. Prediction possibilities

A complete *a priori* prediction of the hydrodynamic behaviour of a system of sorbing bodies in the medium is still impossible in the general case (although it can be made with an acceptable accuracy under some sorption conditions[74,75]). To make the complete prediction, one needs to have methods to calculate the parameters of Eqns (5)–(7) based on data on molecular motion as well as methods to solve the equations specified by accounting for the variety of hydrodynamic behaviour of an ensemble of bodies in the medium. However, no universal methods for such a calculation exist so far.

The methods of molecular dynamics allow prediction of properties of flows of bodies based on data on potentials of interatomic interactions. However, specification of the kind of interatomic potentials is necessary to apply these methods widely to describe flows of particles and the medium. Observations of adatoms of gold in the contact area of two crystals in a tunelling microscope has shown that atoms' behaviour cannot be explained by using the Lennard–Jones potential [see Eqn (8) or other known potentials].[76,77] Therefore, the contemporary conceptions of the potentials of interatomic interactions are approximate. Nevertheless, this does not exclude successful semi-empirical prediction of motion of particles and a medium in narrow intervals of sorption conditions, for instance, upon sedimentation in reactors of different shapes[78,79] or in shearing flows of concentrated suspensions.[67] However, such calculations require expenses which are commensurable to those for experimental

work. Hence, one has to restrict oneself to the estimations obtained using various models, *e.g.* the cell model,[80,81] if the geometry of a system is complex.

IV. Adsorption kinetics

It is convenient to present the velocity of sorption in the form

$$\frac{\mathrm{d}M}{\mathrm{d}t} = \sum_j \int_{-\infty}^{+\infty} (\omega_j a S c - v_j q_{sj}) \varphi \mathrm{d}x_i , \tag{9}$$

where

$$v_j = \frac{kT}{h} \chi_j \exp\left(-\frac{E_j \beta_j}{kT}\right). \tag{10}$$

Here k and h are the Boltzmann and Planck's constants, respectively, χ_j is the frequency factor, E_j is the detachment energy of a sorbate molecule from an adsorption centre, β_j is the ratio of an excess of the activation energy of desorption to the detachment energy. Correlations (9) and (10) demonstrate that it is necessary to take adsorption centres of all sorts into account, although adsorption centres do not always differ by values of v_j as sharply as, for example, for the sorption of antimony by the faces (001) of a GaAs crystal. (Three forms of the antimony are discovered in this case with $E_j\beta_j$ values differing by almost 1 eV.[82]) Nevertheless, three species of adsorbed molecules were also found upon an exploration[83] of the sorption of a 5,10,15,20-tetrakis[3,5-di-*tert*-butylphenyl]porphyrin complex of copper onto the surface of a gold crystal at 420 K from a gaseous environment by scanning tunelling microscopy *in situ*. The central porphyrin part of the molecule was not observable in the microscope against a background of the substrate while the *tert*-butyl groups manifested themselves as bright spots. The conformations of molecules of all species could be judged from the location and the intensity of the spots. The kinetics of mutual conversions of the forms could be deduced from the change in the number of the images. It turned out that one form localised on the steps, the second one on the breaks of rectangular terraces, the third on the terraces. The *tert*-butylphenyl groups of the second from localised at an angle of 65° to the plane of the porphyrin part of the molecule, and those of the third form at an angle of 45°. Heating the substrate till 520 K over 12 min led to the disappearance of the second form from the substrate without any observable desorption of the third form. In this case, the energy of gold atoms on the breaks of the terraces and far from them differed by a few millielectronvolts only.[84] However, such a difference causes a noticeably distinct behaviour of the second and the third forms of the mentioned molecules.

Therefore, an estimation of the role of the centres of all sorts is necessary in any case. Yet it is hard to measure the values of $\omega_j = \omega_j(\vec{v}_L, D)$ for the centres of all sorts, and an *a priori* calculation of these quantities is only possible after a specification of the form of interaction potential.

Specification can be achieved by a search for quantities which are independent of the form of the potential. Such invariants will restrict the possibility of changes in the potential. One of these invariants can be connected with the diffusion constant, D, of the sorbate in the medium and, hence, with ω_j.[85,86] Indeed, D along with self-diffusion constant D_s characterises thermal motion of molecules

$$D = \gamma(y_i) D_s ,$$

where $\gamma(y_i)$ is a function that does not depend on D_s explicitly. The coefficient D_s calculated by the method of molecular dynamics for 1.6×10^4 atoms at different forms of a potential of molecules' interactions can be presented in the following form for a dense monoatomic liquid:[85,86]

$$D_s = \frac{B \exp(S_0)}{g_0 r_0^4} ,$$

where B is a coefficient that does not depend on the form of a potential, S_0 is the difference between the entropy of a liquid and a gas of the same composition, and g_0 is the value of radial distribution function of liquid's atoms at the point of the first maximum of the distribution for which the interatomic distance is equal to r_0.

This correlation indicates the possibility of searching a correlation of coefficient D and, therefore, frequency ω_j with the potential of the interaction of medium molecules through the invariants resembling coefficient B.

Functions $q_{sj} = q_{sj}(y_i, t)$ and $\chi_j = \chi_j(y_i, t)$ reflect the kinetics of all the elementary surface processes leading to sorbate migration between centres of different sorts, chemical transformations of adsorbed molecules and a sorption change of the state of the surface. Rates of elementary processes usually differ significantly, and so functions q_{sj} change with time stepwise. Some steps can be slow in this case.

For instance, a three-step process proceeds during adsorption of oct-1-ene by crystals of aluminosilicate zeolite H-ZSM-5 at 290 K over $10^2 - 2 \times 10^5$ s. A transfer of the oct-1-ene into the adlayer occurs at the first step, the adsorbed oct-1-ene reacts with hydroxy groups of the zeolite, producing carbenium ions at the second step, and at the third step, the carbenium ions undergo a rearrangement

$$CH_2{=}CH(CH_2)_5CH_3 \longrightarrow CH_3C^+H(CH_2)_5CH_3 \longrightarrow$$
$$\longrightarrow CH_3(CH_2)_2C^+H(CH_2)_3CH_3 .$$

These steps were identified by observing ^{13}C NMR spectra *in situ* (in magnetic fields up to 18 T with the sample spinning at a 2–5 kHz frequency at a magic angle, using cross-polarisation). It follows from the intensities of lines in the NMR spectrum at 14.3 ppm which correspond to the terminal groups $^{13}CH_3$ and are given in the study[87] that the third step is determined by the relation

$$\left(\frac{q_{sj}}{q_{0sj}}\right) = 0.31 + 0.69 \exp\left(-\sqrt{\omega_q t}\right),$$

where q_{0sj} and q_{sj} stand for the amount of cabenium ions in the adlayer at the beginning of the third step and at moment t, correspondingly, $\omega_q = 4.5 \times 10^{-5}$ s^{-1} stands for the characteristic frequency of rearrangements.

The three-step nature of the process in question can be explained by the fact that centres of three sorts exist on the surface of the zeolite that differ in composition and mutual location of atoms. The centres of the first sort have a much larger value of ω_j than the other centres, thus, sorption mainly starts with transition of molecules onto these centres. At the second step, the molecules move to the centres of the second sort, which have hydroxy groups reacting with the oct-1-ene. The carbenium ions rearrange in the slow third step, remaining on the centres of the first sort or moving to the centres of the third sort.

The surface processes are so varied that one has to consider their pecularities at a qualitative level. This has been done below using the sorption by single crystals as an illustration and the level of details of description achieved to date is also presented.

1. Accommodation of sorbate molecules

Different sorbing centres have different probabilities of accommodation, so that

$$\omega_j = \alpha_j \frac{S_j}{S} \xi_j , \tag{11}$$

where α_j is the local factor of accommodation at centres of the jth sort, S_j is the area of the body's surface containing these centres, S is the total area of the body's surface, ξ_j is the probability that a sorbate molecule contacts the surface in a unit time as a result of transition of molecules from a gas or a liquid.

A sorbate molecule is promoted to an excited state upon collision with the surface.[88] The promotion proceeds in a period τ_0

in the order of 10 fs. It is accompanied by deformation of electron density and activation of vibrational motion of both the molecule and the body in the contact point and sometimes by a configuration change of the molecule.[89,90] Then the relaxation of the electronic excitement of the molecule proceeds in 10–100 fs, and the relaxation of the vibrations in $\tau_s = 1-10$ ps. Vibrations of atoms of a body can accidentally synchronise giving a molecule sufficient momentum to break it away from the surface. Molecules dwell at the surface of a body for different time τ owing to the accidental character of the synchronisation process and

$$\alpha_j = 1 - \int_0^{\tau_s} \bar{\varphi}_j(\tau)\mathrm{d}\tau,$$

where $\bar{\varphi}_j(\tau)$ is the density of the distribution of molecules occupying centres of the jth sort over τ.

Function $\bar{\varphi}_j(\tau)$ implicitly characterises the dependence of τ on molecule's velocity and orientation at the beginning of the contact. An elastic reflection of the molecules from the surface is observed and $\alpha_j \to 0$, if all the molecules have the velocity and the orientation at which function $\bar{\varphi}_j(\tau)$ is localised in the region of $\tau \approx \tau_0 < \tau_s$. If most molecules have $\tau \approx \tau_s$, then almost complete accommodation takes place and $\alpha_j \to 1$. Coefficient α_j can be determined for the adsorption of a rarefied gas on a homogeneous surface with high accuracy based on the data on a molecular beam reflected from a body. When considering sorption from a liquid medium, one has to content oneself with rough values of α_j. It is of some use to determine the function $\bar{\varphi}_j(\tau)$ characterising the first step of sorption by methods of femtochemistry.[91]

2. Migration on the surface

The sorbate molecules fixed on the surface jump from one adsorbing centre to another. The frequency of the long distance jumps which are accompanied by re-orientation of the molecules increases with increasing temperature. It is established by observation with the tunelling microscope that the jumps of acetylene molecules on faces (111) of a lead crystal occur with a change of orientation at $T > 70$ K, and all six orientations are realised.[92]

Superficial mobility of molecules depends on their configuration.[93,94] Molecules can move from one centre to another due to conformational changes. Increasing the number and the strength of bonds of a molecule with an adsorbing centre weakens the tendency to such changes. This results, for instance, in sorption of a dendritic DNA on a graphite crystal, where DNA molecules can bind to the crystal through numerous guanidine bridges.[95] In the case of adsorption of 1,4-bis[β-(2-pyridyl)vinyl]benzene on face (100) of a silicon crystal, the sorbate molecules that are sufficiently strongly bound to silicon atoms migrate with low velocity so that their motion cannot be detected even on a sufficiently long observation in a tunnelling microscope. Molecules of this sorbate exist as four conformational species on the surface, however, motion with an observable velocity is not a specific feature for any of them. The migration proceeds much faster if it occurs at the face (100) of silicon where every near-surface silicon atom is blocked by a hydrogen atom.[96]

Cooperative effects reveal themselves upon increasing the fraction θ_j of the surface occupied by the sorbate. The mobility gets smaller with the rise of θ_j if the attraction dominates in lateral interaction of sorbate molecules. The mobility increases first and then diminishes if the repulsion dominates.[97]

Thus, the detailed description of molecules' motion over the surface requires that possible changes in their configuration upon jumping from one centre to another and their collective motions be taken into account.

Migration is quantitatively characterised by quantity D_j

$$D_j = \frac{kT}{h}\sum_i \chi_{ji} \exp\left[-\frac{(E_j - E_i)\beta_{ji}}{kT}\right], \qquad (12)$$

where χ_{ji} is the frequency function for the transition of a molecule from the jth sorbing centre to the ith one, E_j and E_i are the energies of interaction of the molecule with the crystal on the jth and the ith sorbing centres, respectively, and β_{ji} is the correction function reflecting cooperative effects of activation.

It is assumed while calculating D_j that the shifts to the nearest vacant sorbing centre dominate among jumps of each molecule, and $E_j = n_j E_{j2}$ and $E_i = n_i E_{i2}$, where n_j and n_i are the number of the crystal's atoms in the nearest neighbourhood of the molecules on the jth and the ith sorbing centres, correspondingly, E_{j2} and E_{i2} are the average energies of the pairwise interaction of the molecules with the nearest neighbours.[98] It is also taken that $\beta_{ji} = 1$ and $\chi_{ji} = \text{const}$.[99] The calculation of E_j and χ_{ji} is attempted based on 'the first principles', but it is a success for the simple sorbates only.[100] It was possible to calculate these quantities for the migration of H_2 on the face (001) of a nickel crystal with a 10% discrepancy with the experimental data. However, one failed to explain the absence of an observable isotope effect in the superficial diffusion of hydrogen at low temperatures.[101]

If the energy of adsorption is sufficiently high, the near-surface layers of a crystal get disordered, molecules come to the surface from these layers, which leads to acceleration of superficial migration.[102] One can get an idea of the scale of such acceleration based on the data on superficial migration of atoms during the adsorption of hydrogen and benzene on the crystals of iron and nickel. For instance, the hydrogenation of the adsorbed benzene is accompanied by a 10^4-10^5-fold increase in the intensity of the superficial migration of iron and nickel atoms.

3. Formation of superficial clusters

Adsorbed molecules can join into clusters that grow up to the size of a whole face for large θ_φ.[103–105] The rate of the formation of the clusters increases quickly if the concentration of the sorbate in the medium achieves a critical value, which is substantially different in the case of the weak and strong bonds of the sorbate molecules with the crystal and with each other.

For example, the clusters can be observed in the sorption of hexadecyltrimethylammonium bromide by the surface of clinoptilolite crystals only at the concentration for which $\theta_j \to 0.25$. In the case of a lesser extent of the adlayer filling, the sorbate exists on the surface as separate molecules, which are observed as oblong knobs of 0.4 nm height in the atomic force microscope.[106] The heights of some knobs double at $\theta_j \to 0.25$, which can be interpreted as the formation of clusters.

The probability of their formation and growing up depends on the extent of conformity between the structures of the sorbate molecules and the near-surface monolayer of the body. In the case of the adsorption of simple molecules, this probability is higher for the sorbates whose crystal lattices have planes with an arrangement of atoms close to that in the near-surface monolayer of the body. The formation of clusters is facilitated in the case of the adsorption of complex molecules at certain configuration of the sorbate molecules.[107,108] This is confirmed by the observation of the adsorption of oligosaccharide polymers on the face (100) of a graphite crystal from an aqueous solution in atomic force microscopy *in situ*.[109,110] The molecule of the polymer, representing a polyvinylamide backbone with numerous dextran and hexanoyl branches, adsorbs so that its backbone is stretched along the surface. The hexanoyl chains contact the carbon atoms of graphite, and the dextran ones are directed outwards.

The orientation of molecules on the surface of a body depends on the ratio between the numbers of the hexanoyl chains and the dextran ones (q_m). The majority of molecules orients along one of two crystallographic directions of the crystal lattice at $q_m = 1/5$. In the case of a sufficiently high concentration of oligosaccharides in solution, a number of molecules successively attach to each molecule fixed on a free surface area, producing a two-dimensional cluster. The clusters spread out over the surface until they merge into a continuous monolayer of 0.7–1.2 nm width. The

orientation of molecules is arbitrary, and no two-dimensional clusters form at $q_m = 1$.

The two-dimensional clusters, enlarging, can turn into three-dimensional formations. For example, the clusters turn with time into epitaxial incrustations [111] upon adsorption of cadmium arachidonate $Cd[CH_3(CH_2)_{12}CO_2]_2$ from the vapour on the face (001) of a crystal of KCl.

Clusters can change their compositions and structures,[112, 113] and successive monolayers of an adsorbed substance can be deposited over the produced ones [114] at certain values of θ_j. Such a phenomenon was *in situ* observed in tunnelling and atomic force microscopies. The conclusions from the observations were confirmed by calculations using the methods of molecular dynamics.[115, 116] In particular, it was established that multi-layer crystals arise, which can have different structures varying in the mutual orientation of molecules, upon the adsorption of H_2O on the face (100) of a crystal of MgO at $\theta_j \to 1$. One of the orientations dominates at $T < 200$ K, and the other one at higher temperatures.[116] Structural transitions occur in the monolayer of lead on the face (100) of a copper crystal: the first one at $\theta_j \to 0.38$, the second, at $\theta_j \to 0.5$, and the third, at $\theta_j \to 0.6$. In this case, each of the structures undergoes 'two-dimensional' fusion [117] on heating. The structural rearrangement of monolayers is accompanied by significant acceleration of adsorption over the adsorption of dodecanethiol and butanethiol on the face (111) of a gold crystal at 298 K.[118]

4. Two-dimensional solid solutions

Adsorbed atoms can be incorporated into near-surface interstices or occupy vacancies in the near-surface monolayer of crystal atoms, *i.e.* form two-dimensional interstitial solid solutions or substitutional ones.[27] This could be observed directly in the case of the sorption of InAs from its vapour on the faces (100) of a crystal of InP by atomic force microscopy.[119] The sorption of vanadium oxide on the face (001) of a crystal of TiO_2 was detected by emergence of an additional component in the band $V2P_{3/2}$ of the photoelectronic spectrum at 623 K. (This band is caused by the transition of a vanadium atom into the lattice of TiO_2.[120]) It was possible not only to detect solid solutions, but also to determine their structures by means of X-ray diffraction analysis while studying the sorption of bismuth from its vapour on the face (001) of a copper crystal.[121] It turned out that the bismuth atoms substitute the copper ones at small θ_j chaotically, and each bismuth atom transferred into the near-surface monolayer is shifted towards the vapour with respect to the copper atoms by 0.06 nm. The sorbed atoms of bismuth form a two-dimensional structure of the type $C(2 \times 2)$ at $\theta_j \to 0.35$, their radius is equal to 0.163 nm, which is considerably smaller than that of a bismuth atom in the bulk of its crystal (0.182 nm). Thus, the structure of two-dimensional solutions can change with increasing θ_j .

The mobility of molecules in the near-surface monolayer of the crystal is far lower than that in the adlayer.[27, 122] Hence, the sorbate transfers to the adlayer at the first stage rather rapidly and forms a two-dimensional solid solution at the second stage slowly. The third stage arises after large periods of sorption, which consists of the transfer of the sorbate to the bulk of the sorbent.

5. Change in the properties of a sorbing body

All properties $\{x_i\}$ of the body change during sorption, and the scale of these changes is nonlinearly connected with the body's state and can be great in a narrow interval of sorption conditions. For example, a change in velocity of the body's motion under the influence of sorption becomes detectable if the body can freely move in the sorbed gas for a long time and the sorption is localised on a portion of the body's surface.[60] The change in temperature is considerable if the medium is characterised by the low thermal conductivity and the great heat of sorption. Sorptive changes in electroconductivity, magnetic, thermophysical and optical properties can turn out to be substantial for porous bodies, which is employed in sensor devices.[123]

There can exist both positive and negative feedback between the sorption and the properties of a sorbing body. For instance, the feedback of the quantity of an adsorbed substance q with the velocity of chemoreactive movement $\vec{v}_k$ is positive since increasing $\vec{v}_k$ leads to growth in ω_j, and growth in ω_j facilitates the acceleration of the movement.[55] The feedback between q and T is usually negative since increasing the temperature leads to growth in the rate of desorption dominating over increasing α_j.[124]

The character of the feedback between q and parameters $\{x_i\}$ is of great significance in the development of sensors.[123, 124]

6. The possibilities of computational experiment

The direct observations of the motion of adsorbed molecules encouraged the application of the methods of molecular dynamics and Monte Carlo for the simulation of elementary processes of sorption under the quantum-chemical interpretation of interatomic interactions or the usage of atom-atomic potentials of the type (8). Simultaneously, the computational methods of chemical kinetics based on differential equations of the type (4) become more widely applied in investigating the sorption processes. As a result, separate elementary processes of sorption could approximately be described for some of the simplest molecules, based on the 'first principles'. It has become clear at the same time that some elementary processes can *a priori* be excluded from the consideration only in the case if we limit ourselves to a narrow set of conditions when modelling sorption. A complete kinetic model of sorption which is applicable for a broad set of conditions must take into account all the details of elementary superficial processes. However, the complexity of the model does not allow making computational experiments *in corpore*.

V. Sorbate migration into the bulk of a body

1. Diffusion into the bulk of crystals

Sorbate migration into the bulk of a body is usually characterised by coefficient D_v reflecting all elementary processes leading to the translation movement of sorbate molecules (ions).[125] Function $W(t)$ can be excluded from Eqn (5) while the sorption at the crystals is described. Coefficient D_v can be considered as a tensor taking into account the anisotropy of crystals' properties in this case. To solve Eqn (5), one should reflect the polyhedral form of crystals and the possibility of their formation with different faces in edge conditions. One also has to take into consideration the fact that the sorbent crystals have 'biographical' structural defects affecting D_v. Besides, the crystals acquire new defects during sorption that are distributed irregularly in their bulk. For example, the defects are localised at the periphery of each crystal for the crystals of K_2SO_4 or NaCl being in an intensely agitated aqueous solution. In this case, the sorbate accumulates significantly faster at the defect areas than at the other ones.[63, 64] The values in the order of D_v of 10^{-25} m^2 s^{-1} are a characteristic of the perfect crystals of $BaSO_4$ with an ion-covalent bond of atoms at 300 K; for the sorption of $SrSO_4$, in particular, by the crystals of $BaSO_4$ with high defectiveness of growing, $D_v = 10^{-16}$ m^2 s^{-1} (see Refs 126 and 127).

The molecules of sodium ethylenediaminetetraacetate and trinitrophenol diffuse into interlayer spaces of the crystals of hydrotalcite $Mg_3[Al(OH)_8][CO_3]_{0.5}$, which have a lamellar structure with the ion-covalent bond of atoms within the layers and the van der Waals one between the layers, with the diffusion constant $D_v \approx 10^{-16}$ m^2 s^{-1} at 300 K.[128]

Diffusion rate is especially high for sorption by the organic analogues of zeolites. The crystals of organic zeolites consist of groups of covalently bound atoms producing ring-shaped formations (blocks).[129] Closing each other up, the blocks produce channels whose width can reach several nanometres. Atoms of the crystal occupy not less than half volume of a channel, the rest space is occupied by molecular pores. Sorbate molecules can migrate along the channels with high values of D_v, which, for example, takes place in the crystals of $C_{72}H_{98}N_{12}O_{40}Zn_3$ with a

trigonal lattice (the diameter of a channel ~ 1 nm, the channels orient along axis c).[130] The channels accounting for 47% of the crystals' volume are filled with water molecules in an aqueous medium. Migration, for instance, of Na^+ ions over the channels proceeds at 300 K with the diffusion constant $D_v \approx 10^{-14}$ m^2 s^{-1}, which was estimated from the data on the rate of ion exchange between the crystals and the solution.

One can judge elementary acts of sorbate migration in molecular crystals by the results of calculations made by the molecular dynamics method.[131–133] The calculations showed a sharp change in the frequency of jumps of sorbate molecules over the channel and the number of molecules in the channel at small changes of the potential of interactions with atoms of the channel's 'walls'. The motions of sorbate molecules lead to significant fluctuations of the number of the molecules localised per length unit of the channel. The scale of such fluctuations also depends on the potential of interaction of molecules with atoms of the channel's walls. Thus, if a carbon nanotube with a diameter of 0.81 nm and a length of $l = 1.34$ nm is placed in a medium containing 10^3 molecules of H_2O, these molecules get into the nanotube and move inside it. If the interaction potential is of the type (8) and $\varepsilon_i = 0.549$ kJ mol^{-1} and $\sigma_i = 0.328$ nm, the molecules of H_2O, having passed through the channel, get out of the tube with the frequency $\omega_\varepsilon = 2 \times 10^{10}$ s^{-1} (see Ref. 133), which corresponds to the coefficient D_v of the order $l^2\omega_\varepsilon = 3.6 \times 10^{-8}$ m^2 s^{-1}. Frequency ω_ε proves to be lower by several times if $\varepsilon_i = 0.272$ kJ mol^{-1} and $\sigma_i = 0.341$ nm. In the channel of the nanotube, H_2O molecules form a monomolecular chain of 2–7 molecules arranged with higher order than in the medium. The molecules of the chain approach each other to a distance at which the hydrogen bond forms much more frequently, existing in such a state for $\tau_\varepsilon = 5.6$ ps ($\tau_\varepsilon = 1.0$ ps in water) on average. In addition, the H_2O molecules possess not only the axial mobility but also the radial one (less frequently). In this case, the average number of molecules in a chain varies from 4 to 6 when $\varepsilon_i = 0.549$ kJ mol^{-1} and $\sigma_i = 0.328$ nm, and from 1 to 2 for $\varepsilon_i = 0.272$ kJ mol^{-1} and $\sigma_i = 0.341$ nm. This example demonstrates the possibility of a sufficiently detailed description of the movement of a sorbate in channels when data on interaction potential of atoms are available.

2. Migration into polymeric grains

Coefficient D_v of the polymeric sorbents has as a rule a complex dependence on their structure, values of θ_j, T, composition of the medium and preliminary swelling of the grains, and this dependence is difficult to predict. For example, $D_v = 3.4 \times 10^{-10}$ m^2 s^{-1} at pH = 1.0 and $D_v = 1.65 \times 10^{-10}$ m^2 s^{-1} at pH = 2.0 for the sorption of $CdCl_2$ by grains of formaldehyde resin from an aqueous solution at 300 K.[134] The value of D_v grows with increasing θ_j first, and then diminishes during the sorption of LiCl by a resin containing sulfo groups.[135] Sorbents based on dendrimers and hydrogels have been obtained in recent years. Their coefficient D_v is almost the same as in the medium surrounding a body.[136] Two models are usually employed to describe sorption by polymeric grains.[137, 138] The first model implies that all grains are quasi-homogeneous and isotropic, *i.e.*, characterised by a unique value of D_v when $\vec{v}_v = 0$ and $W(t) = 0$; the second one assumes a grain to be a population of small polymeric globules jointed by rare molecular bridges. In this model, a grain is characterised by the constants of the sorbate diffusion over the interglobule bulk (the channels) and from the interglobule space into the bulk of a globule. In this case, function $W(t)$ is determined as a total diffusion flux through surfaces of all the globules being in a volume unit, into their bulk. Both models reproduce basic features of the process only approximately.

The calculations[30] have shown that if sorbing bodies are homogeneous and have a Gaussian size distribution, then the time $\tau_{0.9}$ for which they capture 90% of an equilibrium quantity of the sorbate, is

$$\tau_{0.9} = \frac{(0.182 + 0.255\sigma_0 - 0.190\sigma_0^2)\overline{l}^{\,2}}{D_v}, \qquad (13)$$

where σ_0 is the ratio of the root-mean-square deviation of distribution of particles' sizes to their average size $\overline{l}$. The deviation varies in the interval from 0 to 0.45.

For the lognormal distribution over sizes, we have

$$\tau_{0.9} = \frac{(0.1943 + 0.057\sigma_0)\overline{l}^{\,2}}{D_v}. \qquad (14)$$

Correlations (13) and (14) characterise reversible sorption (Fig. 5). It follows from these correlations that it takes sufficiently great time to achieve the sorption equilibrium. One has to restrict oneself to the adsorption if it is required to perform the sorption sufficiently rapidly, *i.e.* within the time $t_k \ll t_{0.9}$. At small t_k, the adsorption behaves as a process with a slight deviation from the reversibility, which is related to the transfer of the sorbate into the bulk of grains. Such a deviation is often revealed in practice.[139, 140]

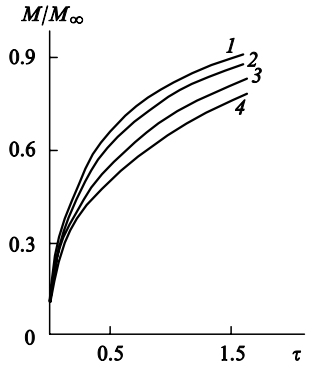


Figure 5. Results of the numerical experiment on sorption by a sorbent with different size distributions of grains.[30]
Normal distribution at $\sigma_0 = 0$ (*1*), 0.1 (*2*), 0.2 (*3*), 0.3 (*4*). $\tau = \pi^2 D_v t/\overline{l}^{\,2}$ is dimensionless time, M_∞ is the equilibrium amount of the sorbate in grains.

3. Sorption by the agglomerates of microparticles

If a body consists of accreted microparticles, coefficient D_v depends on their shape, size, and the character of their packing.[141, 142] The relief of the surface of the particles also affects the value of D_v, which was demonstrated with the use of the molecular dynamics method, employing the diffusion of N_2 and isobutane in a cylindrical space between microparticles of 0.4–1.4 nm size at 200–800 K as an illustration.[143] In addition, the value of D_v can be reduced by infilling the space by the sorbate.

All this suggests that the description of sorption by the agglomerates with the use of coefficient D_v provides little information and shows a necessity to work Eqn (5) out, taking into account the structures of the agglomerates.

Bodies consisting of multiple accrete macroparticles retaining free spaces (macropores) between them are widespread among the agglomerates. In this case, each of the macroparticles is a combination of microparticles divided by the micropores provided that

$$V_k \gg \overline{V}_{k1} \gg \overline{V}_{k2}, \qquad (15)$$

where $\overline{V}_{k1}$ and $\overline{V}_{k2}$ are the average volumes of macro- and microparticles, respectively.

If the state of every particle in an agglomerate is characterised by its size l_i and the volume (V_{pi}) of pores surrounding it, then one can write condition (15) in a continuum approximation

$$c_v = \varepsilon_1 c_{v1} + \int_0^\infty \int_0^\infty m_1 \varphi(l_1, V_{p1}) \mathrm{d}l_1 \mathrm{d}V_{p1}, \quad (16)$$

$$m_1 = \int_{V_{k1}} \left[\varepsilon_2 c_{v2} + \int_0^\infty \int_0^\infty m_2 \varphi(l_2, V_{p2}) \mathrm{d}l_2 \mathrm{d}V_{p2} \right] \mathrm{d}V,$$

where ε_1 is the total volume of macropores in a volume unit of a body, c_{v1} and c_{v2} are the bulk concentrations of the sorbate in macro- and micropores, m_1 and m_2 are the quantities of the sorbate in a macroparticle in state $\{l_1, V_{p1}\}$ and in a microparticle in state $\{l_2, V_{p2}\}$, ε_2 is the porosity of the microparticles, $\varphi(l_1, V_{p1})$ and $\varphi(l_2, V_{p2})$ are the distribution functions of the particles over their states.

Concentrations c_{vi} $(i = 1, 2)$ change during sorption according to a transfer equation, which is analogous with relation (5)

$$\frac{\partial c_{vi}}{\partial t} = \mathrm{div}\,[\varepsilon_i (D_i \,\mathrm{grad}\, c_{vi} - \vec{v}_i c_{v1})] - \int_0^\infty \int_0^\infty \beta_i l_i^2 J_i \varphi(l_i, V_{pi}) \mathrm{d}l_i \mathrm{d}V_{pi}, \quad (17)$$

where D_i is the diffusion constant of the sorbate diffusion into the bulk of pores, $\vec{v}_i$ is the velocity of ordered motion of a liquid or a gas filling the pores, β_i is the shape factor for the particles, J_i is the sorbate flux from the pores through the surface of a particle.

In relations (16) and (17),

$$m_2 = \beta_2 l_2^2 \int_0^t (J_2 + J_{2s}) \mathrm{d}t, \quad (18a)$$

$$J_1 = (\omega_{l_1} c_{v1} - v_{l_1} c_{a1}) a (1 - \varepsilon_2) + D_2 \varepsilon_2 \left(\frac{\partial c_{v2}}{\partial r} \right)_{l_1}, \quad (18b)$$

$$J_2 = (\omega_{l_1} c_{v2} - v_{l_1} c_{a2}) a, \quad (18c)$$

where J_{2s} is the intensity of the sorbate transfer into the bulk of microparticles, ω_i and v_{l_1} are the specific frequencies of the adsorption and desorption, respectively, c_{a1} and c_{a2} are the concentrations of the sorbate in the adsorption layer of microparticles localised on the surface of a macroparticle and in its bulk, $(\partial c_{v2}/\partial r)_{l_1}$ is the normal component of the gradient of sorbate concentration in pores near the surface of the macroparticle, and r is the distance from the centre of the macroparticle to the point where the sorbate concentration is equal to c_{v2}, a is the effective width of the adsorption layer.

Equations (17)–(18a–c) contain only those parameters which can be measured by experiment. Thus, $\varphi(l_i, V_{pi})$, ε_i and β_i can be determined by sectioning the bodies and measuring the sizes of particles and pores on the cuts with the use of optical and electronic microscopy. Frequencies ω_{l_1} and v_{l_1} can be measured upon adsorption by the microparticles which are not assembled into agglomerates. The intensity of sorbate transfer J_{2s} can be determined by the use of single crystals with the same molecular relief that the microparticles have. In addition, quantity J_{2s} can be measured directly observing the motion of adsorbed molecules in atomic force or tunnelling microscopy. The motion of individual molecules and atoms could repeatedly be observed in the tunnelling microscopy.[144, 145] To tell the truth, their trajectories were determined by the electric field of the microscope to a great extent, but there are all reasons to consider that the influence of the field on the surface movement of molecules can be taken into account.

It is not difficult to determine the coefficient D_1, while to determine D_2 is more complicated. This can be made by the conductometric method in the case where the size of sorbate molecules is not more than 0.5 nm. The current strength fluctuates at limits that are proportional to D_2 if two conductive microparticles of size 5–10 nm are approached so as to retain a space of 1–10 nm width between them, and the space is filled up with a sorbate solution containing NaCl, and the current is passed through the electric circuit formed.[146, 147] The volume of the solution determining the electrical resistance of the circuit is very low at the given size of microparticles. Thus, if even one molecule of the sorbate gets into the space, this results in a jump of the electrical conductivity and, therefore, the fluctuation of the current. It appears that a way to conductometric determination of the rate of sorbate accumulation in the bulk and on the walls of an individual micropore was suggested by Bezrukov *et al.*[146, 147] Therefore, a way to the direct measurements of ω_{l_1}, v_{l_1} and coefficient D_2 for molecules of an arbitary size is also open. It was shown[148] that the value of D_2 amounts to $(1-2) \times 10^{-11}$ m^2 s^{-1} at 300 K for the diffusion of polyethylene glycol of a mass of $200-10^3$ a.u. over a channel filled with an aqueous solution of NaCl in the lipid–peptide membrane with a channel radius of 1 nm. This value is lower than that in a free solution by an order of magnitude. This fact confirms the necessity to describe the sorption with Eqns (16)–(18a–b) taking into account possible differences in the values of D, D_1, and D_2.

The use of the functions contained in the indicated equations is complicated by the fact that some of them are unknown even for the most common sorbents. Simplifying assumptions are made for these functions, hence, the description of the sorption kinetics becomes semi-quantitative even if it agrees with the experimental data. The following assumptions are the most widespread:

$$\vec{v}_i = 0,$$
$$\varphi(l_i, V_{pi}) = \mathrm{const} \cdot \varphi(V_{pi}) \delta(\bar{l}_i),$$
$$D_i \neq D_i(\bar{l}_i),$$
$$\beta_i \neq \beta_i(\bar{l}_i),$$
$$\omega_{l_1} = v_{l_1} = 0,$$
$$c_{a2} = B_a c_{v2},$$

where $\varphi(V_{pi})$ is the distribution function of pores over the bulk, $\delta(\bar{l}_i)$ is the Dirac function, and B_a is the equilibrium coefficient of adsorption. As can be seen, the number of *a priori* assumptions is large. Nevertheless, one has to employ most of them even in the most consistent descriptions.[149, 150]

4. Possibilities of prediction

Quantum-chemical methods and correlative empirical dependences give an opportunity to estimate coefficient D_v *a priori* with a relatively small error for the bodies whose structure is near-equilibrium. But the acting sorbents are non-equilibrium as a rule. The structures of their particles depend on the 'biography' of the sorbent. Therefore, the problem of the estimation becomes complicated, and one has to solve it experimentally. Some peculiarities of the migration into the bulk of a body can be predicted by the molecular dynamics method. However, the predicting possibilities of this method are restricted to nanoparticles and small periods of sorption.

VI. Equilibrium sorption

The equilibrium sorption is usually charaterised by a distribution coefficient

$$K = (V_f c N_A)^{-1} \sum_j \int_{-\infty}^{+\infty} \theta_j n_j \varphi(x_f, t) \mathrm{d}x_i,$$

where V_f is the volume of the sorbing phase, and N_A is the Avogadro constant.

Approaching the equilibrium, function $\varphi(x_f, t)$ converges, and parameters θ_j and n_j become independent from $\{x_j\}$, the number of all the centres except the most stable diminishes, and coefficient K tends to a value

$$K_e = \theta_1 N_1 (c N_A)^{-1} = K_0 \exp\left(-\frac{\Delta F}{kT} \right), \quad (19)$$

where θ_1 is the fraction of the most stable filled centres, N_1 is the number of such centres in a volume unit of the sorbent phase, K_0 is

the ratio between the coefficients of thermodynamic activity of the sorbent in the sorbent phase and in the medium, ΔF is the standard change in the free energy of the sorbent during sorption.

A dynamical quasi-equilibrium is achieved between the centres sorbing most rapidly and the medium in the system upon completion of the first step if the sorption proceeds in several steps and adsorption centres of only one type are involved in the process at each step. Many examples of adsorptive quasi-equilibrium on the 'external' surfaces of bodies or on the surfaces of microparticles in the bulk of bodies with a successive transition to the equilibrium in the bulk have been described.

Equilibrium coefficients K_e are determined for several thousands of systems (though often without proof of their equilibrium). K_0 and ΔF are calculated for many systems by the methods of statistical mechanics and molecular dynamics. The matter connected with the differentiation of the partial and total equilibrium and the indentification of centres that are responsible for the quasi-equilibria still remains unclear.

Functions $\Delta F(\theta_j, y_i)$ and $K_0(\theta_j, y_i)$ that can be converted into isotherms of sorption are diverse.[151–154] The Langmuir, Freundlich, Frumkin, Totte, Dubinin–Serpinsky isotherms describing a variety of experimental results are applicable in a narrow range of conditions, as a rule. They are special cases of more complex isotherms. Systems are widespread both with a small entropy contribution in ΔF and with a great one.[155, 156] The great contribution of entropy has been found upon investigation of the sorption of bovine serum albumin and ovalbumin on a series of ion-exchangers.[155] The sorption process of these proteins is endothermic, and coefficients K_e are great.

1. The variety of equilibrium forms

Sorptive centres of several sorts can retain commensurable quantities of a sorbate at the quasi-equilibrium. For instance, it has been proved by the methods of scanning electronic and tunnelling microscopy and also by the diffraction of slow electrons that CO molecules are retained on centres of two sorts on the face (111) of a platinum crystal. In this case, the adsorption on both centres is commensurable if θ_j is high, and the adsorption on one of them dominates if θ_j is low.[157]

Four forms of the sorbate, being present in commensurable quantities and manifesting themselves in its magnetic properties, were discovered in the study of the adsorption of Cu(II) salts at TiO_2 single crystals.[158] Three forms of the sorbate with the adsorption heat of 101.6, 112.4, 178.1 kJ mol^{-1}, respectively, were observed upon the adsorption of NH_3 on crystals of $CdSO_4 \cdot 0.66H_2O$.[23] The presence of these forms can be interpreted as a result of sorbate localisation at the centres of different type. The presence of several adsorptive forms can be related to the different orientation of molecules on the surface in the case of the adsorption of complex molecules.

The forms whose orientations are favourable to produce the largest number of bonds with the surface dominate over the others. This was demonstrated by Diaz *et al.*,[159] for instance, who compared the sorption ability of the SiO_2 surface covered with an alkyl monolayer with respect to eight polyacrylate specimens (sorbates) to which different number of dodecyl radicals was grafted.

2. The role of complex formation

Coefficient K_e increases if centres arise on the surface and in the bulk of a body which act according to the laws of complex formation: the more stable sorptive complexes, the greater values of K_e.[160] This was cogently shown for the sorption of actinides by sorbents containing organophosphorus substances [161] and for the sorbent intended to remove bilirubin from the blood plasma.[162] This fact makes possible the use of ideas of the chemistry of coordination compounds for the interpretation of the sorption, taking into account the fact that the stability of complexes in the bulk or on the surface of the body differs from that in the environment.

Sorbents with centres forming complexes can be selective. For example, the selective adsorption of a lanthanum salt at tetracycline centres is observed if tetracycline hydrochloride is sorbed at zirconium phosphate, and then the resulting sorbent is introduced into a solution of lanthanum, cerium, barium, and thorium salts.[163] If functional groups based on ethylenediamine or diethylenetriamine are grafted to a matrix of mesoporous molecular sieve MCM-41, a possibility will arise to extract Co^{2+} from its aqueous solution selectively due to the formation of amino complexes in the bulk of grains.[159] The selectivity of sorption depends on the difference in the stability of sorptive complexes. The mechanisms of the processes leading to different stability are similar to those determining the selectivities of homogeneous reactions.

3. Deformation of the electronic structure over adsorption

The electronic structures of sorbate molecules change upon sorption of any type, and the changes can be as substantial as for the formation of chemical compounds.[140–145] Thus, the deformation of electronic structure of potassium atoms upon the adsorption of the potassium vapour on the face (110) of a GaP crystal is so strong that lines $2p$(P) and $3d$(Ga) in X-ray electron spectra shift by 1.6 eV at $\theta_j \to 0.1$.[164]

Changes of electronic structure over adsorption affect all atoms of an adsorbed molecule to a greater or lesser extent. However, they are mainly localised on one or several atoms. As a result, some atoms can have great mobility, remaining within a molecule or breaking away from it. In particular, the change of electronic structure affects several atoms connecting the sorbate to the surface over the adsorption of the $H_8Si_8O_{12}$ clusters at the face (100) of a silicon crystal. The evidence for this is the coincidence of a measured reflection IR spectrum and a calculated one (by the method of density functional).[165]

Calculations have shown that an H_2O molecule changes its configuration insignificantly upon its transition on regular adsorption centres localised at the faces (100) of NaCl crystals. But if a molecule of H_2O gets near an anion vacancy in the near-surface monolayer of the crystal, its electronic density changes so much that the molecule dissociates.[166]

It has also been shown by the method of density functional that the electronic structure of a thiophene molecule changes to the configuration η^5 upon the sorption on the (010) surface of a crystal of MoS_2.[167] A cleavage of the C–S bond and the hydrogenation take place in this case. It was established by the same method that a hydrogen bond is formed between hydrogen atoms of the molecule of H_2O and any oxygen atoms of the near-surface monolayer (mostly the oxygen atoms of the vanadyl group) upon the adsorption of H_2O molecules on the face (010) of a perfect crystal of V_2O_5. If the sorbent is non-stoichiometric, the electronic structures of H_2O molecules are deformed so that some of adsorbed molecules dissociate.[168] It was shown by the X-ray electron spectroscopy and temperature-programmed desorption that the adsorption of H_2S on the face (100) of a crystal of FeS_2 at 500 K is accompanied by a strong deformation of electron shells of atoms and dissociation of the sorbate molecules. The hydrogen comes further into the bulk of the crystal and sulfur localises near the vacancies of the near-surface monolayer.[152] The molecules of water adsorbed at the surface containing silicon and aluminium oxygen tetrahedra, are deformed to a lesser extent so that one of the protons of H_2O has an increased mobility without the dissociation of the molecules. Such a conclusion was made as a result of the calculation of configuration and normal vibrations of the molecule of water by the Hartree–Fock method.[169]

The changes of the electronic structure of the sorbate are specific for the centres of a different sort. This manifests itself, for instance, in the adsortion of CO on the surface of crystals with the composition $Cs_2HPW_{12}O_{48}$, where the electronic structure of CO changes in different ways depending on whether it is localised on the atoms of cesium or hydrogen. Adsorption bands with maxima at 2165 and 2145 cm^{-1} emerge in the IR spectra of the sorbate.

The intensity of the former band increases if some of the cesium atoms are replaced with hydrogen ones by changing the conditions of the synthesis of the sorbent.[170]

The examples considered above indicate the variety of the forms of adsorption-induced deformation of the electronic structures of sorbate molecules. Information of such deformation is accumulated rapidly, though the general regularities of the response of an electronic structure to the adsorption are not defined concretely.[154]

It is worth noting that the observation of $R^1-NHCONH-R^2-NHCONH-R^1$ molecules adsorbed on the graphite by scanning tunnelling microscopy revealed that the contrast in the images of carbamide groups is the same if the hydrocarbon chain contains an odd number of carbon atoms. If the number of the atoms is even, the contrast of these images is different.[171] The contrast of the images of the carbonyl group is directly connected with its electronic structure. Therefore, one can conclude that the electronic structure of the sorbate's molecule becomes unsymmetrical with an even number of carbon atoms in the chain. This observation indicates the possibility of a direct microscopic study of some of the peculiarities of the intramolecular distribution of the electronic densities of adsorbed molecules.

4. The relationship between the distribution coefficient and the properties of a body to be sorbed

Experiments have demonstrated that the following condition holds true for some series of sorbates [172]

$$K_e = K_1\left(\frac{P_s}{P}\right)^m + K_2\,, \qquad (20)$$

where K_1, K_2, and m are the characteristic parameters of a series of sorbates, P_s and P are the solubilities (for the sorption from a liquid) or the pressures of saturated vapour (for the sorption from a gas) of the sorbent and sorbate, respectively.

As a rule, $m > 1$ and $K_2 = 0$ in the investigated series. Nevertheless, $m = 1$ and $K_2 > 0$, for instance, for the sorption of α-naphthylamine by the crystals of naphthalene from solutions in various solvents.[173] Series for which $m = -1$ have appeared in the literature, but this can only be explained by the absence of the equilibrium in the system.[172] Correlation (20) reflects a general tendency for substances with low solubility or pressure of saturated vapour to be sorbed predominantly. The results of quantum-chemical calculations do not conflict with such a tendency, though they show that one can expect a monotonic dependence of coefficient K_e on quantities P_s and P in the case of similar properties of sorbed substances only.[174, 175]

Numerous facts indicate the importance of the similarity of sorbate's and sorbent's properties. For example, substances whose crystal lattice is similar to the sorbent one for at least one crystallographic direction adsorb better owing to favourable conditions created for the formation and growth of two-dimensional clusters in this case.[176]

Inert gases dissolved in water are sorbed by the crystal solvate $SO_2 \cdot 6H_2O$ at $T = 268$ K. In this case, coefficient K_e is monotonically reduced by increasing the difference between the molecular mass of SO_2 and the atomic mass of a gas — Ar, Kr, Xe, and Rn (Fig. 6).[177]

A number of admixtures are sorbed by the crystals of germanium and silicon from a melt at the melting point. The smaller the difference in sublimation enthalpy between the sorbed substance and the sorbent, the greater K_e for the formation of solid solutions.[178]

Summarising the results of studies,[172–178] one should note the absence of a determining property, which would uniquely characterise coefficient K_e, among the investigated properties of the sorbate and sorbent. Ratio P_s/P can be considered as such a property as a first approximation. This is indicated by the prevalence of correlation (20). However, the connection of K_e with this correlation is not always unequivocal.

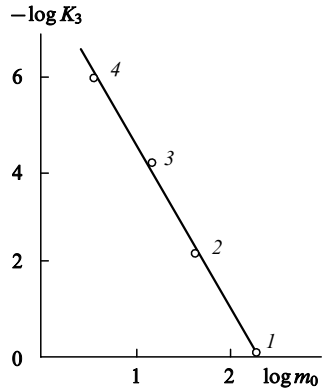


Figure 6. Coefficients of equilibrium sorption by the $SO_2 \cdot 6H_2O$ crystals at 268 K of radon (*1*), xenon (*2*), krypton (*3*) and argon (*4*) *vs.* the sorbate atomic mass;[177]
m_0 is the atomic mass /a.u.; K_3 is co-crystallisation coefficient.

5. Ways of prediction

The qualitative prediction of function $K_e(y_i, \theta_j)$ is possible based on the regularities of equilibrium sorption mentioned above. The semi-quantitative prediction is performed by analogy, using correlation dependences that are similar to Eqn (20). Another way is to employ approximate calculations of functions $\Delta F(y_i, \theta_j)$ and $K_0(y_i, \theta_j)$ with subsequent application of correlations of the type (19). The calculations are performed with the use of statistical thermodynamics and quantum chemistry.[179–181]

One aims to determine the values ΔF regarding the resulting interaction of the sorbate and sorbent as a sum of interactions of different types, by considering their influence to be additive.[182] For example, the dispersion, dipole, and pairwise electronic interactions are discriminated while describing sorption.[183] However, more precise information about the interaction potentials of atoms is required in such a method.

Especially great attention is paid to the calculation of function $K_e(y_i, \theta_j)$ for porous grains.[184–187] Pores of different diameters and configurations have different sorptive capacities usually. In other words, each of them represents a specific sorbing centre. The assumption that pores and adsorbing centres are distributed over the free energy of sorption continuously could be used without a loss of accuracy if there exist many pores.[188–190]

The calculations of sorption are carried out for many systems. Nevertheless, some of them deviate from the experimental results sharply.[191] Other calculations allowed quantitative explanation of the existing experimental results only, but the new data could be explained at the qualitative level only.

VII. Accompanying phenomena

1. Cosorption on the surface and in the bulk

If a sorbent takes several sorbates up simultaneously, the sorption of each sorbate is rarely additive.[15, 192] Sorbate particles usually not simply compete with each other for sorbing centres, but also change the sorptive capacity of these centres with respect to their competitors.[193] If these changes are great, one can speak about negative or positive cosorption of substances. Each cosorption type can be divided into a kinetic one, at which competitors speed up or slow down the sorption of each other, and an equilibrium one, at which they affect not only the rate, but also significantly change the value of K_e.

The range of the kinetic cosorptive effect can be considerable. For example, the rate of the formation of mixed adsorptive layers of $Cu(ClO_4)_2$ and KBr on the faces (100) of a copper crystal in the aqueous medium is so much greater than the rate of the formation of the pure layers of $Cu(ClO_4)_2$ that the adsorption proceeds from the kinetic regime to the diffusion one under the influence of KBr.[194] A powerful negative kinetic effect has been revealed [90] for

the cosorption of H_2 and Cl_2 on the rearranged (2×1) (001) surface of silicon at 300–1500 K, the initial temperature being 300 K. The molecules of HCl are produced in such an excited state upon the reaction of chlorine and hydrogen adatoms that most of them desorb in picoseconds after the beginning of the contact of the adatoms. The probability of desorption increases to 0.18 in a temperature range from 300 to 1000 K. After that, the probability remains constant, which indicates complex forms of functions $\chi_j(T)$ and $\beta_j(T)$ in formula (10). These functions point out the possibility of cleaning the surface from molecules of one sorbate by the molecules of another one owing to the interaction of the sorbates.

The equilibrium cosorption takes place in different systems. Thus, the sorption of strontium from a hydrothermal solution by Montmorillonite increases by 30% if the Sr^{2+} ions sorb together with Li^+ ions.[195] An analogous positive cosorption of these elements by soils was described by Chitra *et al.*[196]

The adsorption of carbon monoxide on SiO_2 from a gaseous phase is negligible under ordinary conditions if the sorbent is not doped with a silver salt. The adsorption is enhanced if the sorbent contains silver. A band at 2169 cm^{-1} has appeared in the IR spectra of the system, which is a characteristic of the Ag–CO bond.[197]

The adsorption of polyvinylpyrrolidone on the crystals of α-Al_2O_3 from an aqueous solution at pH 5–7 is enhanced in the presence of polyacrylic acid.[198] The adsorbed molecules of the acid form hydrogen bonds with the polyvinylpyrrolidone. This results in a positive coadsorption. Such a bond changes the conformations of sorbate molecules, which was proved for samples with a spin label by ESR.

At the same time, the biomass of pine bark sorbs substances from a mixture of aqueous solutions of cadmium, copper, and nickel worse than from an individual solution of each salt.[199] A sterilised soil suppresses the sorption of phenanthrene if the soil contains pyrene in a concentration of 5×10^{-4} mol g^{-1}. The pyrene affects the rate of adsorption slightly, but increases the rate of desorption sharply.[200]

Some sorbents interact with the sorbates, producing microcrystals. This is the case, for instance, for the sorption of $AgNO_3$ from an aqueous solution by copper hexacyanoferrate $Cu_2[Fe(CN)_6]$ (see Ref. 201) or for the sorption of SeO_2 from a gaseous flow by calcium hydroxide.[202] An abnormally strong sorption is observed in the latter case in the interval 770–970 K owing to the formation of $CaSeO_4$.

Thus, cosorption is a consequence of chemical reactions between the sorbates in the bulk or on the surface of sorbing bodies where the conditions of reactions of molecules differ from those in the medium surrounding the bodies. Investigating sorption, one can obtain information about the specificity of the interactions of the sorbate molecules in a force field of the sorbent molecules, which is necessary for a directed search for sorbents.

2. Specific features of biosorbents

Biosorbents consist of plant biomass or microbial cells immobilised on supports.[203–210] Formally, the behaviour of biosorbent grains or separate cells does not differ from that of particles of inorganic sorbents. For example, Madrid *et al.*[205] properly predicted the variation of the concentrations of a number of sorbates in a well-stirred reactor containing algae as sorbents. It was found that biosorbents can be characterised by particular diffusion coefficients D_v and by sorption isotherms and that the surface and volume sorption processes can be simulated in the usual way. If the sorbent is a set of identical cells, the membrane, cytoplasm and internal cell organelles should be regarded as its structural units.[209, 210] Sorbate accumulation by cell membrane can be treated as adsorption, while migration of the sorbate inside the cell, as bulk sorption.

Many biosorbents demonstrate selective sorption by separate structural units.[211] For example, redwood bark and moss cells accumulate cadmium, copper and nickel ions from aqueous solutions by membranes almost without involvement of the cytoplasm.[212]

The sorption capacities of cells depend on their physiological state but, generally, their 'preferences' do not change.[213–215] For example, the sorption sequence $Au^{3+} > Cu^{2+} > Ag^+$ always holds for the *Chlorella vulgaris* cells in aqueous solutions. Inside the cells, the sorbed substance undergoes chemical transformations and passes to the colloidal state.

In a study of sorption of various compounds by seeds of legume crops, it was found [52] that the coefficient K decreases along the series of chromates, molybdates and tungstates: Cr(VI) > W(V) > Mo(VI).

However, no general relationship between the nature of the biosorbent and the D_v or K values has been found so far. Elucidation of this relationship is complicated by strong influence of sorbates on one another [204, 208] and by changes in the sorbate state in the cells or in the physiological state of the cells themselves. The cells or destroyed biomass are to be regarded as 'black boxes'; thus, prediction of sorption becomes groundless, although formally it can provide some results.[207]

3. Structural memory of sorbents

If sorbate molecules are introduced into particles of a sorbent during its synthesis so that the former can escape to the medium, 'imprints' of the sorbate molecules can be retained in the sorbent structure and may play a role of specific sorption sites for this particular sorbate. The sorbent can 'remember' that the sorbate was present in the system during its synthesis. The 'memory' of inorganic sorbents was discovered long ago.[216] It has now been proved that organic polymeric sorbents also possess 'memory'; this fact is used successfully for selective and complete removal of side products of organic syntheses.[217]

4. The influence of external fields on sorbents

Recent studies showed that the sensitivity of a sorbent with respect to an electric field can be increased to a practically significant level without deterioration of their sorption properties. For example, sorbents based on titanium phosphate have been developed the sorption capacity of which changes dramatically upon application of an electric field; these sorbents absorb a number of metal ions from aqueous solutions by the ion exchange mechanism and, after that, desorption can be accomplished by merely changing the potential sign.[218] The application of an electric field accelerates sorbate diffusion inside the bulk of grains.[219] The field also influences the surface mobilities of atoms; this has been demonstrated, for example, by direct observation in a tunnelling microscope of the behaviour of potassium and sodium atoms on the (100) surface of aluminium.[220]

Multiphase sorbents sensitive to acoustic fields have been prepared.[221, 222] The sorbent grains consist of a heat-sensitive polymeric hydrogel, which can undergo a structural phase transition at some temperature T_0. Microcrystals of a poorly soluble substance with high density are introduced in the polymeric matrix, together with particles of a sorption-active phase. When $T < T_0$, the polymer molecules form a three-dimensional network with large cells, which ensures fast diffusion of the sorbate into the grains.

If the acoustic power is relatively low, the properties of the polymer network do not change on direct exposure to an acoustic field but the microcrystals inside the matrix are heated. They absorb most of the field energy and function as 'internal heaters' for the grains. If the grain temperature increases to T_0, the polymer molecules are compacted to form denser stacks and the grain permeability decreases abruptly. Once the sound has been switched off and the grain has been cooled to $T < T_0$, the permeability increases again. Thus, the grain responds to acoustic treatment by a triggered transition from one permeability level to another.

New magnetite-containing sorbents have also been prepared. Particles of such a sorbent can move on exposure to a magnetic field.[223]

5. Phase antagonism and synergism in multiphase sorbents

If a sorbent grain contains several phases, they can compete for a sorbate. In this respect, sorbent phases are antagonists. The points where particles of different phases contact with one another can give rise to specific sorption sites with increased K_e values. If this effect predominates over the antagonistic effect, these phases exhibit a synergistic effect.[224–227] For example, synergism was attained in the synthesis of a fibrous sorbent based on cellulose and zinc or copper ferrocyanide.[224] This sorbent proved to be especially efficient for extraction of cesium salts from aqueous solutions and was recommended for deactivation of natural and technological waters contaminated by ^{137}Cs.

A sorbent based on CuO and γ-$A1_2O_3$ phases with a large internal surface area of microparticles and a high porosity of grains having a narrow size distribution was prepared by the sol–gel procedure.[227] At 790 K, this sorbent showed a sorptive capacity toward sulfur dioxide of no less than 22.5 mass %, which is much greater than the values observed for other sorbents.

6. The molecular electrical conductivity of adsorbed species

If an adsorbed molecule (a two-dimensional cluster) occurs in a flow of electrons coming to the surface from the bulk, then, with some probability, the electrons adhere to a molecule, remain in contact with it for some period, and then pass to the substrate. Thus, the adsorbed molecule influences the electron flow. This influence can be described by attributing to each molecule an individual electrical conductivity. This parameter can be found by observing separate adsorbed molecules through a tunnelling microscope or by measuring the electric current between electrodes bridged by individual adsorbed molecules. For example, by applying a dilute solution of DNA (the length of the molecule is 10.4 nm) onto two platinum nanoelectrodes located at a distance of up to 8 nm using a special application procedure, one can ensure that one end of the molecule is adsorbed to the cathode and the other, to the anode, thus forming a 'bridge' across the gap between the nanoelectrodes.[228] When the electrodes have been dried in a nitrogen flow and the voltage $U = 1-5$ V has been applied, the cathode–DNA–anode circuit carries the current

$$I(U) = \sigma(U - U_\omega),\ U > U_\omega, \tag{21a}$$

$$I(U) = 0,\ U < U_\omega, \tag{21b}$$

where $\sigma = 5.3 \times 10^{-10}\ \Omega^{-1}$ is the molecular electrical conductivity at voltages higher than the threshold value $U_\omega = 1$ V.[229]

The electrical conductivity σ of the DNA molecule is due to tunnelling of electrons through the contact surface between the molecule and the anode and to their one-dimensional diffusion along the molecule.[228,230] However, it is not clear yet what are the contributions of these processes to the DNA conductivity.

Relations (21a) and (21b) reflect the threshold character of the molecular electrical conductivity of DNA. Apparently, this is a typical character of the electrical conductivity of molecules of different nature, as follows from the data on the interaction of adsorbed molecules with a flow of tunnelling electrons.

If a molecule is located on the surface of the substrate electrode, a second electrode represented by a spike with a 'monoatomic' tip is placed at a distance $R = 1-5$ nm, and the voltage U is applied to the spike, then current would flow from the spike to the substrate.[231–233] The current intensity can be expressed by the relation

$$I(U) = \omega\rho_0\varepsilon(\rho_0, U, R)[U\eta_1 + (U - U_\omega)\eta_2],$$

where ω is the probability for an electron to pass from the spike to the molecule per unit time, ρ_0 is the electron density of the substrate under the spike before application of the field, $\varepsilon(\rho_0, U, R)$ is the function characterising transition of electrons from the molecule to the substrate, U_ω is the voltage corresponding to the change in the η_1 and η_2 values from $\eta_1 = 1$ and $\eta_2 = 0$ for $U < U_\omega$ to $\eta_1 = 0$ and $\eta_2 = 1$ for $U > U_\omega$.

The threshold voltages U_ω were found for C_2H_2, CO, benzene and pyridine molecules adsorbed on the surface of copper crystals.[233–235]

The ω value usually depends slightly on ρ_0 and in the $kT < Ue < \varphi_e$ range (e and φ_e are the charge and the work function of an electron), it can be described by the exponent

$$\omega = \exp\left(-\frac{U_0}{U}\right),$$

where $U_0 = 10-100$ V is the characteristic voltage of the tunnelling field emission.[236] The $\varepsilon(\rho_0, U, R)$ function has a discontinuity at $U = U_\omega$. For $U > U_\omega$, it has several maxima; the $\{U_i\}$ values corresponding to these maxima comply with the condition

$$eU_i \to \omega_{hi} h,$$

where ω_{hi} is the frequency of a vibrational transition of the molecule or of the substrate below the molecule. This implies that the tunnelling electrons provide a resonance stimulation of vibrations of atoms in the adsorbed molecule, and the vibrations excited by the electrons are synchronised in such a way as to increase the probability of electron transition onto the substrate. The resonance excitation of intramolecular vibrations was found, for example, in the H_2O molecules adsorbed from vapour at 300 K on the surface of titanium oxidised in air.[231–233] In this case, prior to H_2O adsorption, the $I(U)$ function exhibited maxima corresponding to the stretching vibrations in TiO_2 ($\omega_{hi} h \approx 0.1$ eV). After adsorption, this function acquired large-scale maxima at

$$e(U_2 - U_1) \simeq 0.2 \text{ eV},$$

$$e(U_3 - U_1) \simeq 0.5 \text{ eV},$$

$$e(U_4 - U_1) \simeq 0.7 \text{ eV},$$

$$e(U_5 - U_1) \simeq 1.0 \text{ eV}.$$

The first two of these values are close to the quantum energies of bending (0.2 eV) and stretching (0.46 eV) vibrations of adsorbed water molecules (from IR-spectroscopic data). Hence, the other maxima can be attributed to two-quanta and combined vibration transitions.[233]

When H_2O is replaced by D_2O, the positions of the $I(U)$ maxima shift in conformity with the expected isotope effect. This attests unambiguously to the stimulation of intramolecular vibrations by the tunnelling electrons.

VIII. Sorbent degradation

The properties of a sorbent change inevitably during operation as sorbent bodies are gradually dissolved and destroyed upon collisions and chemical reactions with admixtures. The mass of each grain m varies at the rate

$$\frac{dm}{dt} = \beta_{k0} S(c - P_s) - \gamma_k \omega_k m_f + G_k, \tag{22}$$

where β_{k0} is the kinetic coefficient of dissolution, γ_k is the probability of grain fragmentation, ω_k is the frequency of collisions of the grain with other grains or with reinforcing structures, m_f is the average mass of the chopped-off fragments, G_k is the rate of mass variation caused by chemical reactions between the sorbate and the reagents present in the system as impurities.

Each of the above-mentioned paths of the change in the sorbent properties is characterised by the proper time τ_i:

$$\tau_1 = \frac{\bar{m}}{\beta_{k0} S(c - P_s)},$$

$$\tau_2 = \frac{\bar{m}}{\gamma_k \omega_k m_f},$$

$$\tau_3 = \frac{\bar{m}}{G_k},$$

where $\bar{m}$ is the average mass of grains.

The τ_i values can be predicted;[237, 238] however, the β_{k0} coefficients are unknown for most substances. They should be determined experimentally.

The γ_k value can be estimated using the theory of contact plastic deformation, the frequency ω_k can be determined using the collision theory and m_f is found from the model of fracture of solids.[239, 240] These values can be appreciably different, depending on the reactor shape and the method of stirring of the suspension. If one deals with a block crystal, chopping-off of blocks is the most probable way of destruction. As a result, the m_f value is similar to the average mass of blocks. If the particle is an agglomerate, the points of accretion of microcrystals are the first to be destroyed upon collisions, thus, m_f becomes equal to the average mass of the separate microcrystal.

IX. The search for an optimum sorbent

The quest for the optimal sorbent is carried out more and more often according to the principle: 'a specific sorbent for each system.' An individual system is characterised by a unique set of $K_e(y_i)$, $\tau_{0.9}(y_i)$ and $\tau_1(y_i)$ functions. The sorbent of choice is one ensuring the specified values of these functions. The best sorbent for a given system is usually selected by searching through the sorbents optimum for similar systems.[241, 242] If none of these materials is appropriate, the following multistep procedure is executed.

1. Identification of the substance to form the basis of the desired sorbent

At the stage of looking for the substance that would form the basis of the desired sorbent, correlations such as relation (20) are used and the array of materials with rather high K values and low solubility P_s is identified. The K values for each of these materials are determined experimentally and the material with the greatest K is chosen. This material would form the basis of the optimum sorbent.

2. Study of the kinetics of sorption by the disperse phase of the chosen material

When investigating the kinetics of sorption by the disperse phase of the material chosen as the basis for the optimum sorbent, the kinetics of sorbate absorption by the material particles moving freely in the medium should be measured over a broad range of conditions $\{y_i\}$. Using kinetic equations such as Eqns (3)–(11), the $\alpha_j(y_i)$, $v_j(y_i)$, $\lambda_j(y_i)$, and $\tau_{0.9}(y_i)$ functions are determined, while relations of type (13) and (14) are used to determine the $D_v(y_i)$ function. The $\mu_L(y_i)$ and $\rho_L(y_i)$ functions are also found. Using experimental data on sorption for long sorption times and high concentrations of the sorbate and relations of the type (19) and (20), the $K(\theta_j)$ and $\Delta F(\theta_j)$ values are determined and the isotherms of sorption $\theta_j(y_i)$ by the disperse phase are elucidated. The results of measurements are summarised as $G_i(x_i, y_i)$ and $D_{ij}(x_i, y_i)$ dependences [see relations (1) and (2)]. This stage results in quantitative descriptions of the adsorption and desorption, the formation of two-dimensional solid solutions and surface clusters, the formation of multiatomic layers and particles of the sorbate phase on the surface of freely moving sorbent particles, and migration of the sorbate inside the bulk of the chosen sorbent.

3. Study of the role of agglomeration

Agglomerates of particles differing in porosity are studied to identify the effects of contacts between the particles, capillary condensation and crystallisation in the pores on the $K(\theta_j)$, $\Delta F(\theta_j)$ and $\theta_j(y_i)$ functions. By simulating the sorbate interaction with pore walls, the $D_v(x_i, y_i)$ and $K_e(y_i, \theta_j)$ values for agglomerates can be determined.

The results of investigation of the kinetics of sorption by the disperse phase of the material chosen as the basis of the optimum sorbent and study of the role of agglomeration are generalised as kinetic equations of sorption of the type (1)–(13) devoid of arbitrary assumptions concerning the parameters of elementary steps in the sorption by separate particles and their agglomerates.

4. Determination of the rate of sorbent degradation

The rates of dissolution, fragmentation and chemical degradation of the sorbent for the most drastic operation conditions are determined using Eqn (22), and the $\beta_{k0}(y_i)$, $\gamma_k(y_i)$ and $G_k(y_i)$ functions are found. The ways of sorbent modification aimed at increasing its chemical and mechanical stability are developed.

5. Numerical experiment

The kinetic equations of sorption supplemented by edge conditions for the whole range of $\{y_i\}$ parameters formulated as a closed boundary problem are usually solved by numerical methods. The results are presented as the following functions:

$$K_e(x_{0i}, y_i, t_k),\ \tau_{0.9}(x_{0i}, y_i, t_k),\ \tau_i(x_{0i}, y_i, t_k),$$

where x_{0i} are parameters for the state of sorbent grains before use, t_k is the time period during which operation of the sorbent is planned.

These functions allow one to answer the question what properties are demanded of the initial sorbent for this sorbent to be regarded as optimal. At the stage of numerical experiment, the $\{x_{0i}\}$ values are found.

6. The nearest goal of the search

The stepwise procedure outlined above has been implemented thus far only for systems that are most important for practical purposes. Most often, in choosing the sorbents, the material that provides the most complete, fast and selective sorption and can be recovered from the medium over the shortest period of time is assumed to be the sorbent of choice.

These conditions are met by a sorbent with dendrite-shaped grains consisting of accreted filamentary nanocrystals forming a highly porous texture. The surface of nanocrystals bears functional groups capable of forming complexes as stable as possible with the given sorbate. The structure of nanocrystals allows the sorbate molecules to be inserted into interstices with a high K coefficient. Judging by the experimental results presented above, grains of such a sorbent would form highly porous filter layers characterised by low fluid-flow resistance, high velocity $\vec{v}_L$ and approximately equal accessibilities of grain surfaces for a sorbate and would ensure favourable conditions for adsorption of sorbate molecules on nanocrystals and diffusion of molecules into their bulk.

X. Conclusion

Analysis of the published data shows that the research into sorption is approaching a new stage of development which can be termed as the molecule visualisation stage. There are grounds to expect that the gap between macroscopic and molecular description of sorption would be filled. By the beginning of this stage, conditions have been created for experimental investigation of all elementary processes taking place on the surface and in the bulk of sorbent bodies. To date, these opportunities have not been exploited to a degree sufficient for the elaboration of a theory of sorption able to describe the whole set of elementary processes. Therefore, it is still impossible to predict quantitatively the behaviour of sorbents over a broad range of sorption conditions.

The current level of detail in the description of sorption makes it possible to compose a particular plan for the accumulation of data sufficient for quantitative prediction of the sorbent behaviour under various sorption conditions on the basis of *a priori* semiquantitative estimates ('by analogy').

This plan should include theoretical analysis of the possible variants of implementation of sorption processes and accumulation of missing experimental results. Theoretical analysis implies the solution of evolution equations that describe the variation of the sorbent state during the synthesis and operation, while experimental studies are aimed at 'information loading' of the evolution equations.

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