

Lecture №9. Diffusion of a distributed substance during adsorption

Aim: To characterize the processes of physical and chemical adsorption. Describe the nature of the process of adsorption. Provide a classification of porous materials and the main qualitative characteristics of the porous structure of the material. Describe the four types of diffusion in the pores. To analyze the main forms of isotherms according to the classification of Brunauer.

Lecture summary: Adsorption processes are widely used in industry for cleaning and drying gases, cleaning and clarifying solutions, separating mixtures of gases or vapors, etc. The value of adsorption processes has greatly increased in recent years due to the expansion of the need for high-purity substances. There are physical and chemical adsorption. Physical adsorption is due to the mutual attraction of the adsorbed molecules (sorbate, sorbtiv) and sorbent (adsorbent) under the action of van der Waals forces. During chemical adsorption (chemisorption) a chemical bond arises between the sorbate molecules and the surface sorbent molecules.

The nature of the adsorption process in time depends on the state of the adsorbent layer - whether it is stationary or moving. The processes of adsorption on a fixed bed are periodic. When the adsorbent stream continuously enters the adsorbent layer, a frontal (or frontal) layer is formed in the initial period, on which, due to a sharp drop in the driving force of absorption of the sorbent, it practically stops, and the stream “slips” through this area without changing the concentration, then a parallel transfer of the stationary front occurs adsorption. The time of the layer to saturate its frontal area in a periodic adsorption process is called the period of formation of the adsorption front. From the moment when the gas (or solution) point of the gas front point with a concentration corresponding to the beginning of the “breakthrough” leaves, the time of the adsorption, or protective, action of the layer ends. The area of the adsorbent layer, on which the concentration of the adsorptive in the stream from the initial to zero, occurs, is called the working layer, or the mass transfer zone.

In most cases, the material of the solid phase has a porous structure; such, for example, are technical adsorbents - active carbons, silica gels, zeolites, alumogels.

In adsorption processes, porous materials are divided into pore size by micropores (effective pore radius $r \leq 10^{-9}$ m), transition pores ($r = 10^{-9} - 10^{-7}$ m) and macropores ($r \geq 10^{-7}$ m). A real porous body is a system with complex channels that vary in size and shape. The main qualitative characteristics of the porous structure of the material are: 1) the shape of the lateral surface of the pore; 2) the configuration of its cross section; 3) pore profile in longitudinal section; 4) the tortuosity of the pore channel; 5) the relative position of the pores or elements of the "skeleton" of the body; 6) connectedness of elements with each other; 7) the micro-relief of the surface of the pore walls. The pore profile in the longitudinal section can be tubular, crisp (with constrictions and extensions), bottle-shaped or spheroidal. The presence of pores of a certain profile explains the hysteresis phenomena of sorption – desorption processes.

During adsorption, four types of diffusion in the pores are usually considered: “solid”, surface, Knudsen and free (Fig. 1). The dominance of one of these types of diffusion depends on the porosity of the grain structure and the degree of its filling with

sorbate. "Solid-state" diffusion is observed in pores with a diameter of several angstroms ($d \approx 10^{-10}$ m), and the potential fields of opposite walls overlap. Surface diffusion occurs on almost any surface, both in wide and narrow pores. However, it begins to play a significant role only in fairly narrow pores, when Knudsen diffusion is small.

Under normal physical conditions, the diffusion coefficient of gases and vapors in capillary-porous materials has the following order of magnitude: with free diffusion $D \sim 10^{-5} - 10^{-4}$ m²/s, with Knudsen's $D \sim 10^{-6}$ m²/s, with surface $D < 10^{-7}$ m²/s, with a solid $D < 10^{-9}$ m²/s.

The differential diffusion equation (analogue of the second Fick law) is written for the sum of the densities of sorbate flows in the adsorbent grain in the gas and condensed phases:

$$\frac{\partial c}{\partial \tau} + \frac{\partial a}{\partial \tau} = \text{div}(D' \text{grad} c_2), \quad (27)$$

where D' is the internal diffusion coefficient equal to $D' = D_r + D_n (\partial a / \partial c_r)_t$.

For linear adsorption isotherm $(\partial a / \partial c_2)_t = \Gamma = \text{const}$ therefore, expression (27) can be represented as

$$\frac{\partial c_r}{\partial t} = \text{div}(D_e \text{grad} c_r), \quad (28)$$

where $D_e = D' / (1 + \Gamma)$ is the effective diffusion coefficient during adsorption, which at coincides with the mass diffusivity during adsorption.

$$(\partial a / \partial c_r)_t \gg 1$$

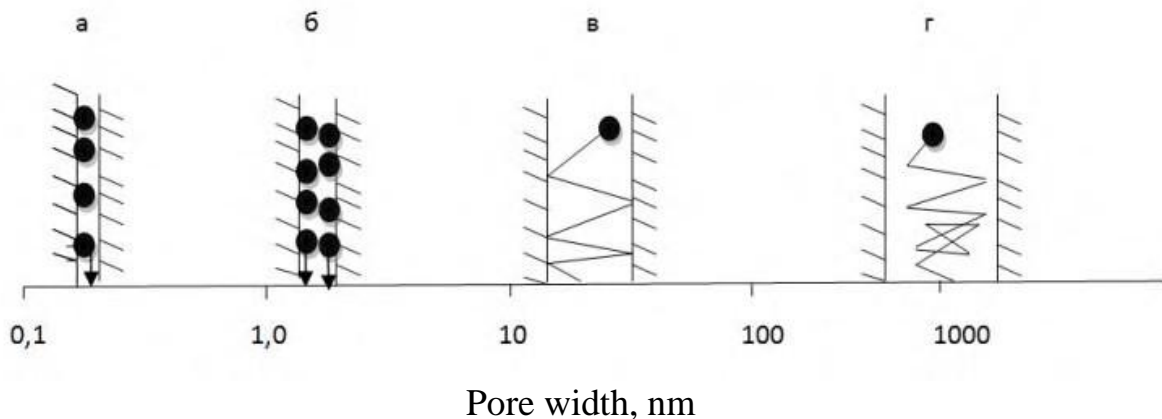


Fig. 1. Types of diffusion in the pores: a) "solid"; б) superficial; в) Knudsen's; г) free.

The coefficients D' and D_e are largely dependent on both the type of adsorbent and the nature of the adsorbate. Zeolites have a particularly strong selective property, which is explained by the molecular sieve effect of these adsorbents. The dependence of the coefficients D' and D_e on the determining factors (temperature, magnitude of adsorption) is complex, therefore, in calculating the kinetics and dynamics of adsorption, the values of diffusion coefficients averaged over the concentration are often used.

In contrast to non-porous materials in capillary-porous materials during physical adsorption the distributed component is held by adsorption and capillary forces. However,

as mentioned above, in the case of a macrocapillary-porous adsorbent (with a radius of $r > 10^{-7}$ m) capillary condensation is absent and the adsorption-bound moisture is negligible, therefore such materials are non-hygroscopic. If capillary-porous material belongs to microcapillary-porous (with a radius of $r < 10^{-7}$ m), then it is characterized by hygroscopic properties.

Depending on the structure of the material, the energy state of the pore walls and the physicochemical properties of sorbate, the equilibrium ratios expressing the relationship between the equilibrium moisture concentration C_{eq} and moisture content φ in the form $C_{eq} = f(\varphi)_\tau$ have a different appearance.

According to the classification of Brunauer, five main forms of isotherms are distinguished (Fig. 2). Type I is characteristic of microporous adsorbents without transition pores. A less steep initial rise of the isotherm indicates the presence of micropores (types II and IV). The relatively rarely occurring isotherms of types III and V are inherent in the systems adsorbate (A) - adsorbent (B), in which the forces of intermolecular interaction between molecules of type A are much greater than the forces of interaction between molecules A and B, i.e. $\mu_{AA} \gg \mu_{AB}$.

Adsorption isotherms are determined experimentally. In the absence of experimental data on equilibrium, isotherm construction is possible using equations derived from various theories of adsorption processes.

The theory of monomolecular adsorption is proposed by Langmuir. According to this theory, localized adsorption occurs on active centers with a small radius of action of adsorption forces capable of saturation. Langmuir equation has the form:

$$\frac{a^*}{a^*_M} = \frac{bp}{1 + bp}, \quad (29)$$

where a^* - is the amount of adsorbate absorbed by a unit of adsorbent according to achieving a state of equilibrium; a^*_M - is the limiting amount of adsorbate that can be absorbed by the adsorbent when filling all the adsorption sites on the surface of the pores of the adsorbent; b - coefficient determining the dependence of the Langmuir isotherm type on temperature. The theory of volumetric filling of micropores with an adsorbed component leads to the Polanyi isotherm equation:

$$a^* = \frac{W_o}{\nu_o} \exp\left[-B\left(\frac{T}{\chi} \lg \frac{p^*}{p}\right)^2\right], \quad (30)$$

where W_o - is the total specific volume of the adsorbent micropores, m^3/kg ; ν_o - molar liquid volume of the adsorptive liquid phase, $m^3/kmol$; B - structural constant, K^{-2} ; χ - affinity coefficient, determined by the adsorbate, taken as a standard substance (benzene - during adsorption by microporous adsorbents and nitrogen - during adsorption by zeolites); T - temperature, K. Values of parameters W_o , B and χ are given in a special temperature.

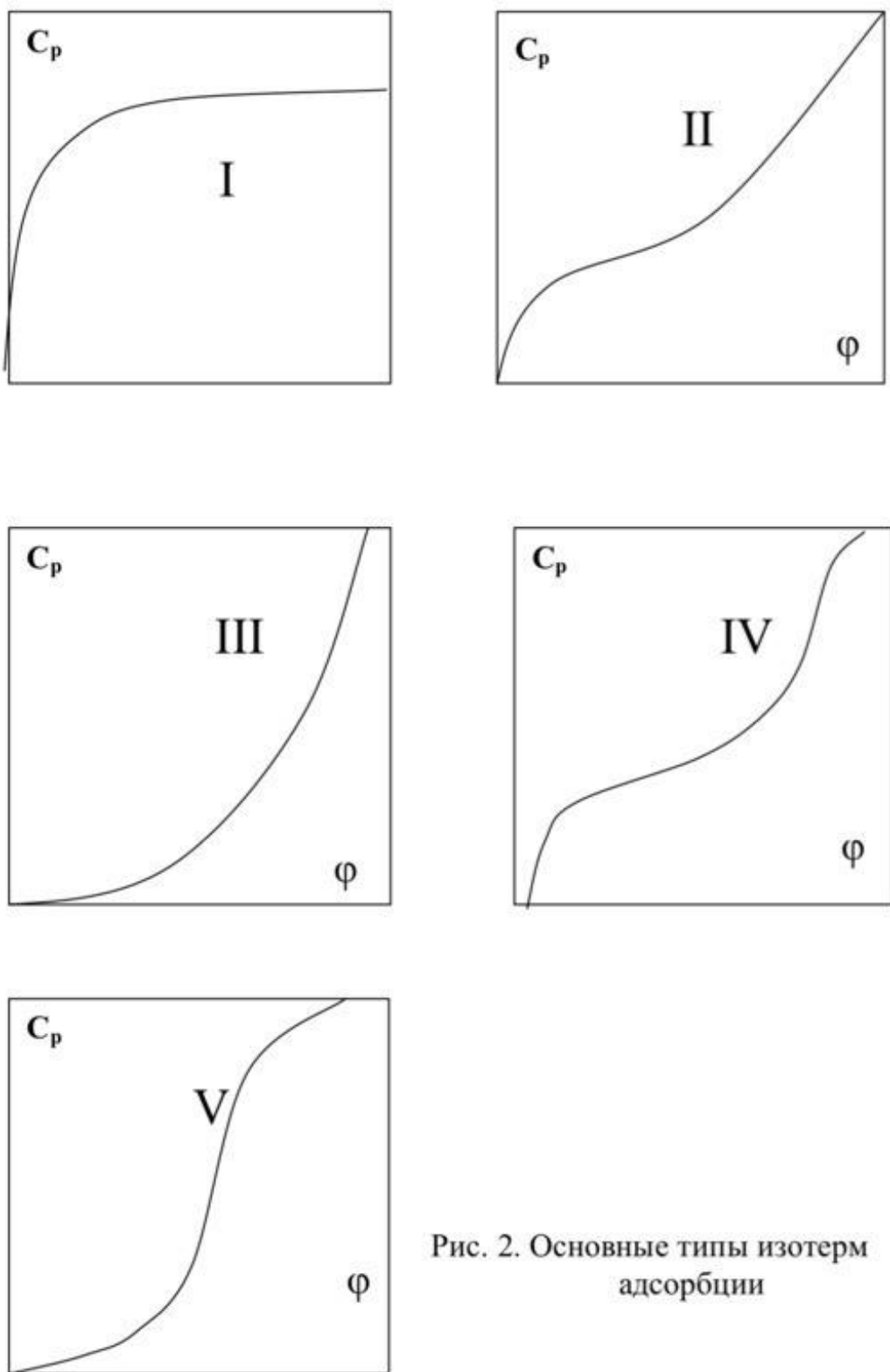


Рис. 2. Основные типы изотерм адсорбции

The theory of polymolecular adsorption BET (Brunauer, Emmett and Teller) was proposed in relation to vapor adsorption.

The isotherm of the BET theory is:

$$\frac{a^*}{a^*_M} = \frac{C_1}{(1 - p/p^*)[1 - (C_1 - 1)p/p^*]} \cdot \frac{p}{p^*}, \quad (31)$$

where p^* - is the saturated vapor pressure of the adsorbate at the temperature of the equilibrium process; C_1 is a constant defined for each pair of adsorbent - adsorbate. Equation (31) describes isotherms with an inflection in the coordinates $a^* - p$, in the interval of relative partial pressures $p/p^* \approx 0.05 - 0.35$.

Questions to control:

1. To characterize the processes of physical and chemical adsorption.
2. Describe the nature of the process of adsorption.
3. Give the classification of porous materials and the main qualitative characteristics of the porous structure of the material.
4. Describe the four types of diffusion in the pores.
5. Analyze the main forms of isotherms according to the classification of Brunauer.

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