Calculation of the Properties of Ternary Systems on the Basis of Binary Data

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A method for the construction of an equilibrium diagram of ternary mixtures on the basis of binary data has been developed. This method is concerned with the freezing points and requires the couples of components to give an equilibrium binary diagram with eutectic point. The method is also of good use for the investigation of the relationship between composition and other properties (solubilities, boiling points, *etc.*) and gives a rapid information provided that the ternary diagram has not been published yet.

The literature seldom furnishes the equilibrium diagrams of freezing points (melting points) for ternary melts which could be used for the balance calculation of crystallization. On the other hand, binary data are available much more frequently. For this reason, several methods have been published which are based on the supposition that the properties are additive and thus they enable us to estimate the properties of ternary system from the known binary data [1—4]. Of course, it does not mean that the melts and their freezing points should always be topical. The property searched for may be the equilibrium solubility in ternary solutions or another property of ternary system.

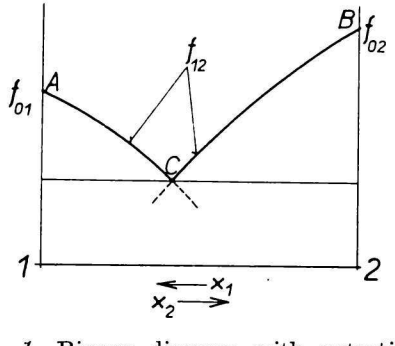

Fig. 1. Binary diagram with eutectic point.

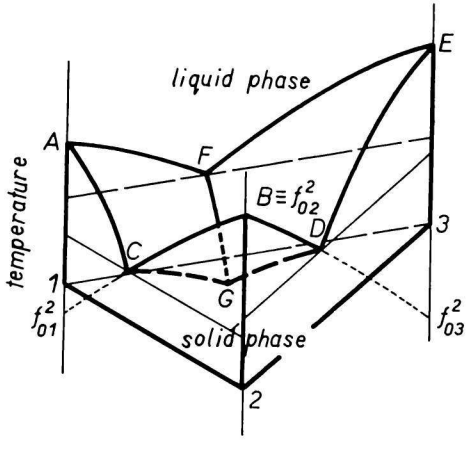

Fig. 2. Equilibrium diagram of the ternary mixtures — the couples of components form eutectics.

For condensed components, the couples of which do not form eutectic in the whole concentration range, the methods cited give results which are in good agreement with the values measured. Provided that the couples of components have an eutectic point in their equilibrium diagram, the above methods give some physically non-justifiable deformations in the course of isotherms. For this case a method [5], which adopts the procedure and symbols of the so-called symmetric correlation method [4], has been proposed. It is based on this consideration: The binary eutectic (point *C*, Fig. 1) is a mixture of two kinds of crystals in the case of crystallization from melt. The eutectic point does not represent a new chemical individuum: it is only a point of intersection of two freezing (melting) point curves. The influence of the component *2* on the melting point in the proximity of the pure component *1* is already expressed by the shape of the line *AC*. Similarly, it is possible to estimate the effect of the component *1* on the section *BC*. Hence, the eutectic *C* is only a passive product of the mutual limitation of components and has no influence on the course of the function f_{12} at different ratios of the components x_1 and x_2.

Analogously, in the system of three components (Fig. 2) where the couples 12, 23, and 31 form the systems with the eutectic (*C*, *D*, *F*), the lines *CG*, *DG*, and *FG* expressing the influence of the third component on the position of the eutectic of the opposite binary system must also be only a passive intersection of the surfaces of the function f_s. The point *G* corresponding to the ternary eutectic point is, therefore, an intersection of the lines *CG*, *DG*, and *FG*.

The method [5] resulting from the above consideration consists of two steps:

1. Construction of a separate point field (surfaces of the function f_s) for each apex of the ternary diagram. Since, for practical reasons, ternary diagrams are not usually drawn as space diagrams, each of these fields is to be characterized by the course of isotherms.

2. Construction of the intersections of three point fields and their plotting in a common diagram. The intersections may be obtained as join lines of the intersection points of equal isotherms in particular fields.

Derivation of mathematical relationships

According to Fig. 3, the following coordinates belong to the points in which the value under consideration has the value f_{mn}:

$$f_s(x_1, x_2, x_3),$$

$$f_{01}(1, 0, 0),$$

$$f_{02}(0, 1, 0),$$

$$f_{03}(0, 0, 1),$$

$$f_{12}\left(\frac{x_1}{x_1 + x_2}, \frac{x_2}{x_1 + x_2}, 0\right),$$

$$f_{23}\left(0, \frac{x_2}{x_2 + x_3}, \frac{x_3}{x_2 + x_3}\right),$$

$$f_{31}\left(\frac{x_1}{x_3 + x_1}, 0, \frac{x_3}{x_3 + x_1}\right).$$

The symbols f_{01}, f_{02}, and f_{03} denote the quantity studied (freezing point) of the pure components while the symbols f_{12}, f_{23}, and f_{31} stand for this quantity in binary mixtures. In this case, it is possible to read the values from the binary diagram.

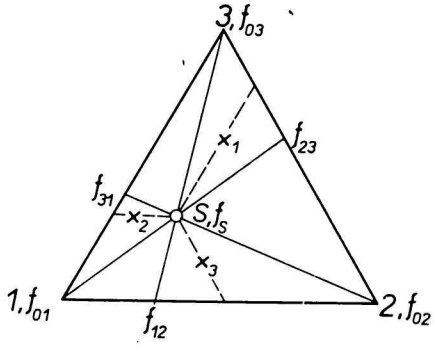

Fig. 3. Symbols used in calculations.

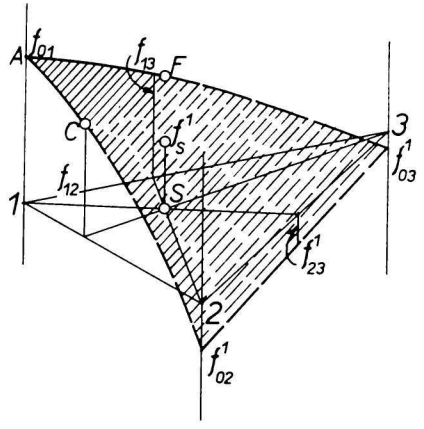

Fig. 4. Example of the point field obtained by calculation.

For the developed method, other six symbols f_{01}^2, f_{01}^3, f_{02}^1, f_{02}^3, f_{03}^1, and f_{03}^2 have to be introduced. Their significance is evident in Fig. 2. They represent an extrapolation of liquidus lines from the apex marked with the upper index behind the eutectic up to the axis of the second binary component. This far-reaching extrapolation is only of a formal importance and as it follows from further explanation it is not really necessary. From the triplets of real and fictional quantities

$$f_{01}, f_{02}^1, f_{03}^1,$$
$$f_{02}, f_{03}^2, f_{01}^2,$$
$$f_{03}, f_{01}^3, f_{02}^3,$$

we may deduce the expressions for three point fields of the function f_s corresponding to individual apices, *i.e.* f_s^1, f_s^2, and f_s^3. One of these surfaces for the value f_s^1 is shown in Fig. 4.

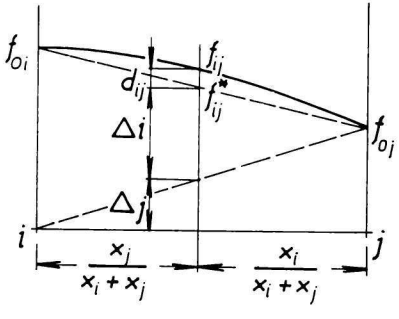

Fig. 5. Estimate of the deviation from ideal course in binary diagram.

In an ideal system, where the function f_s is linear between apices, a simple geometric consideration [4] allows to write for ternary systems at the apex *1*

$$f_s^* = x_1 f_{01} + x_2 f_{02}^1 + x_3 f_{03}^1. \tag{1}$$

The real value of the function f_s at the apex *1* differs from the ideal value by a certain deviation

$$f_s^1 = f_s^* + d_{123}. \tag{2}$$

The difference of the ternary system d_{123} from the ideal state may by calculated from the expression

$$d_{123} = (1 - x_3)\, d_{12} + (1 - x_2)\, d_{31} + (1 - x_1)\, d_{23} \tag{3}$$

where d_{12}, d_{23}, and d_{31} are the deviations from the ideal state in binary systems. For an arbitrary binary deviation d_{ij} it may be written

$$d_{ij} = f_{ij} - f_{ij}^* = f_{ij} - \frac{x_i}{x_i + x_j} f_{0i} - \frac{x_j}{x_i + x_j} f_{0j}. \tag{4}$$

The evidence follows from Fig. 5 because it holds

$$f_{ij}^* = \Delta i + \Delta j = \frac{x_i}{x_i + x_j} f_{0i} + \frac{x_j}{x_i + x_j} f_{0j}.$$

We shall assume the course of the fictional function f_{23}^1 to be ideal (see Fig. 4) so that the deviation d_{23} should be zero in every place. If we cyclically put for the indices in the relation (*4*) the numbers 1, 2, 3 and substitute subsequently in the equation (*3*), we get

$$d_{123} = (1 - x_3)\left(f_{12} - \frac{x_1}{x_1 + x_2} f_{01} - \frac{x_2}{x_1 + x_2} f_{02}^1\right) +$$

$$+ (1 - x_2)\left(f_{31} - \frac{x_3}{x_3 + x_1} f_{03}^1 - \frac{x_1}{x_3 + x_1} f_{01}\right) + (1 - x_1)\, 0. \tag{5}$$

It is valid in a three-component system

$$x_1 + x_2 + x_3 = 1,$$

hence

$$1 - x_3 = x_1 + x_2,$$

$$1 - x_2 = x_3 + x_1.$$

By means of these expressions the equation (*5*) may be transformed into the form

$$d_{123} = (1 - x_3) f_{12} - x_1 f_{01} - x_2 f_{02}^1 + (1 - x_2) f_{31} - x_1 f_{01} - x_3 f_{03}^1. \tag{6}$$

We substitute this expression as well as the relationship (*1*) into the equation (*2*) and after rearrangement we obtain the final equation for the variation of the value under investigation in the point field at the apex *1*

$$f_s^1 = (1 - x_3) f_{12} + (1 - x_2) f_{31} - x_1 f_{01}. \tag{7}$$

The fictional values f_{02}^1 and f_{03}^1 disappeared in the final equation. Analogously, for the fields corresponding to the components *2* and *3* we obtain

$$f_s^2 = (1 - x_1) f_{23} + (1 - x_3) f_{12} - x_2 f_{02}, \tag{8}$$

$$f_s^3 = (1 - x_2) f_{31} + (1 - x_1) f_{23} - x_3 f_{03}. \tag{9}$$

Generally, it holds for an arbitrary apex

$$f_s^i = (1 - x_k) f_{ij} + (1 - x_j) f_{ki} - x_i f_{0i} \tag{10}$$

where the numbers of the triplet 1, 2, 3 are cyclically substituted for the indices i, j, k.

Of course, the practical construction of a ternary diagram does not require three complete point fields. To obtain an intersection, the extrapolation of point fields not too far beyond the eutectic points of binary systems is satisfactory. The extrapolations of binary curves close over the eutectic point may be performed with sufficient reliability.

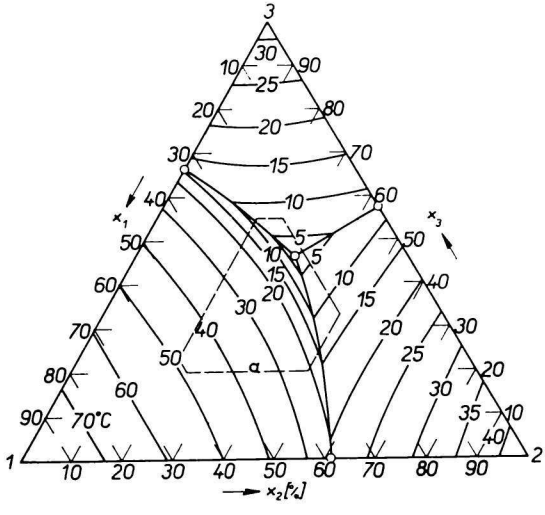

Fig. 6. Ternary diagram calculated for the mixtures of nitrochlorobenzene isomers.
a) limit of the deviations less than +3.0 deg.
1. p-NClB 82.5°C; *2. m*-NClB 43.4°C; *3. o*-NClB 32.0°C.
E_{12} 21.1°C; E_{23} 7.8°C; E_{31} 13.4°C; E_{123} 2.5°C.

The surface of ternary diagram is covered with an arbitrary but possibly regular set of points with the coordinates x_1, x_2, and x_3 in which the values of the searched function f_s^i are subsequently calculated for individual apices according to the equations (7), (8), and (9). It is advantageous to arrange the results of calculation into a table. The course of isotherms is obtained by the interpolation (graphic or numerical) made between the values corresponding to individual points.

Testing of the method

Matz [6] published the ternary diagram of freezing points for the mixtures of nitrochlorobenzene isomers (NClB) which has been experimentally verified. On the basis

Table 1

	Values of the ternary eutectic			
	m.p. [°C]	*o*-NClB [%]	*m*-NClB [%]	*p*-NClB [%]
Values according to [6]	−3.4	47.2	34.2	18.6
Calculated values	2.5	46.3	31.5	22.2

of the binary data available for the mixtures of *o*-NClB, *m*-NClB, and *p*-NClB, a ternary diagram has been calculated and constructed by the above method (Fig. 6). The comparison between the published and calculated ternary system shows that the deviations are only positive and amount to +3.0 deg by individual apices of the ternary system (pure components) at the most. These deviations by apices are characterized as follows:

apex *1*, *p*-NClB from 57 to 100% of the component *1*,
apex *2*, *m*-NClB from 47 to 100% of the component *2*,
apex *3*, *o*-NClB from 55 to 100% of the component *3*.

Since all components are isomers, the numerical data expressing the relative amounts of components are equal irrespectively of weight or molar percentage.

The deviations in the proximity of individual binary systems have been investigated up to the content of 20% of the opposite component. It has been found that the deviations in these zones are less than +3.0 deg.

The comparison between the experimental and calculated values for the ternary eutectic is given in Table 1.

Discussion

The method presented shows only positive deviations in the preceding confrontation. But in other ternary systems, the deviations might also be negative. The deviations result from the simplifying assumption of a linear character of the fictional function f_{23}^{1} (or f_{31}^{2}, f_{12}^{3}) and of the additivity of properties. The real course of the mentioned functions expressing the course of the activities corresponding to different ratios of the components 2, 3 (3, 1 or 1, 2) may be either convex or concave with respect to the comparative line. It is not possible to find out this character without experiment on the basis of binary data themselves. However, the above confrontation shows that the method gives satisfactory results for many problems of engineering practice.

References

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