Lecture 9 «Absorption. Physical bases of absorption process. Influence of temperature and pressure upon absorption process. Material balance of absorption. Absorbing devices»

Aim: Characterize the absorption and physical bases of absorption process. Formulate the influence of temperature and pressure upon absorption process. Describe the material balance of absorption. Characterize the absorbing devices.

Lecture summary: Absorption is the process of selective extraction of one or several components from a gas mixture with a liquid absorber (absorbent). The reverse process – the release of dissolved gases from the absorbent is called desorption.

Absorption processes involve two phases – liquid and gas. When they are in contact, one component (or several) passes from one phase to another. In the presence of a component (components) practically insoluble in the liquid phase in the gas phase, they are called an inert, or carrier gas. A dissolving component – an absorbed component.

In the absence of chemical interaction between the absorbed component and the absorbent, the process is called physical absorption, and in the presence of such interaction – chemisorption.

Absorption is very widely used in the chemical and allied industries. Absorption is used to extract valuable (target) components from the gas mixture, and to purify gas mixtures from impurities before using them in technological processes or before their release into the atmosphere.

In modern industrial practice, the importance of the absorption process is very great for the creation of wasteless technologies.

The main problems in the implementation of absorption are associated with the selection of absorbent and the creation of rational conditions for contacting gas and liquid.

When choosing an absorbent, there are a number of requirements:

1) selectivity, i.e. the ability to selectively absorb the extracted component with the possible minimum solubility in it of the carrier gas;

2) high absorptivity, otherwise high solubility of the absorbed component in the liquid phase under operating conditions (reduces absorbent consumption);

3) possibly lower volatility, i.e. low elasticity of absorbent vapors at operating temperature in order to avoid its losses with the outgoing gas;

4) stability in operation, i.e. the absorbent should not be subjected to changes – decomposition, oxidation, molding, etc.;

5) convenience in work – non-toxicity, incombustibility, low corrosive effect on the equipment;

6) availability and cheapness;

7) easy regenerability during desorption.

Industrial absorbents do not fully meet all of these requirements at the same time. Therefore, in practice, the absorbents are selected from the process conditions (properties and composition of the gas mixture, gas temperature and pressure, the required degree of purification, etc.).

Physical bases of the process of absorption

In the processes of physical absorption, at least three components are involved: two carrier – substances (gas and liquid) and a component that goes from one phase to another. The system of two phases ($\phi = 2$) with the total number of components $k = 3$ according to the phase rule has three degrees of freedom applied to the equilibrium state:

$$\varphi = k - \phi + 2 = 3 + 2 - 2 = 3 \qquad (1)$$

With complete insolubility of the inert in the absorbent and low volatility of the latter, the composition of the phases will be completely characterized by the concentrations of the absorbed component in each of the phases: x – in the liquid phase and y – in the gas phase. The parameters of the equilibrium state of the system are also the temperature and pressure at which this system is located.

Thus, the total number of variables of the equilibrium system is 4. For $\varphi = 3$, three variables can be chosen arbitrarily – according to the conditions of the technological process, and the fourth one will be dependent.

For example, you can arbitrarily choose the temperature and pressure, as well as the concentration of the absorbed component (AC) in the liquid (x). Then for such a system the equilibrium concentration of this component in the gas phase (y^{eq}) will be quite definite. Such a dependence of y on x at a certain temperature and pressure is called the equilibrium curve – the equilibrium line, or the curve of equilibrium (Fig. 1).

$$y^* = f(x) \qquad (2)$$

Let a point A characterizing the working (non-equilibrium) state of the contacting phases lie above the equilibrium lines. Then, when the system approaches equilibrium (in the direction of arrow *1*), the concentration of the absorbed component in the gas phase will decrease, and in the liquid phase – it will increase.

Such a change in the concentration of AC in the phases corresponds to the absorption process. This means that all points lying above and to the left of the equilibrium line form the absorption region. Now let the operating state of the system be characterized by a point D (of concentration x' and y') located below the equilibrium line. Here, on the contrary, when it tends to the equilibrium state (in the direction of the arrow *2*), the concentration of the absorbed component in the liquid phase decreases and its increase in the gas phase, i.e. there is a desorption process. The working area, located below and to the right of the equilibrium line, is called the desorption region.

These curves are also called absorption isotherms. If the temperature of the system t is changed to t_1, then the new AC value in the liquid x will correspond to a new value y_1^{eq}, to the value x' – the value $y_1'^{eq}$. With increasing temperature ($t_1 > t$), the solubility of the absorbed component (gas) in the liquid decreases.
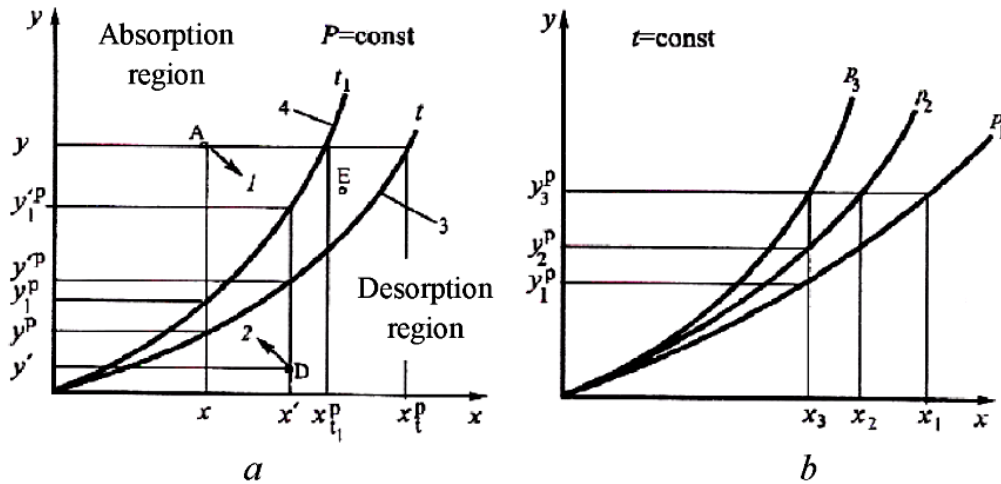
Fig. 1. Phase-balance diagrams of gas – liquid:
a – for p = const, b – for t = const

If the point characterizing the operating state of the system lies between two isotherms *3* and *4*, for example point *E* (Fig. 1), then in such a system absorption will take place – at temperature *t* (absorption region under isotherm *3*) or desorption – at temperature t_1 (desorption region under isotherm *4*). Therefore, by affecting the temperature of the system, it is possible to change the direction of the "absorption-desorption" process.

Let us now consider the effect of the total pressure *P* in the gas-liquid system on the equilibrium distribution of the components between the phases. For small concentrations of the solution (when the gas in the liquid dissolves poorly), Henry's law can be applied, according to which the equilibrium partial pressure of the component in the gas phase above the liquid is proportional to the content of the dissolved gas in the liquid:

$$p^* = \psi x, \tag{3}$$

where p^* – the equilibrium partial pressure of the component in the gas, *mmHg*; ψ – the Henry constant (having the dimension of pressure); x – the dissolved gas content in the solution (kg/kg absorber).

Henry's constant characterizing the solubility of gases in a liquid, it depends on the properties of the dissolved gas and absorber, and also on the temperature. The temperature dependence with some approximation is expressed by the equation:

$$ln\psi = c - \frac{q}{RT}, \tag{4}$$

where q – the heat of dissolution of the gas, *kcal/kgf·mole* of dissolved gas; R – the gas constant; c – the experimental constant.

If the gases are highly soluble and form solutions of high concentration, and gases are under pressures measured in tens of atmospheres, the equilibrium does not follow Henry's law.

For technical calculations, the values of the equilibrium partial pressure of the gas *P** obtained from the experiment are used and the equilibrium content of the component in the gas mixture is calculated from formula

$$y^* = \frac{M_c}{M_{car}} \cdot \frac{p^*}{P - p^*}, \tag{5}$$

where M_c – the molecular weight of the component; M_{car} – the molecular weight of the carrier; P – the total gas pressure over the liquid, *mmHg*.

Material balance and kinetic laws of absorption

The material balance and the working line of the absorption process are characterized by the equations of the material balance of mass exchange and the working line of the mass exchange process.

Kinetic regularities correspond to the general mass transfer equation for two-phase systems

$$M = \beta_y(p - p^*)F, \tag{6}$$
$$M = \beta_x(C^* - C)F, \tag{7}$$

where β_y, β_x – the mass emission coefficients for the gas and liquid phases; p – the partial pressure of the absorbed component in the gas mixture; p^* – the equilibrium partial pressure of the absorbed gas at the interface; C – the concentration of dissolved gas in the liquid; C^* – the equilibrium concentration of the absorbed component in the liquid at the interface; F – the phase interface; M – the amount of gas absorbed.

For systems that obey Henry's law, the equilibrium values p^* and C^* according to Henry's law are related by the relation

$$p^* = \psi C^*, \text{ then } p^* = \psi C \tag{8}$$

Solving jointly equations (6) and (7), we obtain the mass transfer equation for the expression of the driving force through the pressure difference:

$$M = K_y F(p - p^*), \tag{9}$$

where K_y – the total mass transfer coefficient associated with the mass emission coefficients β_y and β_x by the following relation

$$K_y = \frac{1}{\frac{1}{\beta_y} + \frac{\psi}{\beta_x}} \tag{10}$$

Similarly, expressing the driving force through the difference in concentrations, we obtain

$$M = K_x F(C^* - C), \tag{11}$$

where

$$K_x = \frac{1}{\frac{1}{\beta_x} + \frac{1}{\psi \beta_y}} \tag{12}$$

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Absorption devices

Apparatus, in which absorption processes are carried out, are called absorbers. When absorbed, the mass transfer process takes place at the interface of the phases. Therefore, the absorbers must have a developed contact surface between the liquid and the gas. By the way this surface is formed, the absorbers can be conditionally divided into the following groups: 1) surface and film; 2) packed; 3) bubbling (poppet); 4) spraying.

Surface and film absorbers. In absorbers of this type, the contact surface of the phases is a mirror of a stationary or slowly moving liquid, or the surface of a current liquid film.

In surface absorbers, the gas passes over the surface of a stationary or slowly moving liquid (Fig. 2).
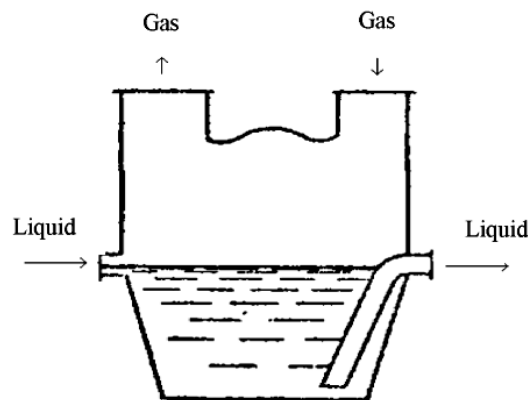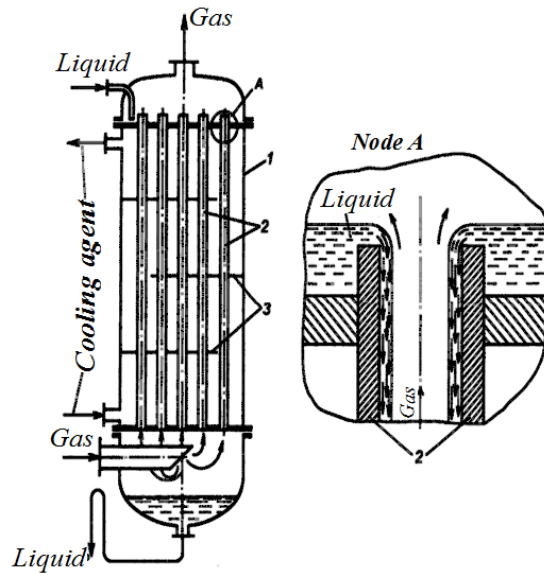

Fig. 2. Surface absorber

Surface absorbers are used to absorb highly soluble gases (for example, to absorb hydrogen chloride with water). Since the contact surface in such absorbers is small, several sequentially connected apparatuses are installed in which the gas and liquid move countercurrent to each other. Surface absorbers have limited application due to their low efficiency and cumbersomeness.

Film absorbers are more efficient and compact than surface absorbers. In film absorbers, the contact surface of the phases is the surface of the current liquid film. Ehe following types of apparatus of this type are distinguished: 1) tubular absorbers; 2) absorbers with a plane-parallel or sheet nozzle; 3) absorbers with an upward movement of the liquid film.

The tubular absorber (Fig. 3) is similar in structure to the vertical casing tubular heat exchanger.

Fig. 3. Tubular film absorber:
1 – housing; *2* – tubes; *3* – partitions

The absorbent enters the upper tube plate, is distributed along the tubes *2* and drains along their inner surface in the form of a thin film. In apparatuses with a large number of pipes, special distribution devices are used to distribute the allocation of liquid more evenly through the pipes. The gas moves along the pipes from below upwards towards the flowing liquid film. To remove the heat of absorption through the intertubular space, water or another cooling agent is passed through.

Absorbers with a plane-parallel nozzle (Fig. 4). This apparatus is a column with a sheet nozzle *1* in the form of vertical sheets of various materials (metal, plastic masses, etc.) or tightly stretched materials from the fabric. In the upper part of the absorber there is a distribution device *2* for uniform wetting of the sheet nozzle on both sides.
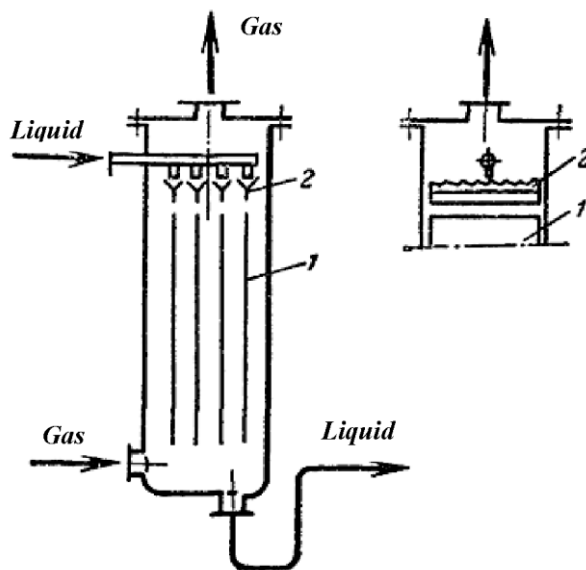
Fig. 4. Absorber with plane-parallel nozzle:
1 – sheet nozzle; *2* – distributive device

Absorbers with an upward movement of the film (Fig. 5) consists of pipes *1* fixed in tube grids *2*. The gas from chamber *3* passes through pipes *4* arranged coaxially with tubes *1*. The absorbent enters the tubes through the slits *5*. The gas moving at a sufficiently high velocity drags the liquid film in the direction of its movement (from the bottom up), i.e. the device operates in the mode of ascending direct flow.

On leaving the pipe *1*, the liquid is drained onto the upper tube plate and discharged from the absorber. A coolant is passed to remove heat of absorption through the intertube space. In apparatus with an upward movement of the film, due to the high velocities of the gas flow (up to 30-40 m/s), high values of the mass transfer coefficients are achieved, but, at the same time, the hydraulic resistance of these devices is relatively large.
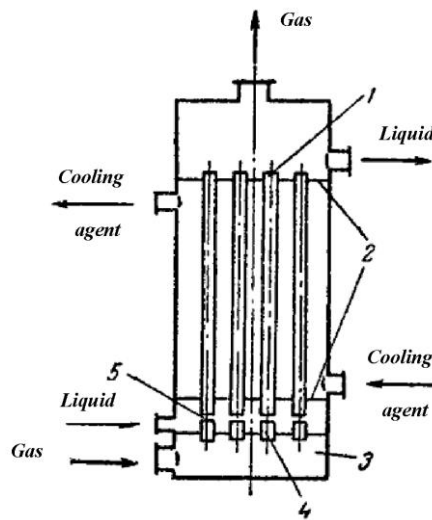

Fig. 5. Absorbers with ascending motion of a liquid film:
1 – pipes; *2* – pipe grid; *3* – the chamber; *4* – a branch pipe for gas supply;
5 – slot for absorbent supply

Packed absorbers. The packed absorbers have found the greatest application in the industry with the absorption of gases by liquids. They are columns loaded with a nozzle, solid bodies of various shapes, through which the liquid flows down from above, towards the rising gas.

As a nozzle, the so-called Raschig rings (thin cylinders, whose height is equal to their diameter) are widely used in the size of 15-150 mm. The rings are made of ceramics, porcelain and less often of steel. In the apparatus, Rashig rings are laid in bulk or in regular rows (with a diameter $d > 50$ mm). The main characteristics of the nozzles are the specific surface area σ (m²/m³) and free volume ε (m³/m³).

To prevent the liquid from spreading to the walls, the nozzle is covered in separate layers (the height of each layer is 1.5-3 m), between which the guide cones are installed.

The packed absorbers, depending on the fluid and gas flow regime, can operate in different hydrodynamic regimes. These modes are visible from the graph (Fig. 6), which expresses the dependence of the hydraulic resistance of the irrigated nozzle on the fictitious gas velocity in the column.
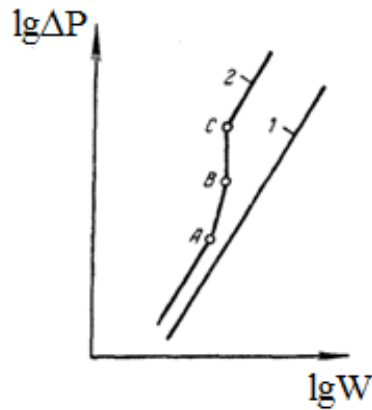
Fig. 6. Dependence of the hydraulic resistance of the nozzle on the gas velocity in the column ($L = $ const): *1* – dry nozzle; *2* – irrigated nozzle

The first mode – *film mode* – is observed at low irrigation densities and low gas velocities. The amount of liquid retained in the nozzle under this regime is practically independent of the gas velocity. The film mode ends at the first transition point (point *A*, Fig. 6), called the hang point.

The second mode – *the hang-up mode*. When the phases are counter-current due to an increase in the frictional forces of the gas against the liquid, there is a brake of a liquid by a gas stream. As a result, the flow velocity of the liquid decreases, and the thickness of its film and the amount of liquid retained in the nozzle increases.

In the hang-up mode with increasing gas velocity, the moistened surface of the nozzle increases and, accordingly – the intensity of the mass transfer process. This mode ends at the second transition point (point *B*, Fig. 6), and in the suspending mode the calm flow of the film is disturbed: vortices appear, splashes appear, i.e. conditions for the transition to bubbling are created. All this contributes to an increase in the intensity of mass exchange.

The third mode – *the emulsification mode*. In these conditions, the liquid occupies the entire free volume of the nozzle, which is not occupied by gas. The liquid is a continuous phase, and the gas is a dispersion phase. The role of the nozzle is reduced to the fragmentation of gas vortices into a large number of small vortices piercing the liquid, to distribute them throughout the entire column section, and the swirling of the liquid itself.

By carefully adjusting the gas supply, the emulsification mode can be set at the entire height of the nozzle. The hydraulic resistance of the column thus increases sharply (in Fig. 6, this mode is characterized by an almost vertical segment *BC*).

The fourth mode – the mode of *entrainment*, or reversed motion of the liquid, carried from the apparatus by a gas stream. This mode is not used in practice.

Bubbling (poppet) absorbers. In bubbling absorbers, the gas is distributed in the liquid in the form of bubbles, on the surface of which absorption takes place. The most common absorbers are in the form of columns with cap and sieve plates (Fig. 7 and 8).
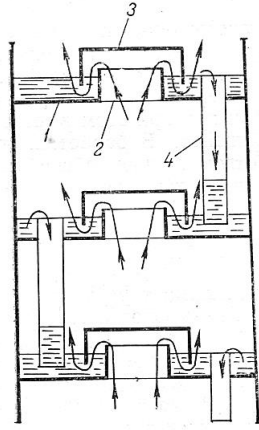
Fig. 7. Column with cap plates:
1 – plates; *2* – branch pipes;
3 – caps; *4* – overflow pipes
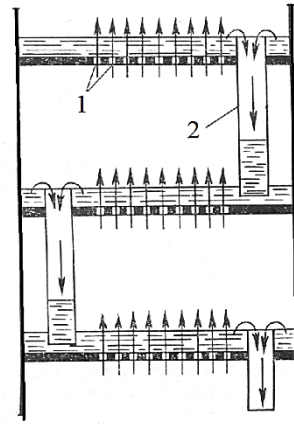
Fig. 8. Column with perforated
plates: *1* – holes; *2* – overflow pipes

Captive plates are equipped with nozzles, covered with caps. Gas passes through a layer of liquid, the level of which on the plate is supported by overflow tubes. The lower ends of the overflow tubes are lowered to the level of the liquid of the next plate, so that a hydraulic seal is created to prevent the passage of gas through the overflow tubes. The liquid from the plate to the second plate flows over the overflow pipes. The number of caps on a plate is not the same in different columns.

Sieve plates have holes (2-5 *mm* in diameter) through which gas flows. The liquid on plates with a height of about 25-30 *mm* is determined by the position of the upper ends of the overflow tubes, is supported from below by gas pressure and flows to the next plate only over the overflow pipes.

Bubbling absorbers are complex in design and have high hydraulic resistance caused by a large amount of gas being passed. Therefore, bubble absorbers are used mainly in those cases when absorption is carried out under increased pressure, since at the same time high hydraulic resistance is insignificant. In bubbler absorbers, the removal of the heat of absorption can be carried out with the help of coils installed on the plates of the column, through which the coolant is passed.

Spraying absorbers. In spray absorbers, the contact surface of the phases is created by spraying the liquid into small droplets in the mass of the gas. Spraying the liquid is done from above, and the gas moves from the bottom up. Spraying absorbers are used to absorb highly soluble gases.

Spraying of liquid is carried out by mechanical or pneumatic nozzles or centrifugal sprayers. Pneumatic injectors operate under the influence of compressed air or steam under excess pressure up to 5 *atm*. Centrifugal sprayers are made in the form of discs rotating at high speed. The speed of the discs is 4000-20000 *rpm*.

The injection absorbers operate at low gas velocities (1-1.5 *m/s*) and irrigation densities of at least 0.003 *m³/(m²·s)* [2, 3].

Questions to control:
1. Explain the principles of absorption and desorption processes. To solve what practical problems are these processes used?
2. Formulate Henry's law. For which systems is this law applicable?

3. How is the material balance of absorption compiled? Explain the notion of the working line of absorption and desorption processes.

4. How does the change in temperature and pressure in the system affect the position of the equilibrium line?

5. List the main requirements for absorption devices. Give them a classification.

6. Expand the principle of the action of film absorbers. In what cases is the use of these devices the most rational?

7. Give a comparative description of packed, bubbling and spraying absorbers.

Literature

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