Lecture 10 «Distillation. Characteristic of two-phase systems liquid-steam. Simple distillation. Distillation with water vapor»

Aim: Characterize the distillation process and types of distillation. Formulate the material balance is simple distillation. Describe the steam distillation.

Lecture summary: In chemical technology, petrochemical and a number of other industries (food, pharmaceutical, metallurgical) use a wide variety of liquid and gas mixtures to be separated into sufficiently pure components or fractions of different composition. The separation of such mixtures, accompanied by a redistribution of the components between the phases upon contact of the liquid and vapor phases, is called distillation. At the basis of the distillation lies the varying volatility of the components of the mixture, which has a different propensity to transition from the liquid phase to the vapor phase (or from the vapor phase to the liquid phase). Different propensities of the components of the mixture to the transition to the vapor (or liquid) state are due to the difference in their boiling point (condensation).

The possibility of enriching the vapor or liquid phase with a component is at the basis of separation processes by distillation and rectification methods, united under a common name as distillation processes. During distillation, all the components of the mixture pass to the vapor state in quantities proportional to their fugacity (volatility). When the mixture is separated by a distillation process, the steam contains a relatively large amount of a volatile or low boiling point component (LBC) than the original mixture.

Consequently, during the distillation process, the liquid phase is depleted, and the vapor phase is enriched by the LBC. An unevaporated liquid naturally has a composition that is richer in a non-volatile, or high-boiling component (HBC).

This liquid is called the residue, and the liquid obtained as a result of the condensation of the vapors – a distillate or rectificate.

The degree of enrichment of the vapor phase of the LBC, other things being equal, depends on the type of distillation: distillation and rectification.

Distillation is the process of separation of a mixture of volatile liquids into components or fractions of various compositions by evaporation and subsequent condensation of the formed vapors.

Distillation is subdivided into simple distillation and equilibrium distillation. Simple distillation refers to the process of a single partial evaporation of a boiling liquid mixture with continuous evacuation and condensation of the formed vapors.

Equilibrium distillation is characterized by evaporation of a part of the liquid and prolonged contact of the formed vapors with an unevaporated liquid until phase equilibrium is reached.

To achieve a more complete separation of components, a more complex type of distillation, rectification, is used. Rectification – the process of separating homogeneous mixtures of volatile liquids by two-way mass and heat exchange between nonequilibrium liquid and vapor phases having different temperatures and moving relative to each other.

The main and cardinal difference in the processes of distillation and rectification is as follows: distillation is a non-counterflow process, rectification is essentially counter-current process.

Physico-chemical basics of the distillation processes

Composition and properties of mixtures. In systems subjected to distillation, as a rule, there is no inert that does not pass from phase to phase: all the components participate in different phases in the interfacial exchange. Therefore, there is no reason to use relative concentrations based on constant flows (amounts) of inert; the absolute concentrations – mole and mass – are applied.

The phase rule and equilibrium in liquid-vapor systems. With an infinitely long contact between the liquid and vapor phases, an equilibrium is established between them in an isolated system. In this case, two intensive parameters in the existing phases –

temperature and pressure (vapor pressure), as well as the chemical potentials of each of the components are equalized. Because these potentials are inconvenient to use for practical purposes, they pass to concentrations: instead of equal chemical potentials of components operate with their equilibrium concentrations in the liquid and vapor phases.

If the system consists of two components ($C = 2$) and there is no chemical interaction between them, then in the presence of liquid and vapor phases, the number of phases is $\phi = 2$. According to the phase rule, the number of degrees of freedom of such a system is:

$$NDF = C + 2 - \phi = 2 + 2 - 2 = 2 \tag{1}$$

Hence, in the general case, two limitations can be imposed (set), for example, the pressure and composition of the liquid mixture, and the remaining quantities (boiling point and composition of the vapor mixture) can not be varied. They will take certain values that meet the accepted restrictions. It also answers that for a given pressure and boiling point, the liquid and vapor phases have quite definite compositions.

Classification of binary mixtures. Depending on the mutual solubility of the components, mixtures of liquids are distinguished: 1) with unlimited mutual solubility; 2) mutually insoluble; 3) limitedly soluble in each other. Mixtures with unlimited mutual solubility of components in turn are divided into ideal and real mixtures.

Ideal mixtures are called, the components of which do not change the volume when mixing, and the mixing itself occurs without the thermal effects of the interaction of the components. Ideal mixtures obey Raoult's law, according to which the equilibrium partial pressure (vapor pressure) of an *i*-component over a mixture at a certain temperature is equal to the product of its vapor pressure over a pure component at the same temperature by its mole fraction in the liquid mixture (x_i):

$$P_i = P_i^0 \cdot x_i \tag{2}$$

The sum of the partial pressures of all components of the vapor mixture is equal to the total (working, external) pressure P:

$$P = \Sigma P_i = \Sigma P_i^0 \cdot x_i \tag{3}$$

For a binary mixture consisting of components *A* and B according to Raoult's law

$$p_A = P_A^0 x_A \quad \text{and} \quad p_B = P_B^0 x_B = P_B^0 (1 - x_A) \tag{4}$$

At the same time, according to Dalton's law, the total vapor pressure over the solution P is equal to the sum of the partial pressures of its components:

$$P = p_A + p_B = P_A^0 x_A + P_B^0 (1 - x_A) \tag{5}$$

From the equations expressing the laws of Raoult and Dalton, it can be seen that, at a constant temperature, the partial pressures of the components, as well as the total vapor pressure over the mixture, are linearly related to the mole fraction x_A of the low-boiling component.

For physicochemical characteristics of binary liquid-vapor systems, it is convenient to use the so-called *phase* diagrams (Fig. 1 and 2).
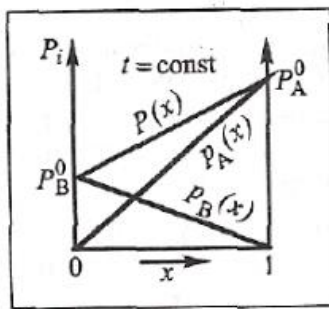

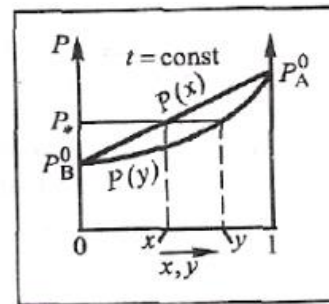**Fig. 1.** To the Raoult's law for ideal binary systems

Fig. 2. Dependences of $P(x)$ and $P(y)$ and equilibrium concentrations for ideal binary systems

According to (5), the quantity $x = 1$ corresponds to $P = P_A^0$ (pure low-boiling component A), and $x = 0$ corresponds to $P = P_B^0$ (pure high-boiling component B).

In the overwhelming majority of cases, the distillation processes are carried out at constant pressure. Therefore, technologists are more interested in isobaric dependencies and diagrams of the type $t(x)$ and $t(y)$.

At $t = t_B$, we have $P = P_B^0$ and we get $x, y = 0$ – pure HBC. For $t = t_A$, we have $P = P_A^0$ and $x, y = 1$ – pure LBC (Fig. 3.14).

To determine the equilibrium phase compositions using the isobaric diagram $t - x, y$, it is also necessary to equalize the temperatures. For a certain temperature t^* (corresponding to the horizontal in Fig. 3), the equilibrium concentrations x and y are obtained as the abscissas of the points of intersection of this horizontal line with the curves $t(x)$ and $t(y)$.
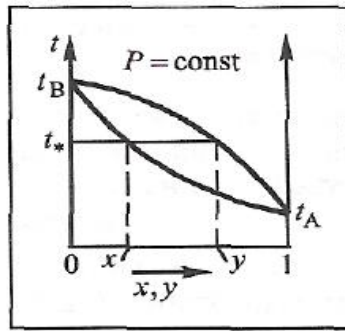
Fig. 3. Dependences $t(x)$ and $t(y)$ and equilibrium
concentrations for ideal binary systems

Real mixtures. In real systems there is an interaction of components – usually weak in the vapor phase and often substantial – in the liquid phase. This interaction affects the equilibrium, leading to a deviation from ideality (in particular, from Raoult's law). Such systems in practice are found much more often than close to ideal ones.

It is very difficult to calculate the interaction between a pair of components in a mixture, so equilibrium in real binary systems is established experimentally.

The "small" and "large" deviations of binary systems from ideality are distinguished.

Small deviations from ideality. In the case of small deviations from ideality, the lines $P(x)$ cease to follow a linear (additive) dependence (equation (5)). In this case, the $P(x)$ curves can pass below the straight line corresponding to the Raoult's law (negative deviation) or higher (positive deviation), but remain ascending in the entire range of x from 0 to 1 (Fig. 4). Otherwise, the tangent to the curve $P(x)$ here always forms an acute angle with the x axis, i.e. $dP/dx > 0$. Such mixtures are called *zeotropic*.

Konovalov's first law retains the sense characteristic of ideal mixtures: in an equilibrium state, the vapor phase is enriched in the low-boiling component in comparison with the liquid phase. The equilibrium phase compositions using the diagrams $t - x - y$ and $x - y$ are determined graphically – by the same construction as for ideal binary systems.
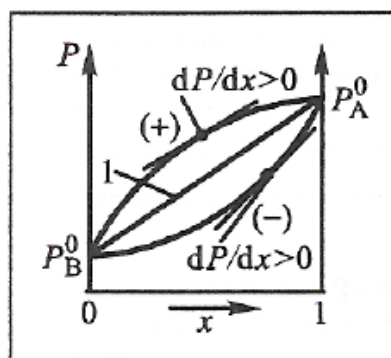

Fig. 4. The diagram $P(x)$ for real binary mixtures:
1 – the straight line following Raoult's law; (–) and (+) – negative and positive deviations from Raoult's law

Great deviations from ideality. For some mixtures, deviations from ideality are so great that the curves $P(x)$ pass through an extremum. The specific value x for the extremum point depends on the properties of the components. The diagrams $P(x)$ with the extreme pressure (maximum or minimum) are shown in Fig. 5, *a,d.*

Mixtures with an extreme deviation of ideality follow the second law of Konovalov (see Fig. 5,*a,b,d,e*): the maximum on the pressure curve corresponds to a minimum on the boiling curve; the minimum on the pressure curve corresponds to a maximum on the boiling temperature curve.

Since systems with a maximum pressure and a minimum boiling point are encountered more often, we consider in more detail. There are two branches on the curve $P(x)$ (Fig. 5,*a*): the ascending $dP/dx > 0$ for it and the descending $dP/dx < 0$, and also the maximum point, where the tangent is horizontal and $dP/dx = 0$.

In the diagram $t - x, y$ (Fig. 5,*b*), the first region, as in the case of zeotropic mixtures, is characterized in the equilibrium state by the inequality $y > x$. However, for the second region $y < x$, i.e. the vapor phase in comparison with the liquid is enriched in HBC.

If for $dP/dx > 0$ the $y > x$ is fair, and for $dP/dx < 0$ the $y < x$ is true, then the equation $dP/dx = 0$ corresponds to $y = x$, i.e. equality of equilibrium concentrations in the liquid and vapor phases for a certain composition of the liquid mixture x_{az}. A mixture of such a composition is called *azeotropic* or inseparably boiling, and a mixture of components having an azeotropic point A at a certain concentration x_{az} – is azeotrope-forming. In the diagram $y - x$ (Fig. 5,*c*), for such a mixture there are also regions $y > x$ and $y < x$; the point of intersection of the equilibrium line with the diagonal corresponds to azeotrope $(y = x)$.
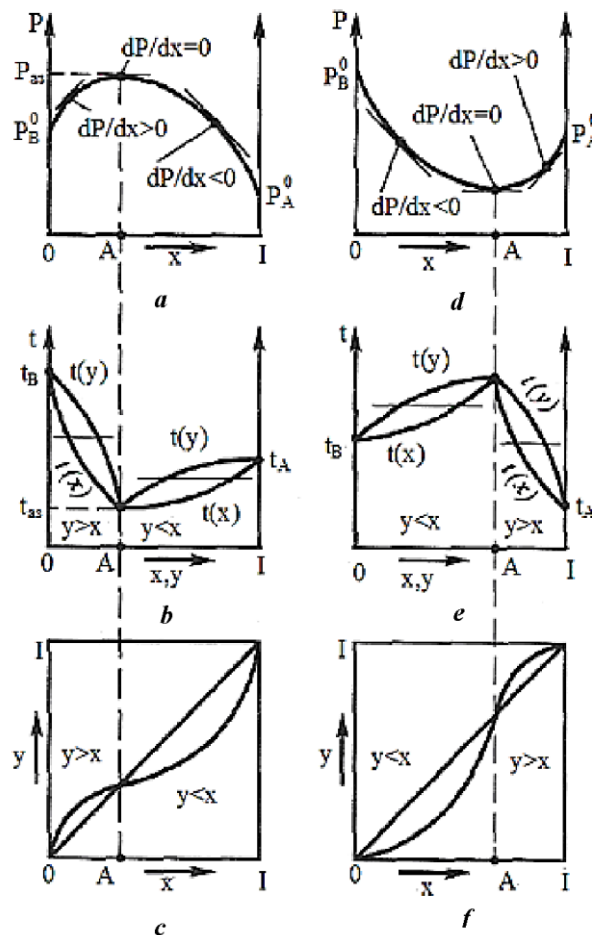
Fig. 5. The diagrams $P - x$ (a, d), $t - x, y$ (b, e) and $x - y$ (c, f)
for azeotrope-forming mixtures

Compositions of azeotropic points, depending on the properties of the components, are mixed with a change in pressure in accordance with the rule of Vrevsky: in the case of mixtures with a minimum of boiling points, with increasing pressure, the concentration of the component with a higher molar heat of vaporization increases, and in the case of mixtures with a maximum boiling point – a smaller one.

The displacement of the point of the azeotrope with a change in pressure can be used to separate the azeotrope-forming mixtures, including mixtures of an azeotropic composition, into very pure components.

Mixtures of mutually insoluble components. Practically mutually insoluble are liquids with negligible solubility in each other. Such mixtures form two layers and can be separated by upholding.

A system consisting of two mutually insoluble components and three phases (two liquid and one vapor), according to the phase rule, has one degree of freedom. It follows that each temperature of the mixture corresponds to a strictly defined pressure, and each component of the mixture behaves independently of the other. Accordingly, the partial pressure of each component does not depend on its content in the mixture and is equal to the vapor pressure of the pure component at the same temperature.

In the $P - x$ diagram (Fig 6,a), the partial pressure and total pressure lines are straight lines parallel to the abscissa.

In Fig. 6 also shows the phase diagrams $t - x - y$ (b) and $x - y$ (c) for binary mixtures of mutually insoluble components. In the diagram $t - x - y$, the values t_A and t_B – the boiling points of the pure components A and B, and S – the boiling point of the mixture. The boiling point of the mixture is always below the boiling point of the pure components that make up the mixture. This property is used in the technique to separate water-insoluble liquids by distillation with water vapor.

Mixtures of liquids that are limitedly soluble in each other. For such systems, when one liquid is added to another (for example, phenol to water), they first completely dissolve into each other, then form two layers at certain concentrations and behave like insoluble liquids: their amounts change, but the liquid phase remains constant. Such mixtures are called *heteroazeotropic*.

Heterozeotropic mixtures can be considered as general, including as a partial mixture with both an azeotrope and mutually insoluble components. As shown in Fig. 7 when the points S' and S'' are shifted to the point S (i.e., when the horizontal plateau $S'S''$ is contracted at the point), an azeotropic mixture is obtained. When the point S' is shifted to the vertical $x = 0$ and the point S'' to the vertical $x = 1$, we have a mixture of mutually insoluble components [2].
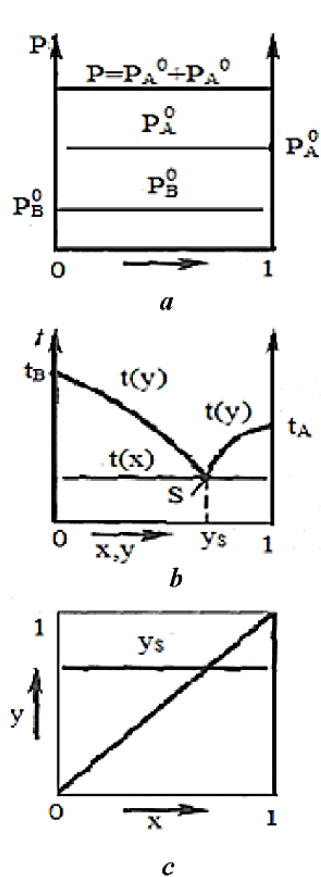
Fig. 6. Diagrams $P - x$ (*a*), $t - x, y$ (*b*) и $x - y$ (*c*) for mutually insoluble components
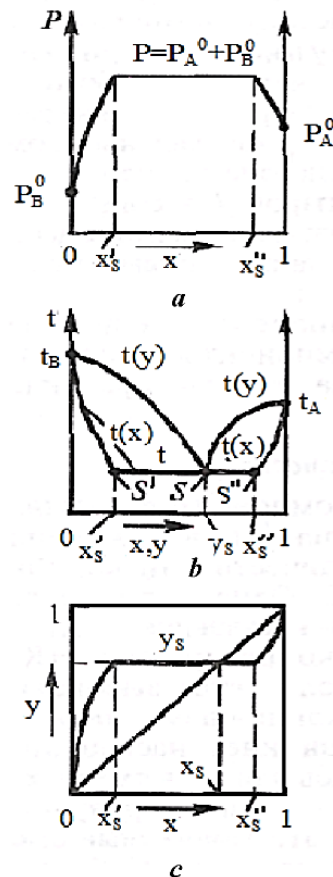

Fig. 7. The diagrams $P - x$ (*a*), $t - x, y$ (*b*) и $x - y$ (*c*) for the mixtures with a limited mutual solubility

Material balance of simple distillation

When considering the processes of distillation, it is assumed that the vaporization takes place very slowly and that equilibrium is established between the liquid and the vapor.

Consider the material balance of simple distillation. We denote by G – the amount of liquid in the cube, and by x – its composition. The content of the low-boiling component in the liquid is Gx.

When a small amount of liquid dG having a composition x evaporates, the liquid concentration decreases by dx and the remainder of the liquid in the cube is expressed by the quantity

$$G - dG \tag{6}$$

and its composition will be

$$x - dx \tag{7}$$

The content of the low-boiling component in the liquid residue is

$$(G - dG)(x - dx) \tag{8}$$

7

The amount of the distillate is equal to the amount of the evaporated liquid dG, and the composition of its y is in equilibrium with x.

The material balance of the volatile component can be represented by the time interval under consideration in the following form

$$Gx = (G - dG)(x - dx) + ydG \tag{9}$$

or

$$Gx = Gx - xdG - Gdx + dGdx + ydG \tag{10}$$

Neglecting the product $dGdx$ as an infinitesimal second-order quantity, we obtain

$$Gdx = dG(y - x) \tag{11}$$

or

$$\frac{dG}{G} = \frac{dx}{y-x} \tag{12}$$

We denote the amount of liquid in the cube after distillation through G_1 and its composition through x_1, equation (12) can be integrated in the range from G_1 and x_1 to G and x. We get

$$\int_{G_1}^{G} \frac{dG}{G} = \int_{x_1}^{x} \frac{dx}{y-x} \tag{13}$$

or

$$2{,}3 lg \frac{G}{G_1} = \int_{x_1}^{x} \frac{dx}{y-x} \tag{14}$$

The integral of the right-hand side of equation (14) is determined graphically. To do this, plot the x values on the abscissa and the corresponding $\frac{1}{y-x}$ values along the axis and find the area bounded by the curve, the x axis, and the vertical ones drawn through the abscissas x_1 and x. This area is equal to the desired integral (Fig. 1).
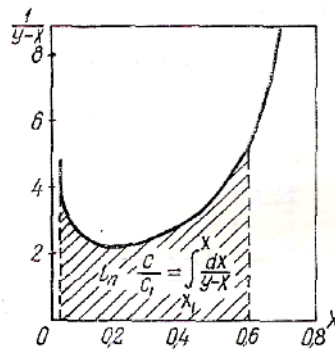

Fig. 1. To the calculation of simple distillation

The amount of distillate $G - G_1 = G_{eq}$ obtained and its composition x_{eq} are determined from the equation of material balance of the volatile component

$$Gx = G_1 x_1 + (G - G_1)x_{eq} \tag{15}$$

whence

$$x_{eq} = \frac{Gx - G_1 x_1}{G - G_1} \qquad (16)$$

A simple distillation is carried out at atmospheric pressure or under vacuum, connecting the distillate collectors to a vacuum source. The use of vacuum makes it possible to separate thermally low-stable mixtures and, due to a decrease in the boiling point of the solution, to use for the cube heating a steam of lower parameters.

Distillation with water vapor

The boiling point of an inhomogeneous mixture of insoluble liquids is always below the boiling point of the lowest boiling point. It follows that if water is added to a liquid that is immiscible with water and boiled at high temperatures, the boiling point of such a mixture at atmospheric pressure will be below 100 ºC. The total vapor pressure over the mixture is equal to the sum of the elasticities of the components in pure form at the same temperature

$$P = p_A + p_B, \qquad (17)$$

from which the partial pressure of water vapor over the mixture

$$p_B = P - p_A \qquad (18)$$

At atmospheric pressure, *p = 760 mm Hg. col.* the partial pressure of water vapor will be

$$p_B < 760 \qquad (19)$$

and a saturated water vapor with a pressure of less than 760 *mm Hg.col.* is below 100 ºC.

Due to the low boiling point of water with water vapor, liquids are easily distilled in a pure form having a very high boiling point at which the substance can partially decompose. In this way, with water vapor under atmospheric pressure at temperatures below 100 ºC, fatty acids, aniline, nitrobenzene, turpentine, etc are distilled.

Distillation with water vapor is usually carried out in distillation cubes equipped with a steam jacket to preheat the original mixture to the distillation temperature and a bubbler through which the hot steam is supplied. If the initial mixture contains water, the "sharp" steam is started to pass only after the water distillation from the mixture. The distillable product after condensation is separated from the water with which it is not mixed, by sedimentation or centrifugation.

The steam flow rate for distillation is theoretically determined from the relationship

$$G_B = \frac{p_B \cdot M_B}{p_A \cdot M_A} \qquad (20)$$

In practice, the water vapor leaving the distillation apparatus is not completely saturated with the vapors of the distilled component. Therefore, practical G_B is always more theoretically determined. Taking this into account, the saturation factor φ

$$G_B = \frac{p_B \cdot M_B}{\varphi p_A \cdot M_A} \qquad (21)$$

The value φ depends on the hydrodynamic mode of distillation [3].

Questions to control:
1. What is meant by simple distillation? What are the types of simple distillation?
2. Show the scheme of the distillation process with dephlegmator, expand its advantages over simple distillation.
3. Give the rule of phase and equilibrium in liquid-vapor systems.
4. What is the difference between real and ideal mixtures?
5. Expand the principle of drawing up the material balance of simple distillation, determining the amount of vat residue, distillate and its composition at simple distillation.
6. What is the essence of steam distillation?

Literature
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