Lecture 12 «Adsorption. Balance between phases. Material balance of process of adsorption. Kinetics of adsorption»

Aim: Formulate the adsorption and balance between phases. Describe the material balance of process of adsorption. Explain the kinetics of adsorption.

Lecture summary: Adsorption is the process of selective absorption of one or several components of a gas or liquid mixture by the surface of a solid absorber (adsorbent).

The absorbed component (AC) contained in a continuous environment (gas, liquid) is called the adsorbtive contained in the sorbent – adsorbate.

The adsorption process is accompanied by the release of heat, the value of which depends on the nature of the interaction of adsorbed molecules with the surface. According to this, physical and chemical adsorption are distinguished.

Physical adsorption is due to the action of van der Waals forces. The amount of heat released during adsorption roughly corresponds to the evaporation heat values (1-5 *kcal*/*mol* for simple molecules and 10-20 *kcal*/*mol* for large molecules). Physical adsorption – a reversible process. Chemical adsorption – an irreversible process. The amount of heat released during chemical adsorption is close to the amount of heat of the chemical reaction (10-100 *kcal*/*mol*). Chemical adsorption increases with increasing temperature, physical adsorption decreases with increasing temperature – desorption occurs.

Adsorption is used to purify gas (liquid) mixtures from undesirable impurities or to isolate this impurity as a target product; optimal is the realization of both objectives together, i.e. approach of technology to wasteless. Due to selectivity of absorption of various components, adsorption is one of the effective separation processes. At the same time, it constitutes one of the stages of carrying out a heterogeneous chemical reaction, catalytic or non-catalytic.

After adsorption, the adsorbent is desorbed. This allows you to extract AC (often – the target product) from the sorbent and reuse the sorbent released from it. To do this, it is necessary to activate the sorbent to restore its adsorption properties. The stages of desorption and activation of the adsorbent are its regeneration.

Adsorption is widely used in chemical technology:

- for drying of gases and their purification with allocation of target components;
- for extraction (regeneration) of solvents from gas or liquid mixtures;
- for clarifying solutions;
- for cleaning gas emissions and waste water;
- for analytical purposes (chromatography method).

The success of the adsorption process is largely determined by the choice of adsorbent.

Basic requirements for adsorbents:

- selectivity;
- possible high absorption capacity;
- acceptable cost and availability;
- ease of desorption and regeneration;
- high mechanical strength;
- convenience in work;
- incombustibility, low erosive impact on the elements of equipment.

In accordance with the requirement of high absorptivity, adsorbents – most often highly porous solids used in the form of grains ranging in size from a fraction of a millimeter to several millimeters.

Depending on the size, micropores, intermediate pores (mesopores), macropores are distinguished. Micropores include pores with a radius of up to 20 $Å$ (1 $Å = 10^{-10}$ m), they are commensurable with the size of AC molecules. The specific surface area ranges from several hundred to 2000 m^2/h.

Intermediate pores with a radius of 20 to 1000-2000 $Å$ are considered; the specific surface area is from 10 to 500 m^2/h. It is believed that the mesopores perform two roles: the proper adsorption and transport (transfer of AC molecules to micropores).

Macropores (their radius exceeds 2000 $Å$) differ by a small specific surface (up to several square meters per gram). Their main role – transport: the transfer of AC to micro- and mesopores.

The most common industrial sorbents include: activated carbons (AC), silica gels and alumogels, zeolites, ion exchangers.

Equilibrium between phases

During adsorption, gas or vapor molecules concentrate on the surface of the adsorbent under the influence of molecular forces of attraction. This process is often accompanied by chemical interaction, as well as condensation of steam in the capillary pores of the solid adsorbent. There is no generally accepted theory of adsorption. According to the widespread view, adsorption occurs under the action of electrical forces caused by interaction of charges of molecules of the adsorbent and the substance being placed. According to another theory, adsorption forces are of a chemical nature, and their nature is explained by the presence of free valences on the surface of the adsorbent.

Regardless of the nature of the forces that cause adsorption, with sufficient contact time of the phases, an adsorption equilibrium occurs, at which a definite relationship is established between the concentration of the adsorbed substance X (in *kg*/*kg* of the adsorbent) and its Y concentration in the phase contacting with the adsorbent:

$$X = AY^{1/n}, \tag{1}$$

where Y – the equilibrium concentration (*kg*/*kg* of the inert part of the vapor-gas mixture or solution); A and n – coefficients determined experimentally, with $n \geq 1$.

Dependence (1) corresponds to a certain temperature and is depicted by a curve, which is called *the adsorption isotherm*. The adsorption isotherms of some substances are shown in Fig. 1.

The concentration of the adsorbed substance in the mixture at constant temperature is proportional to its pressure. Therefore, the equation (1) can be represented in the form

$$X = A_1 P^{1/n}, \tag{2}$$

where A_1 – the proportionality coefficient; P – the equilibrium pressure of the absorbed substance in the vapor-gas mixture.

The main factors influencing the course of the adsorption process are: the properties of the adsorbent, temperature, pressure, properties of the substances absorbed and the composition of the phase from which they are adsorbed.

The equilibrium concentration X decreases with increasing temperature and increases with increasing pressure. Thus, adsorption accelerates with decreasing temperature or with increasing pressure.

The same factors influence the desorption process, which is usually carried out after adsorption, in the opposite direction. Desorption is accelerated with an increase in the temperature of the adsorbent and a decrease in the pressure above it, as well as when passing through the adsorbent the vapors that displace the absorbed substance.

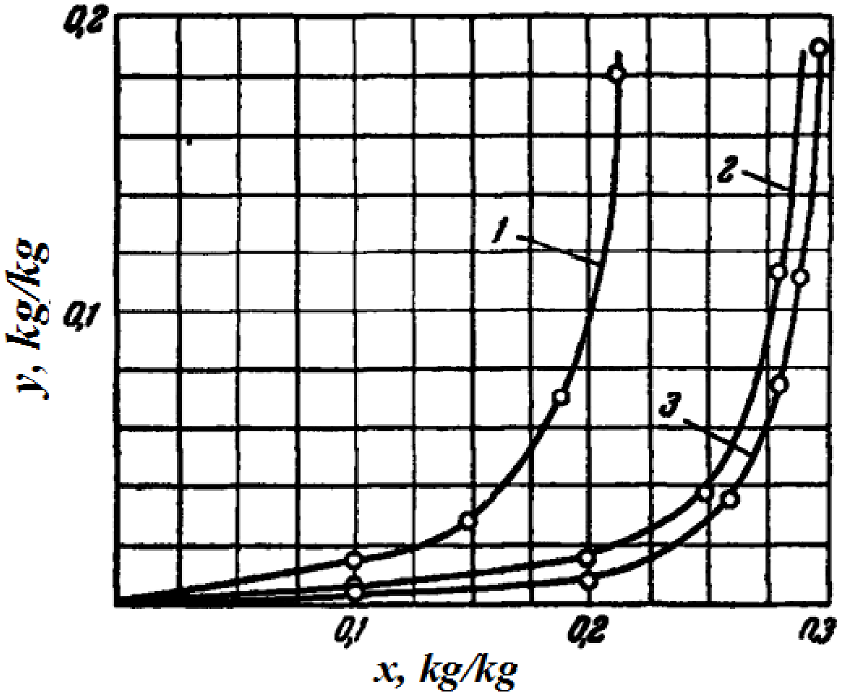

Fig. 1. Adsorption isotherms (at 20 °C):
1 – for ethyl ether; *2* – for ethyl alcohol; *3* – for benzene

Adsorbents are characterized by *static* and *dynamic* activity. After a certain period of work, the adsorbent ceases the completely absorb the extracted component and begins to “slip through” the component through the adsorbent bed. From this moment, the concentration of the component in the off-gas vapor mixture increases until equilibrium is reached.

The amount of substance absorbed by a unit of weight (or volume) of the adsorbent during the time from the beginning of adsorption to the onset of a “slip through” determines *the dynamic activity* of the adsorbent. The amount of substance absorbed by the same amount of adsorbent during the time from the onset of adsorption to the establishment of equilibrium, characterizes the *static activity*.

The activity of the adsorbent depends on the gas temperature and the concentration in it of the absorbed component. The consumption of adsorbent is determined by its dynamic activity, since dynamic activity is always less than static activity [2].

Material balance of adsorption process

Adsorption processes are carried out periodically or continuously. If the adsorbent moves through the apparatus, adsorption occurs continuously and the material balance of the process is expressed by equation, which is common for all mass transfer processes.

Adsorption in a layer of a fixed adsorbent is a periodic (batch) process in which the concentration of the absorbed substance in the adsorbent varies in time and in space. Assume that the gas (in the amount G per unit time), passing through the time $d\tau$, the adsorbent layer with a height dh, changes its concentration by a value dy and, consequently, gives the substance in an amount

$$Gdyd\tau \tag{3}$$

At the same time, the concentration of the absorbed substance in the layer element increases by dx, and the amount of substance absorbed by the layer with a height dh at the cross-sectional area of sorbent S will be

$$dhSdx\rho_{bulk}, \tag{4}$$

where ρ_{bulk} – the bulk weight of the adsorbent.

Then the equation of material balance will have the form:

$$-Gdyd\tau = Sdh\rho_{bulk}dx \tag{5}$$

or

$$dy = -\frac{S\rho_{bulk}dh}{Gd\tau}dx \tag{6}$$

Kinetics of adsorption

Adsorption refers to the processes of mass exchange occurring with the participation of the solid phase. Within the solid phase, the substance moves due to mass conductivity.

But experience shows that the internal diffusion resistance of the sorbent can be neglected, the calculation of the process of mass exchange during adsorption can be carried out using the equation of convective diffusion. The mass emission coefficient is determined from the following equations:

1) for a granular adsorbent under laminar motion (Re <30)

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

2) under turbulent motion (Re 30 ÷ 150)

$$Nu'_g = 0{,}53Re^{0{,}54}\left(Pr'_g\right)^{0{,}3} \tag{8}$$

In these equations, the defining geometric dimension in the criteria Nu'_g and Re is the equivalent diameter (d_{eq}), calculated from equation $\frac{l\rho w}{\mu} = \mathrm{Re}$.

3) for a fine-grained adsorbent in the fluidized bed

$$Nu'_g = 46{,}25 \cdot 10^{-6} Re_0^{1{,}67} \quad (9)$$

In equation (9) Re_0 is determined by the formula $Re = w\rho d/\mu = wd/\nu$. To determine the mass emission coefficient, the formula (10) is used:

$$Nu'_g = \frac{\beta_{vol} d^2}{D_г}, \quad (10)$$

where β_{vol} – the volume mass emission coefficient, kg/m^3·s·kg/m^3 or *1/s*; d – the average grain diameter, *m* (which is also the determining geometrical dimension in the *Re* criterion); D_g – the diffusion coefficient in the gas phase, m^2/s.

Questions to control:

1. What are the most rational application fields of adsorption?
2. Describe the main industrial adsorbents.
3. Expand the essence of the static and dynamic activity of adsorbents.
4. Describe the equilibrium in adsorption.
5. How is the material balance of adsorption compiled?
6. Explain the features of the kinetics of the process of equilibrium adsorption.
7. What devices exist for the industrial implementation of adsorption processes?
8. List the methods for regenerating adsorbents.

Literature

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