Lecture №1. General information on the course “Mass transfer processes in a system with solid phase”. Course content and its purpose.

Aim: Acquaintance with the course content and its objectives. Formulate the general laws of diffusion processes. Explain the laws of Fick. Discuss the physical meaning of the differential equation of convective diffusion.

Lecture summary: Introduction. Concentration diffusion plays an important role in the mass transfer processes occurring in systems with a solid phase; is a necessary part of many productions and significantly influences the quality of the products used.

The general laws of mass transfer with participation of the solid phase underlie such widespread processes of chemical technology as adsorption, drying, extraction from solid materials, etc.

In recent years, in connection with the production of plastics and the widespread use of solvents, a new area of diffusion processes has arisen, requiring specific attention. Such phenomena as the distribution of diffusing matter in polymers and porous materials, the separation of low- and high-molecular components, structural changes in pasty materials during drying, etc., often accompany technological processes and are the object of increased attention.

In addition, with the development of synthesis of high molecular substances, a wide application of world practice for the sealing of chemical, food, pharmaceutical and other products, as well as expensive devices and installations for the purpose of preserving them qualitatively, has received polymer films. Therefore, the study of the processes of vapor permeability, and hence diffusion processes in polymer materials – the actual need for industrial production.

In order to solve practical problems of diffusion mass exchange in heterogeneous systems with the participation of a solid phase, it is necessary to rely on the basic laws and general principles of modeling and calculation of these processes.

1. General regularities of diffusion processes of mass transfer

Mass exchange, or mass transfer, is a complex process involving a complex process involving the transfer of substance within a single phase, then the transfer of substance through the interface and its transfer within another phase.

The transfer of a distributed substance within one phase from the main volume of the flow to the interface with another phase is called *mass emission*; the process of transferring substance from one stream to the bulk of another substance through the interface – *mass transfer*.

The rate of mass exchange processes is often limited by molecular diffusion, so mass transfer processes are sometimes called *diffusion* processes.

Equations that formally describe the diffusion motion of atoms in solids were proposed by Fick.

The first law of Fick has the form:

$$I_i = -D_i grad\,\overline{C_\iota}\,, \tag{1}$$

where I_i – the flux density of the i-th component, mol/(m^2·s) or kg/(m^2·s); D_i – the diffusion coefficient of the i-th component, m^2/s; $grad\ \overline{C_i}$ – gradient of its concentration, mol/m^4 or kg/m^3/m. The minus sign corresponds to the positive value of the diffusion flux in the direction of decreasing concentration.

In thermodynamics of irreversible processes it is clearly shown that the flux of particles in a chemical (concentration) field is determined by the gradients of the chemical potential. Calculation of the chemical potential for real systems presents certain difficulties, therefore, in practical calculations of mass-transfer processes, the cause of the diffusion flux of a component is the presence of a gradient of its concentration. At the same time, it must be remembered that the phase equilibrium does not mean a numerical equality of the content of each distributed component in each phase. It should be noted that Fick's first law is purely empirical and does not reveal the nature of diffusion phenomena.

The second law of Fick, describing the dependence of concentration on time, follows directly from the first, taking into account the law of conservation of substance. An increase in the concentration of particles in some isolated element of the volume in the absence of extraneous sources is possible only due to the difference in the fluxes of these particles entering and leaving the volume element and is described by the formula:

$$\frac{\partial C_i}{d\tau} = -divI_i, \tag{2}$$

Substituting the flow from (1) into (2), we obtain the expression of the *second Fick's law*. In most practical problems, the diffusion coefficient is assumed to be independent of the concentration, and therefore of the coordinates. In this case, Fick's second law is expressed by the equation:

$$\frac{\partial C_i}{d\tau} = D_i \nabla^2 C_i\ , \tag{3}$$

where $\nabla^2 = div(grad)$ – the Laplace operator.

In the simplest case of one-dimensional diffusion, when the concentration gradients and fluxes are directed along the x axis, the equation of the second Fick's law takes the form:

$$\frac{\partial C_i}{d\tau} = D_i \partial^2 C_i / \partial x^2, \tag{4}$$

The diffusion coefficient D_i is a fundamental characteristic of the diffusion environment and plays an extremely important role in the theory of all diffusion processes. An ideal thermodynamic system is an ensemble of noninteracting particles that diffuse as a result of chaotic "wanderings". The theory of chaotic "wanderings" is based on the strict laws of static mechanics and is well developed. Therefore, the diffusion coefficient in this case can be calculated quite accurately, which creates the conditions for the development of a theory of more complicated diffusion processes.

Thus, the coefficient of molecular diffusion D_i is a physical quantity that characterizes the ability of a given substance to penetrate due to diffusion into a stationary environment that does not depend on *the hydrodynamic conditions* in which the process proceeds. The value of the molecular diffusion coefficient D_i is a function of the properties of the distributed substance and the environment into which it diffuses, temperatures and pressures. Usually, D_i grows with increasing temperature and decreasing pressure (for gases). In each specific case, the value D_i is determined from experimental data or from theoretical and semi-empirical equations, taking into account the temperature and pressure at which diffusion takes place.

By analogy with the equation of the molecular diffusion process expressed by equation (1), *turbulent diffusion* is described by the equation: $I_i = -\varepsilon_i grad\,\overline{C_\iota}$. Here ε_i – the turbulent diffusion coefficient, which is not a physical constant; it depends on the hydrodynamic conditions, determined mainly by the flow velocity and the scale of the turbulence.

The transfer of substance along with the environment itself in a direction that coincides with the direction of the total flow is described by the equation:

$$\overrightarrow{I_\iota} = \vec{\omega}\overrightarrow{C_\iota}\,, \tag{5}$$

where $\vec{\omega}$ – the component flow velocity, m/s.

Through molecular diffusion, a substance moves only in a stationary environment. In a moving environment, the substance can move both as a result of molecular diffusion, and the environment itself (convective transport) in the direction of its motion or its individual particles in various directions. In a turbulent flow, the transfer of substance by molecular diffusion predominates only near the phase boundary.

1.1. Differential equation of convective diffusion

The total transfer of substance due to convective transport and molecular diffusion is called convective mass transfer, or *convective* diffusion. The differential equation of convective diffusion, expressing the law of distribution of the concentration of a given component in a stationary environment moving under an unsteady mass exchange process, has the form:

$$\frac{\partial C}{\partial \tau} + \omega \cdot gradC = D \cdot \nabla^2 \cdot C. \tag{6}$$

For mass exchange in a stationary environment, the convective component in (6) is zero and equation (6) becomes the differential equation of molecular diffusion of the second Fick's law (4).

In the differential equation of convective diffusion (6), in addition to the concentration one, the flow velocity ω is variable. Therefore, this equation must be considered in conjunction with the differential equations of hydrodynamics (the Navier-Stokes equations and the equation of continuity of the flow). However, this system of equations does not have an analytical solution, and to obtain the calculated dependencies on mass exchange one has to resort to the transformation of the differential equation of convective diffusion by the methods of the theory of similarity.

Questions to control:

1. Give the course content and its objectives.
2. Formulate general patterns of diffusion processes.
3. What does Fick's first law mean? Give the formula.
4. What does Fick's second law describe? What does the equation look like for the simplest case of one-dimensional diffusion?
5. What equation describes the turbulent diffusion equation?
6. Give the differential equation of convective diffusion. What does it express?

Literature:

1. Ishanhodjaeva M.M. Physical chemistry. Part 1. Diffusion in systems with a solid phase. - SPb.: SPbGTURP, 2012. - 35 p.
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