4D space models of quaternary systems for the phase diagrams graphics correction

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Abstract. The methods of T-x-y-z diagrams invariant point determination by the “geometrical calculations” are analyzed, and the appearance of ambiguous and multiple solutions are shown. The inaccuracies of experimentally constructed isopleths and invariant point detection are analyzed.

1. Introduction

The space model of phase diagram contains information about each geometric element. The computer 3D model of T-x-y-z diagrams can be visualized both in the concentration projections and in the projections taking into account the temperatures [1]. Using of T-x-y-z diagrams computer models gives the possibility not only to analyze the structure of studied systems, but also to choose the arrangement of vertical and horizontal sections, since already on the arrangement of section it is possible to assume the section view and to avoid the errors with its interpretation [2].

The determination of invariant points compositions within the T-x-y-z diagrams is possible both by the selection of the hyper surfaces models and by the use of tie-lines method. In the first case the invariant points are calculated as the intersection of hyper surfaces (in the simplified variant their additive approximation by hyper planes is used) [3-5].

In the second case the coordinates of invariant points is determined from the series of vertical sections [1-2]. Let's consider the calculation methods for the invariant points coordinates and the detection of errors at the interpretation of experimental data by the use of 4D space model for T-x-y-z diagram of eutectic type.

2. Calculation of invariant points by the solution of equations of liquidus (hyper)surfaces of T-x-y-z diagrams

The linear approximation of liquidus surfaces for T-x-y diagrams with the calculation of invariant points coordinates can give both the good agreement with the experimental data and the negative values of coordinates. For example, the linear models of ternary systems (NaNO₃)₂-(LiNO₃)₂-Ba(NO₃)₂, AgCl-ZnCl₂-CdCl₂, (KCl)₂-K₂WO₄-K₂SO₄, CsJ-NaJ-KJ, FeCl₃-PbCl₂-AgCl, FeCl₃-PbCl₂-PdCl₂, SnCl₂-NaCl-TeCl₃, SnCl₂-FeCl₃-Cl₂, SnCl₄-FeCl₃-LaCl₃, RbF-LiF-NaF, NaOH-NaJ-NaBr, (CsNO₃)₂-(NaNO₃)₂-Ba(NO₃)₂, (NaNO₃)₂-(KNO₃)₂-Ba(NO₃)₂, NaCl-SrCl₂-BrCl₂, CsCl-TiCl₃-KCl, (NaCl)₂-(NaF)₂-NaAlF₆, (KCl)₂-(KF)₂-K₂AlF₆, CaCl₂-BaCl₂-CaMoO₄, (KF)₂-(LiF)₂-K₂AlF₆, (KCl)₂-(LiCl)₂-K₂AlF₆, LiCl-NaCl-LiBO₂, LiCl-RbCl-LiF, NaBO₂-LiBO₂-NaCl, Na₂SO₄-PbSO₄-PbMoO₄, K₂Cr₂O₇-(NaNO₃)₂-Na₂Cr₂O₇, (NaCl)₂-Na₂SO₄-BaSO₄, BaCl₂-(NaCl)₂-BaSO₄, (AgJ)₂-(AgCl)₂-CdCl₂
contradict their physico-chemical sense, because the coordinates of three planes intersection is situated outside the concentration triangle [6]. Analogous problems should appear at the construction of linear models of T-x-y-z diagrams. Furthermore, the ambiguous solutions are possible, and they depend of the methods of hyper plane determination.

2.1. Calculation of invariant points by the solving of three equations system for the surfaces euEukEul on the liquidus hyper surfaces intersection

In [3] authors suggest the calculation method of the point of quaternary eutectic point by intersection of three planes passing through one binary and two ternary eutectic points euEukEul (figure 1). Since T-x-y-z diagram includes six such surfaces, then four different systems of three equations can be combined, which gives the ambiguous solution. Using as an example a T-x-y-z diagram model we produced the different variants of calculation of quaternary eutectic point ε by intersection of three planes adjoining to different vertexes of tetrahedron in two coordinate systems: T-Σzi and Σzi. As a result 8 variants of coordinates of quaternary eutectic point were obtained (figure 1, table 1). The intersection of planes adjoining to vertex D gives the negative values of coordinates at the calculation in coordinates Σzi. The calculation in the coordinates T-Σzi give two cases with negative coordinates for the planes adjoining to vertexes B and D.

![Figure 1](image-url)

*Figure 1. Calculation of point ε by the intersections of three planes adjoining to vertex A (eABeABCeABD, eACeABCeACD, eADeABDeACD) in coordinates Σzi (a) and T-Σzi (b)*

|   | z1   | A (a) | B   | C   | D   | z2   | A (a) | B   | C   | D   |
|---|------|-------|-----|-----|-----|------|-------|-----|-----|-----|
| z1| 0.387| 0.356 | 0.263| 0.435| -0.115| 0.253| -0.294| 0.420|
| z2| 0.093| 0.180 | 0.187| -0.017| 0.261| 0.493| 0.121| -0.017|
| z3| 0.311| 0.134 | 0.270| 0.284| -0.184| -0.248| 0.245| 0.275|
| z4| 0.209| 0.330 | 0.280| 0.298| 0.670| 0.870| 0.928| 0.322|

2.2. Calculation of invariant points by the solving of system of four equations leuEukEul [4]
Calculation method of quaternary eutectic point of system Cd-Pb-Sn-Bi with binary incongruently melting compound and two quaternary points (eutectic and quasiperitectic) is based on the solving of...
the system of four hyper planes. As the authors said, “because the presence of the peritectic compound Pb:Bi has essentially no influence on the liquidus surface, Bi, Pb, Sn and Cd were used as components of the system” [4, P. 78]. Each their hyper plane passes through the vertex with initial component (I), the binary eutectic point \( e_{IJ} \) and two ternary eutectic \( E_{IJK} \), \( E_{IJL} \): \( Ie_{IJ}e_{IK}E_{IJK}E_{IJL} \). The authors obtained a good agreement between the calculated and experimental data. But this method does not have the unique solution because each liquidus can be defined by three equations and therefore there are different variants of equations system.

2.3. Calculation of invariant points by the solving of system of four equations \( Ie_{IJ}e_{IK}e_{IL} \).
The description of the liquidus by hyper planes \( Ie_{IJ}e_{IK}e_{IL} \) [5] has a unique solution, and the coordinates of ternary and quaternary eutectics are calculated. The coordinates of initial component and binary points were used as initial data. But the positive and negative coordinates of calculated points can be obtained in depending of the structure of T-x-y-z diagrams. E.g., the present model of T-x-y-z diagram (table 2) gives the negative values of coordinates of ternary eutectic points \( E_{ABC} \) and quaternary eutectic \( \varepsilon \) (table 3a, figure 2a). To solve this problem, we propose to use a nonlinear model of T-x-y-z diagram (table 3b, figure 2b). Using of the curvature of liquidus hyper surfaces increases the equations degree, but it makes possible to avoid the intersection outside of the concentration tetrahedron.

### Table 2. Initial data for linear model

|   | A  | B  | C  | D  | eAB | eAC | eAD | eBC | eBD | eCD |
|---|----|----|----|----|-----|-----|-----|-----|-----|-----|
| z1| 1  | 0  | 0  | 0  | 0.71 | 0.58 | 0.50 | 0   | 0   | 0   |
| z2| 0  | 1  | 0  | 0  | 0.29 | 0    | 0    | 0.17 | 0.60 | 0   |
| z3| 0  | 0  | 1  | 0  | 0    | 0.42 | 0    | 0.83 | 0   | 0.55 |
| z4| 0  | 0  | 0  | 1  | 0    | 0    | 0.50 | 0   | 0.40 | 0.45 |
| T | 600| 850| 710| 900| 500  | 310  | 400  | 680  | 550  | 520  |

### Table 3. Calculated coordinates of ternary and quaternary eutectic points

|   | EABC | EABD | EACD | EBCD | \( \varepsilon \) | EABC | EABD | EACD | EBCD | \( \varepsilon \) |
|---|------|------|------|------|---------|------|------|------|------|---------|
| z1| 0.857| 0.397| 0.422| 0    | 0.494   | 0.528| 0.405| 0.430| 0    | 0.381   |
| z2| -0.732| 0.226| 0    | 0.291| -0.239  | 0.056| 0.254| 0    | 0.261| 0.096   |
| z3| 0.875| 0    | 0.272| 0.333| 0.403   | 0.416| 0    | 0.277| 0.392| 0.280   |
| z4| 0    | 0.377| 0.306| 0.376| 0.342   | 0    | 0.341| 0.293| 0.347| 0.243   |
| T | 248.14| 371.29| 289.8| 500  | 267.14  | 301.69| 346.66| 278.36| 477.15| 269.55  |

**Figure 2.** Linear model of T-x-y-z diagram with negative value of coordinates of points \( E_{ABC} \) and \( \varepsilon \) (a), non-liner model (b)
2.4. Modernized tie-lines method
The alternative method of determination of invariant points coordinates is the tie-lines method. Earlier we proposed the modernization of this method, based on the construction of three nonplanar two-dimensional vertical sections [1-2]. In the first stage the section for determination of point belonging to the general two-dimensional simplex $I_{JE}$ of two linear hyper surfaces $Q^{UK}$ and $Q^{IM}$ at the temperature of quaternary eutectic $\varepsilon$ is constructed. It is necessary to take into account the arrangement of section relative to the forming two-dimensional simplexes of different linear hyper surfaces. Let's consider the possible variants of section arrangement near the edge $AB$ (figure 3). The section $S_{12}$ is located so that the point $S_{1CABC}$ is inside simplex $A_{E}BCE$ and the point $S_{2CABD}$ is inside simplex $A_{E}ABD$ (figure 3a). Such section (figure 3b) intersects the hyper surface of liquidus $Q_{A}$ (line 1-2), linear hyper surface $Q_{AB}$ with forming segment $A_{E}AB$ (line 3-4), two linear hyper surfaces with forming two-dimensional simplexes $Q_{ABC}$ (5-6), $Q_{ABD}$ (6-7) and hyperplane $H_{E}$ at $T_{E}$ (8-6-9). The point $S_{4}$ of section $S_{34}$ is located in simplex $A_{E}ABD$ (after the line $AE_{D}$). Such section additionally intersects two linear hyper surfaces $Q_{AD}$ and $Q_{ABD}$ with one-dimensional (4-7) and two-dimensional (4-10) forming simplexes, but lines of hyper surfaces $Q_{AB}$ and $Q_{ABD}$ is decreased: (3-4) and (4-6) (figure 3c). Since the ending points of section $S_{56}$ are arranged in simplexes $AE_{E}BC$ and $AE_{E}BD$, then else two linear hypersurfaces ($Q_{ABC}$ and $Q_{AEB}$) are intersected: $Q_{AB}$ (4-5), $Q_{AC}$ (3-4), $Q_{AD}$ (5-8), $Q_{ABC}$ (4-6), $Q_{ACB}$ (4-7), $Q_{ABD}$ (5-6), $Q_{EADB}$ (5-9) (figure 3d).

Figure 3. Possible variants (a) of arrangement of section $SS_{6}$ for the determination of point (6) on the forming two-dimensional simplex $A_{E}B_{E}$ of two linear hyper surfaces $Q_{ABC}$ and $Q_{ABD}$ at the temperature of quaternary eutectic: $S_{12}$ (b), $S_{34}$ (c), $S_{56}$ (d)

The point 6 of sections $S_{12}$, $S_{34}$ and $S_{56}$ is located on the forming simplex $A_{E}B_{E}$ at $T_{E}$, therefore any section ($S_{78}$) constructed through the arbitrary point of edge $AB$ and given point (6) intersects the one-dimensional forming section $A_{E}E$ of linear hyper surfaces $Q^{AB}$ (in point $t_{E}$). Then third section is constructed along a ray $Ar_{E}$ and includes the point of quaternary eutectic. The matrix conversions is used for the calculation of points coordinates, which determine the arrangement of vertical sections [7].

3. Graphic correction of T-x-y-z diagrams
The view of section can be assumed based on its arrangement into tetrahedron and avoid the mistakes in interpreting of experimental data. Authors of [7] are located the two dimensional vertical section into tetrahedron so that its ends are arranged in the different simplexes (as the section $S_{34}$ in figure 3a). Whereas the authors give the section with the intersection of liquidus hyper surface and three linear
hyper surfaces similar the section $s_{132}$ (figure 3b). Whereas the section with such arrangement really intersect five liner hyper surfaces as the section $s_{334}$ (figure 3c).

The using of computer models also allows to correctly interprets the experimental data according with determination of eutectic point. Authors of [8] at the study of system Li,Ba,Mg,Zr/F suggest that the section passing through vertex ZrF$_4$ and opposite ternary eutectic point Li,Ba,Mg/F contain the quaternary eutectic point.

While the tie-line constructed from the vertex and containing ternary and quaternary eutectic points may corresponds to very particular case of phase diagram structure. Figure 4 shows the possibility sections constructed from tetrahedron vertexes and the ternary eutectic points for the model of T-x-y-z diagram.

Figure 4. T-x-y-z diagram model (a), vertical sections D-E$_{ABC}$ (b), C-E$_{ABD}$ (c), B-E$_{ACD}$ (d), A-E$_{BCD}$ (e)

The modernized tie-line method are described in [10]. In the first step the three dimensional vertical section mnk is given. Then two-dimensional section fg for determination of point r is constructed in plane mnk (figure 5a). In the next step the section sv (not belonging to the plane mnk) passing through point r (figure 5b) is calculated by simultaneous reducing of the concentrations of components A and D in the ratio given by the point s and the increase at the same value of the concentration of components B and C. Such method provides the moving on the plane $A_{\varepsilon}$ and the finding of tie-line $A_{\varepsilon}$ in point $r_{\varepsilon}$. In the last step section Ap is constructed along the ray $A_{\varepsilon}r_{\varepsilon}$, which contains the quaternary eutectic e (figure 5c). Authors combine second and third sections (figure 5b and 5c) on one
figure as $rr', \epsilon$ and give the smooth curve of intersection of liquidus hyper surfaces. But the sections $rr', \epsilon$ (figure 5b) and $r, \epsilon$ (figure 5c) are constructed on the axes located with different angles. Therefore the combination of these two sections should give the inflection on the liquidus isopleth 1-2-3 in point 2 (figure 5d).). The liquidus curve can be smooth only when the sections sv and $A, \epsilon, r' \epsilon$ belong to one line.

![Figure 5. Schema of sections arrangement (a), sections sv (b), Ap (c), rr' (d)]](image)

4. Conclusions
The computer model of T-x-y-z of diagram is not only the example for 3D visualizations of studied system, but also it contains the information about all geometric elements. Using these models allows to understand the structure of the phase diagram and predict the view of horizontal or vertical sections on its arrangement relative to the elements of phase diagram in the concentration tetrahedron. And then - to avoid the errors at its interpretation. The model of phase diagram also can be used to predict the experimental work. It can be constructed using partial experimental data and then rebuilt at the new data appearance.

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