CHEMISTRY

A. F. FROLOV

1964

SovietRxiv

Abstract

Full Text

CHEMISTRY

A. F. FROLOV

A NEW METHOD OF REPRESENTING EQUILIBRIUM BETWEEN TWO LIQUID PHASES OF A FOUR-COMPONENT SYSTEM

(Presented by Academician N. M. Zhavoronkov, January 15, 1964)

Equilibrium isotherms of two separating liquid phases of a four-component system are usually represented graphically in a tetrahedron in the form of spatial diagrams.

Below a new, simpler method is described for representing the equilibrium of the indicated system on a plane, based on the fact that equilibrium lines located within the volume of a tetrahedron can be represented in the form of the corresponding projections onto its adjacent triangular faces; the tetrahedron itself is unfolded and takes the form of a square (or rhombus) with crossed diagonals. In this case the compositions of the four-component mixture, inherent to the tetrahedron, are resolved into three-component compositions corresponding to plane projections.

Table 1

Decomposition of a four-component mixture into two three-component ones

Components	four-component	three-component in triangle $A\Gamma B$	three-component in triangle AB
A	a_4	a_3^{Γ}	a_3^{B}
	$_4$	$^{\Gamma}_{3}$	$^{B}_{3}$
	$_4$	—	$^{B}_{3}$
	$_4$	$^{\Gamma}_{3}$	—

The method of processing experimental data by this method is as follows.

First, the initial data of single-stage extraction processes, including the compositions of the initial mixture entering mixing and the obtained compositions of the coexisting phases, are resolved into three-component compositions, which are located in plane projections, as shown in Table 1.

Then the data from Table 1 are placed in the two triangles of the square, as shown in Fig. 1 for the system studied by us: acetic acid—nitric acid—water—chloroform.

As is evident from the data of Table 1 and Fig. 1, each point expressing a definite composition of a four-component mixture corresponds to two points on the plane, one of them on the triangle $A\Gamma$ (for example, the point R_1^Γ) and the other on the triangle A (for example, the point R_1^B). Points such as R_1^Γ and R_1^B will hereafter be called paired points.

The analytical dependence between the compositions in the four-component and three-component mixtures can be expressed in the form of the following relations:

$$\frac{a_4}{1 - {}_4} = a_3^\Gamma, \qquad (1)$$

$$\frac{{}_4}{1 - {}_4} = {}_3^\Gamma, \qquad (2)$$

$$\frac{{}_4}{1 - {}_4} = {}_3^\Gamma, \qquad (3)$$

$$\frac{a_4}{1 - {}_4} = a_3^B, \qquad (4)$$

$$\frac{{}_4}{1 - {}_4} = {}_3^B, \qquad (5)$$

$$\frac{{}_4}{1 - {}_4} = {}_3^B, \qquad (6)$$

Expressing these equations in terms of the components in the quaternary mixture, we obtain, for

$$a_4 = 1, \tag{7}$$

$$b_4 = \frac{b_3^\Gamma}{a_3^\Gamma}, \tag{8}$$

$$v_4 = \frac{v_3^{\mathrm{B}}}{a_3^{\mathrm{B}}}, \tag{9}$$

$$g_4 = \frac{g_3^\Gamma}{a_3^\Gamma}. \tag{10}$$

Equation

$$\frac{a_3^{\Gamma}}{b_3^{\Gamma}} = \frac{a_3^{\mathrm{B}}}{b_3^{\mathrm{B}}}, \tag{11}$$

obtained from (1), (2), (4), (5), determines the arrangement of paired points on the diagram on paired rays. By paired rays, in the present case, we mean rays issuing from opposite corners of the quadrilateral and intersecting on its diagonal at one point (for example, Γ1 and B1). As is evident, in order to determine the compositions of a four-component mixture from the available compositions of ternary mixtures on the triangles, using the diagram, it is sufficient to apply equations (7), (8), (9), (10).

Considering the quadrilateral diagram obtained, the following properties may be noted.

1. For each composition of the initial four-component mixture it is always possible to calculate two corresponding compositions in ternary mixtures; however, not every arbitrary pair of compositions of two ternary mixtures taken on the triangles corresponds to a composition of a four-component mixture. In accordance with equation 11, only compositions of ternary mixtures lying on paired rays correspond to definite compositions of the four-component mixture.
2. The points on both triangles representing the composition of the initial mixture and the compositions of the coexisting phases lie on straight lines (on triangle $A\mathrm{B}B$, the lines $R_1^{\mathrm{B}}M_1^{\mathrm{B}}E_1^{\mathrm{B}}, R_2^{\mathrm{B}}M_2^{\mathrm{B}}E_2^{\mathrm{B}}$, etc.; and on triangle $A\Gamma B$, the lines $R_1^{\Gamma}M_1^{\Gamma}E_1^{\Gamma}, R_2^{\Gamma}M_2^{\Gamma}E_2^{\Gamma}$, etc.), and, consequently, the lever rule applies to the quantities of phases and to the tie-line segments on which they are located, for example: $R_1^{\Gamma} \cdot \overline{M_1^{\Gamma}R_1^{\Gamma}} = E_1^{\Gamma} \cdot \overline{M_1^{\Gamma}E_1^{\Gamma}}$ and $R_1^{\mathrm{B}} \cdot \overline{M_1^{\mathrm{B}}R_1^{\mathrm{B}}} = E_1^{\mathrm{B}} \cdot \overline{M_1^{\mathrm{B}}E_1^{\mathrm{B}}}$.
3. Through the points corresponding to the compositions of the coexisting phases, smooth lines—binodals—can be drawn in each of the triangles. The role and significance of these binodals in combination with the tie-lines are apparently analogous to those in the Gibbs triangle.
4. The possibility of obtaining new equilibrium data by interpolation and extrapolation.

One of the possible methods of interpolating data here, based on the noticeable proportionality of the binodal segments in the extract and raffinate phases between tie-lines, is given below.

Let it be necessary in Figs. 1, 2 to obtain additional data on the composition and amount of phases between the pairs of tie-lines $R_5^{\Gamma}E_5^{\Gamma}$–$R_6^{\Gamma}E_6^{\Gamma}$ and $R_5^{\mathrm{B}}E_5^{\mathrm{B}}$–$R_6^{\mathrm{B}}E_6^{\mathrm{B}}$. On the line AB between points 5 and 6 we choose an arbitrary point 7 and through it draw the rays 7Γ and $7B$; the latter intersect the binodal

Fig. 1

Figure 1: Fig. 1

Fig. 2

Figure 2: Fig. 2

segments $R_5^{\Gamma}R_6^{\Gamma}$ and $R_5^{\mathrm{B}}R_6^{\mathrm{B}}$, respectively, at points R_7^{Γ} and R_7^{B}, giving the raffinate composition. Through these points new tie-lines $R_7^{\Gamma}E_7^{\Gamma}$ and $R_7^{\mathrm{B}}E_7^{\mathrm{B}}$ are drawn. The intersections of these tie-lines with the binodal segments $E_5^{\Gamma}E_6^{\Gamma}$ and $E_5^{\mathrm{B}}E_6^{\mathrm{B}}$, at points E_7^{Γ} and E_7^{B}, respectively, indicate the extract composition; and their intersections with the diagonal $B\Gamma$, at points M_7^{Γ} and M_7^{B}, indicate the composition of the initial feed mixture. Given the phase compositions in the ternary mixtures, the phase compositions in the four-component mixture are found from equations 7, 8, 9, 10 and then from the material-balance equations for a single-stage extraction process

$$R + E = M = 1, \tag{12}$$

$$Ra_4^R + Ea_4^E = Ma_4^M = a_4^M. \tag{13}$$

the quantities of the phases R and E are found. When carrying out additional tie-lines by the interpolation method, two cases may be considered: the first, apparently particular, case shown in Fig. 1, when pairs of tie-lines (for example,

Fig. 1. Liquid—liquid equilibrium in the system: acetic acid—nitric acid—water —chloroform

Fig. 2. Interpolation of tie-lines

$R_5^{\Gamma}E_5^{\Gamma}$—$R_6^{\Gamma}E_6^{\Gamma}$ and $R_5^{B}E_5^{B}$—$R_6^{B}E_6^{B}$) are parallel and the compositions of one of the phases (in Fig. 1, the extracts) practically lie on one pair of rays ($\Gamma 8$—$B8$), and the second (more general case), when the tie-lines are located at a considerable-

angle, and the compositions of both phases are located on different paired rays (Fig. 2).

In the first case the geometrically correct solution consists in drawing, for example, the points indicated above under $R_7^{\Gamma}E_7^{\Gamma}$ and $R_7^{B}E_7^{B}$, while maintaining the ratios

$$\frac{R_5^{\Gamma}R_7^{\Gamma}}{R_6^{\Gamma}R_7^{\Gamma}} = \frac{E_5^{\Gamma}E_7^{\Gamma}}{E_6^{\Gamma}E_7^{\Gamma}}, \tag{14}$$

$$\frac{R_5^B R_7^B}{R_6^B R_7^B} = \frac{E_5^B E_7^B}{E_6^B E_7^B}, \tag{15}$$

respectively (parallel lines on the sides of an angle cut off proportional segments). In the second case interpolation may be carried out by the graphical method shown in Fig. 2. From the points R_5^Γ, R_6^Γ, and R_7^Γ on the triangle $A\Gamma B$, three lines are drawn parallel to the side $A\Gamma$, and from the points E_5^Γ, E_6^Γ two lines are drawn parallel to the side $B\Gamma$. The intersection of two pairs of parallel lines occurs on the line $\Gamma_5\Gamma_6$. Next, from the point Γ_7 a third line is drawn, parallel to the side $B\Gamma$, which intersects the binodal at the point E_7^Γ. In an analogous manner the position of the point E_7^B is found in the triangle ABB.

Diagram 1 should be regarded only as one system of a complete diagram, on which experimental data at different ratios of components A/B are plotted (on it only data for relatively equal amounts of components A and B in the initial mixture are plotted). This complete diagram, including several systems with their binodals and nodes, makes it possible to solve more complex problems on it, including extraction calculations.

A description of such complete diagrams will be considered in our subsequent papers.

Accepted notation. M, R, E are the compositions (amounts) of the initial mixture, raffinate, and extract, respectively; a, b, v, g are the concentrations of components A, B, V, Γ, respectively. The indices attached to component concentrations indicate: 3, 4 —belonging of the composition to a three- or four-component mixture (for example, a_3), respectively; g, v —the same, to the triangle Γ or V (for example, a^Γ), respectively; M, R, E —the same, to the initial mixture, raffinate, and extract (for example, a^M), respectively.

Yaroslavl Technological Institute

Received
15 I 1964

Note: Figure translations are in progress. See original paper for figures.