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MASS TRANSFER PROCESSES

WITH A SOLID PHASE PARTICIPATION

Tutorial

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Учебное пособие предназначено для обучения магистров по направлению «Химическая технология» и его содержание соответствует ФГОС 3-го поколения для дисциплины «Процессы массопереноса в системах с участием твердой фазы». Изложенный в учебном пособии материал позволяет студентам восполнить и систематизировать знания по теории массообменных процессов, знакомит со спецификой массопереноса в системах с участием твердой фазы, а также с такими процессами, как адсорбция, ионный обмен, кристаллизация, растворение, мембранное разделение, конструкциями соответствующих аппаратов и методами их расчетов.

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Tutorial is intended for the course «Mass Transfer Processes with a Solid Phase Participation» of Masters Degree Program in «Chemical Technology». Contents of the tutorial introduces students to the fundamentals of mass transfer processes theory and peculiarities of the methods of calculation of adsorption, ion exchange, crystallization, dissolution and membrane separation processes.

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ABBREVIATIONS

a **–** active; adsorption; adsorbent
b – boundary
bd – bulk density
c - convective; concentration
d – diffusion; dynamic
dr - drying
e – equivalent; effective; electric
f – fluid; phase (surface)
fin – final; output
in – initial; input
ion - ionite
id - ideal
L - liquid
lam – laminar

^ - laboratory (frame of reference, etc.)
lw - lower
m – medium; mass; mean
n – nucleus
s – solid; saturated
skc – skipping concentration
skt – skipping time
ss - supersaturated
T – turbulent; thermal; temperature
skti – skipping time (ideal)
up – upper
v - volume

CHAPTER 1.   FUNDAMENTALS OF MASS TRANSFER PROCESSES

1.1.   Mass Transfer Mechanisms and Equations

We can distinguish three mechanisms of transfer: ***molecular, convective and turbulent (eddy).*** Molecular mechanism of transfer is due to the thermal motion of molecules. Interaction between molecules can be imagined roughly as "hard" repulsion at short distances between their centers (ℓ) and "soft" attraction at large distances. A typical view of the potential energy of intermolecular interaction $\varphi(\ell)$ is shown on fig.1.1.
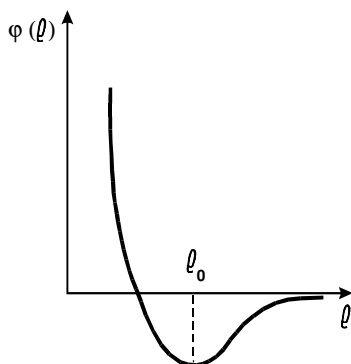
Fig. 1.1. A typical view of an intermolecular interaction potential: ℓ - distance between the centers of molecules

The force of interaction $\mathbf{F = d\varphi/d\ell}$ is negative at distances $\ell < \ell_0$ (repulsion) and is positive if $\ell > \ell_0$ (attraction).

The nature of molecular motion can be different, depending on the phase state of a substance. Molecules in gases move chaotically. A larger share of the time of molecular` movement here constitutes the so called «free path» (collisions free) rundown, i.e. due to the low density of the system the movements of molecules are virtual - without any interaction with each other. Lowering temperature of system leads to the decrease of kinetic energy of molecules. They loose the ability to overcome the intermolecular forces of attraction, and a system condenses – transforms

from the gaseous state into the liquid state. The chaotic nature of molecular motion in this case mainly remains. However, the role of intermolecular interaction becomes much more substantial because of a considerable increase of density, and a large share of the volume of a system is occupied by molecules. As the result, exit of a molecule out of its nearest environment becomes hampered.

Majority of molecular systems transforms into a crystalline state in case of a further lowering of temperature, when the kinetic energy of a molecule becomes not enough to exit a cell, formed by surrounding molecules. From the energy point of view, it leads to the formation of the most advantageous structure of the crystal lattice. Movement of molecules from one node to another is possible only with the help of violations of structure regularity - dislocations, "holes". Thermal motion of molecules within the cell becomes prevailing.

Molecule, moving from one point of space to another, transports all three types of substance parameters (or «substances») - mass, momentum and energy. Visible macroscopic transport of substances is not observed in the conditions of equilibrium, because the transfer of molecules in any direction is equally probable, when system rests and concentrations of components and temperature in all points are of the same value. In the absence of equilibrium, a predominant probability of molecular transfer of masses appears in the direction from a larger values of concentration to a lower, of momentum - from a large values of velocities to a smaller, of energy - from a higher temperature to a lower. This leads to the observed macroscopic phenomena of transfer.

Convective mechanism of substance transfer is caused by the motion of macroscopic volumes of a medium (fluid) as a whole. The characteristic scale of engineering tasks allows you to operate on macroscopic values, that can be specified in each point of space by averaging the microscopic values. The whole set of quantities of physical values, clearly defined at each point of some part of space, is called a field of this value (field of density, concentration, pressure, velocity, temperature, etc.).

The motion of macroscopic volumes of a fluid leads to transfer of mass ρ, momentum $\rho \vec{W}$ and energy $\rho E'$ of a single volume (ρ- density or mass of a unit volume, $\rho \vec{W}$□ - momentum of a single volume, $\rho E'$ - energy of a single volume).

We distinguish free and forced convection according to the causes, which create convective flows. Free convection is due to natural causes and occurs under the action of force of gravity, but forced convection arises as the result of artificial (external) affect, what can be realized with the usage of pumps, compressor machines, by mixing, etc.

Turbulent mechanism of transfer occupies an intermediate place between molecular and convective mechanisms from the point of view of the space-time scale. It is necessary to perform maximum number of conditions for creation of a turbulent motion. So, molecular thermal motion occurs in any system (including the equilibrium systems), which temperature differs from the absolute zero, i.e., almost always. The convective motion is observed only in non-equilibrium systems in case of displacement of macroscopic volumes of the medium. Turbulent motion arises only under the certain conditions of the convective motion: a sufficient distance from a phase boundary and heterogeneity of convective velocity field.

Macroscopic layers move regularly, parallel to each other, in case of a small convective velocity of a medium (gas or liquid) motion with respect to a phase boundary. This kind of movement is called *laminar*. Incidental or artificial small perturbations, arising in real conditions, impact the regularity of movement (roughness of a surface, limiting the flow, etc.) and do not increase over time, but, on the contrary, dampen. However, the sustainability of the motion with respect to small perturbations is violated if heterogeneity of velocity and distance from a boundary of the phase exceed a certain value. Therefore begins the development of irregular chaotic movement of individual volumes of the medium (vortices). This movement is called *turbulent.*

Here are introduced the values, characterizing turbulent motion, which are analogous to the characteristics of molecular movement, where are used mean square speed of molecules and their size. The notion of the scale of turbulence, which determines the size of vortices, is used too. In contrast, for example, of molecules, vortices are not sustainable, clearly limited in space formations. They arise, break down into smaller vortices and vanish up with the transition of energy to heat (dissipation of energy). Therefore, the scale of turbulence - is an averaged statistical value. And turbulent vortex (vortex flux) carries out all kinds of transfer - mass, momentum and energy - similarly to the random motion of molecules.

Equations of transfer. Let us consider the local equations of mass transfer, i.e., equations that are true for each point of space. The examination is conducted at macroscopic level - all used values are macroscopic. The task is to obtain a mathematical expression for *mass flux* (quantity of mass, transferred per unit of time through a unit surface area) under the action of various transfer mechanisms.

Convective mechanism. Flow of mass (**m**) for the account of convective mechanism in any point of a system in the laboratory (**^**) frame of reference $\wedge \vec{j}^m$ is connected with convective speed:

$$\wedge \vec{j}^m = \rho \wedge \vec{W}, \quad \text{kg/m}^2\text{s.} \qquad (1.1)$$

In case of multi-component environment we can consider the flow of mass of each component:

$$\wedge \vec{j}_i^m = \rho_i \wedge \vec{W}, \qquad (1.2)$$

where *i* is a number of components, ρ_i - density of component *i*.

Often it is more convenient to use the flow of substance, and not of mass:

$$\wedge \vec{j}_i = \wedge \vec{j}_i^m \Big/ m_i = c_i \wedge \vec{W}, \quad \text{kmol/m}^2\text{s,} \qquad (1.3)$$

where m_i - mole mass of component *i*, kg/kmol; c_i - mole concentration, kmol/m³. Note that convective velocity and flow are analyzed in the laboratory system of reference, i.e. relative to the reference frame, associated with a device. Convective velocity relative to a machine in the conditions of hydro-mechanical equilibrium is not only a constant value, but the constant value, equal to zero.

Molecular mechanism. Actually molecular mechanism of mass transfer can be observed in thermodynamically equilibrium system, where are present only the gradients of concentration of marked particles of the sort *i* (**i'** - isotopes of molecules of the sort *i*):

$$\wedge \vec{j}_{i'} = -D_i \vec{\nabla} c_{i'} \qquad (1.4)$$

The sign «minus» testifies to the opposite direction of vectors of substance flow and gradient of concentration. Gradient of concentration

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