Lecture №4. Diffusion of components in systems with a solid phase. General regularities of mass transfer in systems with a solid phase

Aim: Explain the phenomena of internal and external diffusion. Give the physical meaning of the mass diffusivity. Give an equation for the process of mass conductivity.

Lecture summary: The general laws of mass transfer with a solid phase take into account the mass emission (output) of the substance to be distributed in a solid material (which can be called *mass conductivity*) due to *internal diffusion* and the transfer of a substance in the liquid or gas phases due to *external diffusion*. The specific nature of the processes involving the solid phase is that the transfer of substance in a fixed layer of solid material is an unsteady process, i.e. the concentration of substance in the solid phase changes not only in space (C = f (x)), but also in time (C = f(τ)). Therefore, the process of *mass conductivity* can be represented by the equation:

$$M = -D_M F\tau \frac{\partial C}{\partial n}. \qquad (12)$$

Here D_M – *the mass diffusivity coefficient*, which is the internal diffusion coefficient.

The mass of a substance removed from the interface by mass emission (output) is determined as follows:

$$M = \beta_c F\tau(C_{boun} - C^*) = \beta_c F\tau\Delta C, \qquad (13)$$

where β_c – the mass emission (output) coefficient. Equating the relations (12) and (13) and considering the mass transfer along the *x* axis, we get:

$$\beta_c \Delta C = -D_M \frac{\partial C}{\partial x} \qquad (14)$$

The mass transfer coefficient is *a kinetic* constant depending on the physical properties of the phase and the hydrodynamic conditions in it, related to the physical properties of the phase, the geometric characteristics and the size of the mass transfer apparatus. The most rigorous way to determine the mass emission (output) coefficients is to integrate the diffusion equation in a moving medium together with the Navier-Stokes equations and the flow continuity equation for given initial and boundary conditions. However, the system of these equations has practically no common solution. Therefore, it is possible to find the connection between the variables characterizing the process in a phase flow in the form of *a generalized (criterial) mass emission (output) equation* using the methods of the similarity theory.

Taking into account that for such processes the ratio of similar values is equal to the ratio of values proportional to them, we replace in (14) ∂C with a finite difference ΔC and ∂x – with some linear dimension l. Dividing the left side of equation (14) into its right side, reducing similar terms and lowering the minus sign, we obtain the dimensionless similarity criterion:

$$\frac{\beta_c \cdot l}{D_M} = Bi' = idem. \qquad (15)$$

This criterion reflects the similarity of the transfer of the substance to be distributed at the boundary of the solid and liquid (gas or vapor) phases and is called *the Biot diffusion criterion* (Bi'). The Biot criterion includes the ratio β_c and D_M, which characterize the rates of external and internal diffusion. For small values of Bi', the rate of mass transfer is limited by external diffusion, and for large values of Bi' – by the rate of internal diffusion (the process takes place in the intradiffusion region).

To find the conditions for the similarity of mass transfer processes in the core of a solid phase, carry out a similar transformation of the differential equation of mass conductivity:

$$\frac{\partial C}{\partial \tau} = D_M \left(\frac{\partial^2 C}{\partial x^2} + \frac{\partial^2 C}{\partial y^2} + \frac{\partial^2 C}{\partial z^2} \right). \qquad (16)$$

From it, using the usual methods of the similarity theory, one can obtain the relation:

$$\frac{D_M \tau}{l^2} = Fo' = idem. \qquad (17)$$

This dimensionless complex of quantities, which describes the similarity of the rate of mass transfer of substance by mass conductivity through the solid phase, is called *the Fourier diffusion criterion* (Fo').

In addition to these similarity criteria, when considering the transfer of a substance by mass conductivity, the geometric similarity expressed by the simplex x/δ, where x – the coordinate of a given point in a solid, and δ – *the defining* geometric size, must be observed. The *determined* value is the dimensionless simplex of concentrations, presented as a ratio: $\frac{C - C_{boun}}{C_{init} - C^*}$, where C – the concentration at a given point of the solid phase for the time τ. Thus, in the simplest case of a one-dimensional flow, the generalized mass conductivity equation involving the solid phase has the form:

$$\frac{C - C_{boun}}{C_{init} - C^*} = f\left(Bi', Fo', \frac{x}{\delta} \right). \qquad (18)$$

Using equation (18), we find the average concentration of solid particles as a function of time. Knowing this value, you can get the necessary information about the kinetics of the process and its effectiveness.

Questions to control:

1. Explain the phenomena of internal and external diffusion.
2. Give the physical meaning of the mass diffusivity.
3. Give an equation for the process of mass conductivity.
4. Write a generalized mass diffusivity equation involving the solid phase for a one-dimensional flow.

5. What is the defined value in this equation?

Literature:

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

2. Tsvetkov S.K. Mass transfer processes in systems involving the solid phase. - SPb.: SPbU, 2017. - 50 p.

3. Kasatkin A.G. Basic processes and devices of chemical technology. – M: Alliance, 2006. – 752 p.

4. Romankov P.G., Frolov V.F., Flisyuk O.M. Calculation methods of processes and devices in chemical technology (examples and tasks). – St.-Petersburg: Himizdat, 2011. – 544 p.