Lecture №6. Diffusion in non-porous materials

Aim: Discuss diffusion in non-porous materials. Describe diffusion in capillary-porous materials. Define anomalous diffusion.

Lecture summary: In non-porous materials, the absorption of a substance distributed in the solid phase by them occurs by the mechanism of absorption, and its transfer by molecular diffusion. Typical representatives of non-porous materials are many polymers used in the chemical industry. Depending on the method of preparation and the characteristics of the morphological structure, the polymers may have a porous or non-porous structure. In a non-porous polymeric material, the absorption mechanism of absorption of the substance being distributed is confirmed by experiments, which are characterized by the coincidence of the sorption and desorption curves, as well as the presence of contraction during moisture absorption. The diffusion of the dispersed substance in a partially swellable polymer obeys Fick's law, which is described by equation (1).

Non-porous polymeric materials are usually heterogeneous in composition and contain microregions consisting of amorphous and crystalline phases of the polymer. The substance is absorbed mainly by the amorphous phase, characterized by a looser packing of macromolecules and greater mobility of the segments of macromolecules. Migration of the molecules of the substance to be distributed occurs only through the amorphous parts of the polymer, and the diffusion conductivity of the crystallites can be taken equal to zero. A characteristic feature of the migration of the substance to be distributed in non-porous polymeric materials is that it occurs not through strictly fixed channels (pores), but through windows and holes, which periodically appear and disappear in the polymer matrix as a result of thermal movement of macromolecular segments.

The diffusion rate of the distributed substance in a non-porous polymeric material depends on the volume fraction of the amorphous phase, its structure, geometry, and the nature of crystallite incorporation in the polymer, and the transfer of the distributed substance obeys, as mentioned above, the Fick molecular diffusion law.

Diffusion in capillary porous materials

Mass transfer in capillary-porous bodies is a complex process, which is caused by several reasons: 1) the type of technological process: drying, desorption, extraction or heterogeneous catalysis on porous catalysts, etc.; b) the characteristic of the porous medium: the size and configuration of the pores, the distribution of pore sizes, the nature of their connection with each other, etc.; c) the energy state of the surface of the pore walls; d) the magnitude of the physicochemical affinity of the molecules of the extracted substance (diffusant) and the "skeleton" of a solid body; e) the degree of filling of the pores with the extracted substance; e) process conditions: temperature, pressure, etc.

Migration of the substance to be distributed in some porous materials occurs through the pore system, which retains its shape and size during the entire diffusion process. The main mechanisms of isothermal mass transfer of substances in such materials are, for large moisture contents – the capillary flow, for small moisture – the normal or constrained

vapor diffusion, film flow and surface diffusion. The contribution of individual mechanisms to the total flow is determined by the pore size, the distribution function of their size, the energy state of the substance being distributed and the skeleton of the porous material. In other porous materials, a change in the framework in the diffusion process is observed. An example would be porous materials containing a solid phase that is removed by extraction. The transfer of substance in the pores of such bodies is carried out by molecular diffusion, but the changing skeleton of a solid has an effect on the diffusion rate, which is reflected in a numerical change in the diffusion coefficient and an increase in the solution viscosity due to partial solubility of the solid phase.

The affiliation of a material to a particular class is determined on the basis of structural sorption studies.

Colloidal capillary-porous bodies include materials of plant and animal origin, which are sometimes used in chemical technology, as well as porous polymers. In colloidal capillary-porous materials, the distribution of the substance being distributed occurs both through the pore system and through their walls due to diffusion in porous materials with permeable pore walls.

The transfer of substance through the pore walls, carried out by molecular or osmotic diffusion, can either obey Fick's law or be characterized by *anomalous diffusion*, depending on the scale and speed of the structural changes taking place. In addition, in colloidal capillary-porous materials, the nature of diffusion depends on whether the pores are closed or form end-to-end, interconnected channels. In materials with closed pores, diffusion of molecules through the pore walls (the slowest stage of the process) limits the overall diffusion rate; however, the diffusion coefficient is of the same order of magnitude as in the material constituting the pore walls.

Anomalous diffusion in polymeric capillary-porous materials manifests itself during the diffusion of liquid molecules, which in the thermodynamic sense is a "good" solvent in relation to the solid phase itself, which can cause structural changes in the polymeric material during the process.

Questions to control:

1. Describe the diffusion in non-porous materials.
2. List the causes of diffusion in capillary-porous materials.
3. What materials are related to colloidal capillary-porous bodies?
4. What substance transfer is called anomalous diffusion?

Literature:

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