Lecture №3. Determination of mass transfer coefficients in systems involving the solid phase

Aim: Bring molecular diffusion equations (Fick's first law). Formulate the basic law of mass emission (output) (convective) diffusion. Analyze the mass emission (output) equations for the gas and liquid phases. Write the dimension of the mass emission (output) coefficient in a general form and explain its physical meaning. Describe the criteria for diffusion similarity.

Lecture summary: The basis of such common processes of chemical technology as adsorption, drying, extraction from solid porous materials, are the general laws of mass transfer involving the solid phase. The mass transfer between the solid and moving liquid (gas) phase consists of two processes: 1) moving the distributed component inside the pores of the solid to (or away from) the interface due to internal mass emission (output), or *mass diffusivity*; 2) transfer of the same substance from the interface to the flow of liquid (gas, vapor) due to mass emission (output).

The elementary laws that govern the transfer of a substance being distributed from one phase to another are the laws of molecular diffusion, mass emission (output), and mass conductivity.

Molecular diffusion in gases and liquids occurs as a result of the chaotic movement of molecules, not associated with the movement of fluid flows. The transfer kinetics in this case obeys Fick's first law, according to which the amount of substance diffused within the phase is proportional to the concentration gradient, the area perpendicular to the direction of the diffusion flow, and time

$$dM = - D(\partial c / \partial x) dF d\tau, \quad (1)$$

where D – diffusion coefficient.

The basic law of mass emission (output), or convective diffusion, was first formulated by Shchukarev when studying the dissolution kinetics of solids. The amount of substance transferred from the interface to the perceiving phase is proportional to the difference in concentration at the interface and in the core of the perceiving phase, the phase contact surface and time:

$$dM = \beta(c_b^* - c) dF d\tau, \quad (2)$$

where β – mass emission (output) coefficient characterizing the transfer of substance within the phase by convection and diffusion simultaneously; c_b^* – the concentration of the distributed component at the interface of the distributing phase; c – the concentration of the component to be distributed in the core of the flow of the distribution phase.

For the established process, the mass emission (output) equation takes the form:

$$dM = \beta F(c_{гр}^* - c). \quad (3)$$

Due to the complexity of the mechanism of mass emission (output) processes in phases for practical purposes, it is assumed that the rate of mass emission (output) is proportional to the driving force equal to the concentration difference in the core and at the phase boundary.

The mass emission (output) equations for each of the phases are as follows:

$$M = \beta_y F(y - y_{boun}); \qquad M = \beta_x F(x_{boun} - x). \tag{4}$$

where β_y, β_x – mass emission (output) coefficients in the gas and liquid phases; F – the interfacial area; y, x – the concentrations of the target component in the bulk of each phase; y_{boun}, x_{boun} – concentrations of the target component at the interface. The concentration differences included in these equations ($y - y_{boun}$) and ($x_{boun} - x$) are the driving force of the mass emission (output) process, respectively in the gas and liquid phases.

Depending on the method of expressing the composition of phases, the dimensions and numerical values of the mass emission (output) coefficient can be different. If we assume that the amount of the target component is measured in kilograms, then in general terms the mass emission (output) coefficient will be expressed as follows:

$$[\beta] = \left[\frac{kg}{m^2 \cdot s \cdot (unit\ of\ movement)}\right]$$

Due to the complex dependence of the mass emission (output) coefficient on many factors, it is extremely difficult to obtain a generalized dependence for determining the β_y or β_x value. Therefore, in an experimental study of the kinetics of mass transfer processes, the processing and presentation of experimental data are performed using similarity theory methods.

$Nu' = \frac{\beta l}{D}$ – the Nusselt diffusion criterion, which characterizes the similarity of mass transfer processes at the phase interface and is a measure of the ratio of the intensity of the total transfer of a substance (convective and molecular) to the intensity of molecular transfer.

$Fo' = \frac{\tau D}{l^2}$ – the Fourier diffusion criterion characterizing the similarity conditions for unsteady mass emission (output) processes.

$Pe' = \frac{wl}{D}$ – the Péclet diffusion criterion, which is a measure of the ratio of the mass transfer intensities of substance by convection and molecular diffusion in a moving stream.

The Peclet diffusion criterion can be represented as the product of two dimensionless complexes $Pe_D = Re \cdot Pr_D$.

$Pr' = \frac{\mu}{\rho D} = \frac{\nu}{D}$ – the Prandtl diffusion criterion, which characterizes the similarity of the physical properties of the moving carrier medium and is a measure of the ratio of viscosity and diffusion properties in the flow.

Mass transfer in a solid phase system is a particularly complex process. In it, besides the mass transfer from the interface to the liquid flow, there is a movement of the substance in the solid phase - mass diffusivity. As a law that governs the kinetics of transfer of a substance being distributed in a solid, a law has been adopted that is analogous to the law of thermal conductivity: the amount of substance that has moved in the solid phase due to mass diffusivity is proportional to the gradient of concentration, area, perpendicular to the direction of substance flow, and time

$$dM = -K(\partial c/\partial x)dFd\tau. \tag{5}$$

In this equation, the process rate coefficient K is called the mass diffusivity coefficient. The mass diffusivity coefficient is similar to the diffusion coefficient.

To solve the problem of the movement of a substance within a solid phase, the differential equation of mass conductivity must be supplemented by an equation characterizing conditions at the interface between the solid and liquid phases. The elementary site at the interface is supplied with a substance from the solid phase in the amount of dM, which can be determined on the basis of the law of mass conductivity $dM = -K(\partial c/\partial x)dFd\tau$.

From the elementary site, the same amount of substance dM is diverted into the washing phase, which can be determined on the basis of the law of convective diffusion, $dM = \beta(c^*_{boun} - c)dFd\tau$.

Equating the right-hand sides of these equations, we obtain a differential equation characterizing the conditions at the interface: $-K(\partial c/\partial x) = \beta\Delta c$. By dividing the right into the left-hand side of the last equation, we obtain a complex, which is called *the Biot diffusion criterion*

$$Bi' = \frac{\beta \cdot l}{K}. \tag{6}$$

The Biot criterion expresses the ratio of the intensity of substance transfer in the core of the washing phase to the intensity of transfer in a solid material, where mass transfer is associated with mass conductivity.

One of the common mass transfer processes involving the solid phase is adsorption. The values of the mass emission (output) coefficient for the granular adsorbent can be determined by the following equations:

– at the laminar movement (Re < 30)

$$Nu' = 0{,}883Re^{0{,}47}(Pr')^{0{,}33}; \tag{7}$$

– during turbulent motion (Re = 30–150)

$$Nu' = 0{,}53Re^{0{,}54}(Pr')^{0{,}33}. \tag{8}$$

In these equations, the determining geometrical size in the criteria of Nu’ and Re is the equivalent diameter d_{eq}.

To determine the mass emission (output) coefficients β (in s^{-1}) from the vapor – gas mixture flow filtered through the fixed bed of the adsorbent particles to the outer surface of the particles, correlation ratios found on the basis of a generalization of the corresponding experimental data can be used:

$$Nu' = 0{,}515 Re^{0{,}85} (Pr')^{0{,}33},\ Re < 2; \tag{9}$$

$$Nu' = 0{,}725 Re^{0{,}47} (Pr')^{0{,}33},\ Re = 2 - 30; \tag{10}$$

$$Nu' = 0{,}395 Re^{0{,}64} \left(Pr'\right)^{0{,}33},\ Re > 30. \tag{11}$$

Here, Nu’ = $\beta d^2/D$ – the Nusselt diffusion criterion; Re = $4w\cdot\rho/(\sigma\cdot\mu)$ – Reynolds criterion; Pr’ = $\mu/(\rho D)$ – Prandtl criterion; d – the grain diameter of the adsorbent; D – the molecular diffusion coefficient; w – the gas velocity calculated for the free section of the apparatus; μ – the dynamic viscosity of the gas; ρ – the gas density; σ – the specific surface of the particles of the adsorbent.

Questions to control:

1. Write the equation of molecular diffusion (Fick’s first law).
2. Give the wording of the basic law of mass emission (output) (convective) diffusion.
3. Give a comparative analysis of the mass emission (output) equations for the gas and liquid phases.
4. Write the dimension of the mass emission (output) coefficient in general form. What is its physical meaning?
5. Describe the criteria for diffusion similarity.
6. What is the physical meaning of the coefficient of mass diffusivity?
7. Give the Biot diffusion criterion. How is it derived?

Literature:

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