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Handling multicomponent systems in $\mathbb{R}^n$. I: Theoretical results

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The phases of multicomponent systems (mixtures, states, etc.) containing the compounds $A_1, \ldots, A_n$ are $x_1A_1 + \cdots + x_nA_n$, where $0 \leqslant x_i \leqslant 1$ and $x_1 + \cdots + x_n = 1$. For $n \geqslant 4$ (quaternary or higher dimensional systems), the displaying methods and visual investigations in the n-dimensional Euclidean space $\mathbb{R}^n$ are tangentially or not at all described in the literature. In this paper we first develop the theoretical (both mathematical and computational) background in any dimension in $\mathbb{R}^n$. We focus not only on the important points, lines, surfaces of these systems, and computing method of the states of some processes in such systems, but also on the approximating methods of the above mentioned lines and surfaces, and, finally, on the question "*which is the region where a state (a point) falls into*". Using the above results a computer program for PC's was created for evaluating and displaying the approximated surfaces. This program is described in I. Szalkai, SALT3DIM.exe – A program for handling 4 component mixtures, Preprint No. 047, University of Veszprém (1996), and the computing results are planned to be published in a forthcoming paper (I. Szalkai, Handling multicomponent systems in $\mathbb{R}^n$. II: Computational results, J. Chem. Inf. Comput. Sci., submitted).

0. Introduction

The starting point of our research was motivated by inorganic chemistry: how to handle and display *several* component mixtures, their exact compounds, marking and investigating the important lines and surfaces which separate the distinct phases of the system. Since similar problems arise (at least from an abstract mathematical point of view) in several other disciplines, not only in the theory of mixtures, we focus mainly on the common *general* mathematical tools of these problems and not on their applications (which could include residue curves, distillation boundaries, liquid composition profiles, eutectic surfaces, etc.).

Our second (but not lesser) goal was to develop general methods which work also in *higher dimensions*, for systems/mixtures formed from *many* compounds. Even quaternary systems are shortly described and investigated in the literature because of the geometrical difficulties in higher dimensions. We overcome this difficulty by using co-ordinate geometry in *any* dimension in $\mathbb{R}^n$ and by using computer calculations. For

human 3D and 2D pictures we may want to make pictures using intersections with 2D or 3D hyperplanes, these problems are also discussed in section 1.3.

Since the sum of the percentage of the compounds must be equal to 1, the so-called barycentric co-ordinates are preferable, requiring higher dimensional simplexes, but calculations and diagrams are made in the usual rectangular Cartesian co-ordinate system. These problems (from the beginning of building higher dimensional simplexes) with transformation methods among the different co-ordinate systems are discussed in sections 1.1 and 1.2. Though isothermical diagrams are drawn not in simplexes but in prisms instead, converting methods are also introduced at the end of section 1.2.

Further, when approximating (e.g., eutectic) surfaces/lines/points from a dataset, first the problem of approximating many-variable functions in the case of *scattered data points* arises. This is not only because we have to transform data from barycentric to Cartesian co-ordinates, but from the nature of these surfaces and lines. In the present paper (in section 1.3), we use the simplest method (Shepard's method); this applied method will be discussed in more detail in our forthcoming paper [10].

We also highlight in our research the question "*which is the region where a point (representing a state of the system) falls into*". We discuss this problem in section 1.4. Other questions with solutions are mentioned in sections 1.5 and 1.6.

Our theoretical investigations have been also applied in a practical computer software which is introduced with some output pictures in [8].

1. Mathematical tools

1.0. Introduction

Though our method was originally developed for mixtures of several chemical compounds, which we are talking about throughout the whole paper, the method is also applicable for describing any system, in which the sum of the co-ordinates of any state (phase) is equal to 1.

In general, n-ary systems contain the components $A_1, A_2, \ldots, A_n$ and X (H_2O in general). A state P denotes a mixture, having the proportion α_i of the component A_i for $i = 1, 2, \ldots, n$. Of course, we must have

$$0 \leqslant \alpha_i \leqslant 1 \quad \text{for } i \leqslant n \tag{1}$$

and

$$\alpha_1 + \alpha_2 + \cdots + \alpha_n + \delta = 1, \tag{2}$$

where δ denotes the remainder, i.e., the proportion of X. Clearly also,

$$0 \leqslant \delta \leqslant 1. \tag{3}$$

In other words, the state (mixture) P corresponds to the vector

$$\mathbf{p} = [\alpha_1, \alpha_2, \ldots, \alpha_n, \delta]$$

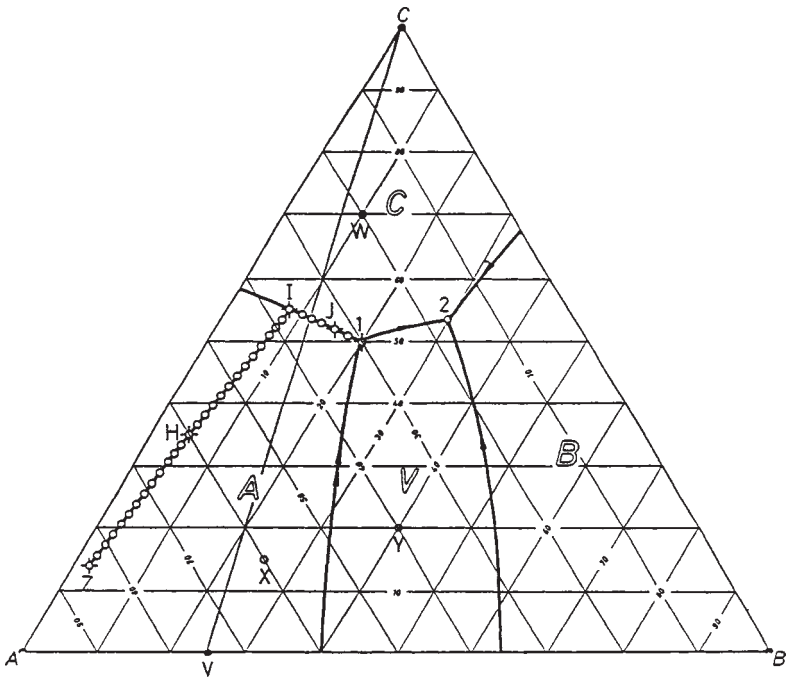


Figure 1. A typical 2-dimensional diagram with an application. Reproduced from [11].

satisfying (1)–(3). Turning to geometry, if $A_1, A_2, \ldots, A_n, X$ are represented by *any* vectors (points) $\mathbf{a}_1, \mathbf{a}_2, \ldots, \mathbf{a}_n, \mathbf{x}$ in the n-dimensional Euclidean space $\mathbb{R}^n$, and we take

$$\mathbf{p} := \alpha_1 \cdot \mathbf{a}_1 + \alpha_2 \cdot \mathbf{a}_2 + \cdots + \alpha_n \cdot \mathbf{a}_n + \delta \cdot \mathbf{x}, \tag{4}$$

then $\mathbf{p}$ runs all the internal and marginal points of the convex hull of the points $\mathbf{a}_1, \mathbf{a}_2, \ldots, \mathbf{a}_n, \mathbf{x}$ as the coefficients $\alpha_1, \alpha_2, \ldots, \alpha_n, \delta$ take all their possible values satisfying (1)–(3).[1]

It is advisable to choose the base vectors $\mathbf{a}_1, \mathbf{a}_2, \ldots, \mathbf{a}_n, \mathbf{x}$ as the vertices of a full-dimension regular simplex (i.e., an n-dimensional tetrahedron). The vertices and the geometry of these simplexes in *any* dimension $n \in \mathbb{N}$ will be discussed in detail in the next section.

The above sketched method is widely used for ternary systems in dimension two ($n = 2$), where the base vectors (points) $\mathbf{a}_1, \mathbf{a}_2, \mathbf{x}$ are $(0; 0)$, $(0; 1)$ and $(1/2; \sqrt{3}/2)$, in the usual rectangular Cartesian co-ordinate system. This special 2-dimensional method can be found in detail in any stoichiometry book, and we can also refer to the exhaustive introductory paper of Tamás [11]. A typical diagram with an application is shown in figure 1. Hartman and Haase explained a slightly different approach in [3].

[1] $[\alpha_1, \alpha_2, \ldots, \alpha_n, \delta]$ are called the *barycentric* co-ordinates of the point P with respect to the base $\{\mathbf{a}_1, \mathbf{a}_2, \ldots, \mathbf{a}_n, \mathbf{x}\}$. Converting barycentric and Cartesian co-ordinates is discussed at the end of section 1.1

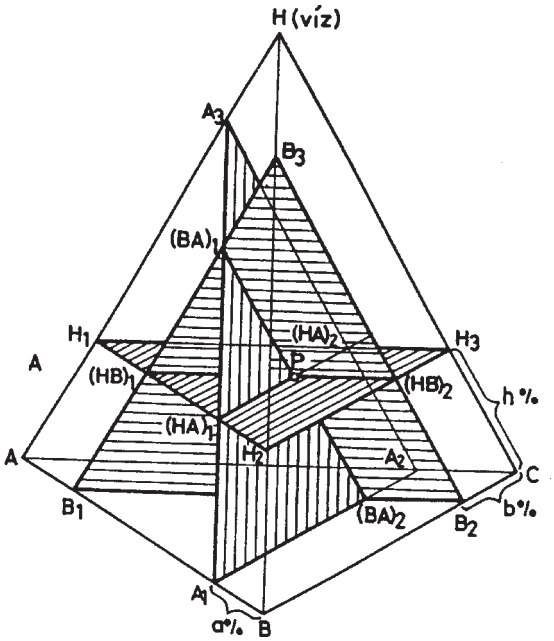


Figure 2. The usual 3-dimensional diagram for determining co-ordinates. Reproduced from [6].

Unfortunately, the geometry of quaternary systems A–B–C–X requires the 3-dimensional unit simplex in the space $\mathbb{R}^3$. Standard (manual) computations by rulers and pencil are no longer valid as was in the case in 2 dimensions, so this 3-dimensional case is only tangentially discussed in the literature. The difficulties of diagram-drawing can be seen in figure 2.

Our theoretical method and computational ideas can be used in *any* dimension!

1.1. Simplexes in $\mathbb{R}^n$

The following theorem helps us to determine the (usual) rectangular Cartesian co-ordinates of the vertices of a regular simplex (all edges are of unit length) in $\mathbb{R}^n$ with the property:

(L): The first n vertices of this simplex form a "similar" regular, but lower dimensional simplex in $\mathbb{R}^{n-1}$ also with property (L).

(Some low-dimensional examples are given in tables 1 and 2.)

Table 1
The vertices of the 3-, 4- and 5-dimensional simplexes.

$$S_3\text{:}\quad \mathbf{a}_1^3 = \begin{bmatrix}0\\0\\0\end{bmatrix},\quad \mathbf{a}_2^3 = \begin{bmatrix}1\\0\\0\end{bmatrix},\quad \mathbf{a}_3^3 = \begin{bmatrix}1/2\\\sqrt{3}/2\\0\end{bmatrix},\quad \mathbf{a}_4^3 = \begin{bmatrix}1/2\\\sqrt{3}/2\cdot 1/3\\\sqrt{3}/2\cdot\sqrt{8}/3\end{bmatrix}$$

$$S_4\text{:}\quad \mathbf{a}_1^4 = \begin{bmatrix}0\\0\\0\\0\end{bmatrix},\quad \mathbf{a}_2^4 = \begin{bmatrix}1\\0\\0\\0\end{bmatrix},\quad \mathbf{a}_3^4 = \begin{bmatrix}1/2\\\sqrt{3}/2\\0\\0\end{bmatrix},\quad \mathbf{a}_4^4 = \begin{bmatrix}1/2\\\sqrt{3}/2\cdot 1/3\\\sqrt{3}/2\cdot\sqrt{8}/3\\0\end{bmatrix},$$

$$\mathbf{a}_5^4 = \begin{bmatrix}1/2\\\sqrt{3}/2\cdot 1/3\\\sqrt{3}/2\cdot\sqrt{8}/3\cdot 1/4\\\sqrt{3}/2\cdot\sqrt{8}/3\cdot\sqrt{15}/4\end{bmatrix}$$

$$S_5\text{:}\quad \mathbf{a}_1^5 = \begin{bmatrix}0\\0\\0\\0\\0\end{bmatrix},\quad \mathbf{a}_2^5 = \begin{bmatrix}1\\0\\0\\0\\0\end{bmatrix},\quad \mathbf{a}_3^5 = \begin{bmatrix}1/2\\\sqrt{3}/2\\0\\0\\0\end{bmatrix},\quad \mathbf{a}_4^5 = \begin{bmatrix}1/2\\\sqrt{3}/2\cdot 1/3\\\sqrt{3}/2\cdot\sqrt{8}/3\\0\\0\end{bmatrix},$$

$$\mathbf{a}_5^5 = \begin{bmatrix}1/2\\\sqrt{3}/2\cdot 1/3\\\sqrt{3}/2\cdot\sqrt{8}/3\cdot 1/4\\\sqrt{3}/2\cdot\sqrt{8}/3\cdot\sqrt{15}/4\\0\end{bmatrix},\quad \mathbf{a}_6^5 = \begin{bmatrix}1/2\\\sqrt{3}/2\cdot 1/3\\\sqrt{3}/2\cdot\sqrt{8}/3\cdot 1/4\\\sqrt{3}/2\cdot\sqrt{8}/3\cdot\sqrt{15}/4\cdot 1/5\\\sqrt{3}/2\cdot\sqrt{8}/3\cdot\sqrt{15}/4\cdot\sqrt{24}/5\end{bmatrix}$$

Table 2
The matrix A_{10}.

$$\begin{bmatrix}
1 & 1/\sqrt{4} & 1/\sqrt{4} & 1/\sqrt{4} & 1/\sqrt{4} & 1/\sqrt{4} & 1/\sqrt{4} & 1/\sqrt{4} & 1/\sqrt{4} & 1/\sqrt{4}\\
0 & \sqrt{3/4} & 1/\sqrt{12} & 1/\sqrt{12} & 1/\sqrt{12} & 1/\sqrt{12} & 1/\sqrt{12} & 1/\sqrt{12} & 1/\sqrt{12} & 1/\sqrt{12}\\
0 & 0 & \sqrt{4/6} & 1/\sqrt{24} & 1/\sqrt{24} & 1/\sqrt{24} & 1/\sqrt{24} & 1/\sqrt{24} & 1/\sqrt{24} & 1/\sqrt{24}\\
0 & 0 & 0 & \sqrt{5/8} & 1/\sqrt{40} & 1/\sqrt{40} & 1/\sqrt{40} & 1/\sqrt{40} & 1/\sqrt{40} & 1/\sqrt{40}\\
0 & 0 & 0 & 0 & \sqrt{6/10} & 1/\sqrt{60} & 1/\sqrt{60} & 1/\sqrt{60} & 1/\sqrt{60} & 1/\sqrt{60}\\
0 & 0 & 0 & 0 & 0 & \sqrt{7/12} & 1/\sqrt{84} & 1/\sqrt{84} & 1/\sqrt{84} & 1/\sqrt{84}\\
0 & 0 & 0 & 0 & 0 & 0 & \sqrt{8/14} & 1/\sqrt{112} & 1/\sqrt{112} & 1/\sqrt{112}\\
0 & 0 & 0 & 0 & 0 & 0 & 0 & \sqrt{9/16} & 1/\sqrt{144} & 1/\sqrt{144}\\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \sqrt{10/18} & 1/\sqrt{180}\\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \sqrt{11/20}
\end{bmatrix}$$

The rows of the left upper submatrix of size $n \times n$ give the vectors $\mathbf{a}_2^n, \ldots, \mathbf{a}_{n+1}^n$.

The two vertices of the 1-dimensional simplex (interval) $[0;1]$ with property (L) in $\mathbb{R}^1 = \mathbb{R}$ are clearly (0) and (1). Further, for the sake of unique notation, from now on we will denote the last vector of our simplex by $\mathbf{a}_{n+1}$ instead of $\mathbf{x}$, as in the previous section.

Theorem 1. If $\{\mathbf{a}_1^n, \mathbf{a}_2^n, \ldots, \mathbf{a}_{n+1}^n\} \subset \mathbb{R}^n$ are the vertices of the (unique) simplex with property (L), where $\mathbf{a}_i^n = [a_1^{n,i}, a_2^{n,i}, \ldots, a_n^{n,i}] \in \mathbb{R}^n$ ($i \leqslant n+1$), then the vertices of the unique simplex in $\mathbb{R}^{n+1}$ with property (L) are $\{\mathbf{a}_1^{n+1}, \mathbf{a}_2^{n+1}, \ldots, \mathbf{a}_{n+1}^{n+1}, \mathbf{a}_{n+2}^{n+1}\} \subset \mathbb{R}^{n+1}$, where

$$\mathbf{a}_i^{n+1} = \left[a_1^{n,i}, a_2^{n,i}, \ldots, a_n^{n,i}, 0\right] \in \mathbb{R}^{n+1} \quad (i \leqslant n+1)$$

and

$$\mathbf{a}_{n+2}^{n+1} = \left[a_1^{n,n+1}, a_2^{n,n+1}, \ldots, a_n^{n,n+1} \cdot \alpha_{n+1}, a_n^{n,n+1} \cdot \beta_{n+1}\right] \in \mathbb{R}^{n+1},$$

where

$$\alpha_{n+1} = \frac{1}{n+1} \quad \text{and} \quad \alpha_{n+1}^2 + \beta_{n+1}^2 = 1.$$

Let us highlight that $a_j^{n,i}$ denotes the jth co-ordinate of the vector $\mathbf{a}_i^n \in \mathbb{R}^n$ ($1 \leqslant j \leqslant n,\ 1 \leqslant i \leqslant n+1$).

In other words, we have (only!) to split the last co-ordinate of $\mathbf{a}_{n+1}^n$ to get the last two co-ordinates of $\mathbf{a}_{n+2}^{n+1}$ according to α_{n+1} and β_{n+1}. It is interesting that we do not need any value of the functions sine and cosine, as one might think at the first glance of the co-ordinates of the last vertex of the 2-dimensional triangle: $(1/2; \sqrt{3}/2)$. However, we still have the equality $\alpha_{n+1}^2 + \beta_{n+1}^2 = 1$. For illustration, the vertices of our 3-, 4- and 5-dimensional simplexes are listed in table 1 and, in a simplified form, in table 2.

Proof of theorem 1. Property (L) is clear by induction. So, the only thing left for us to confirm is that $\mathbf{a}_{n+2}^{n+1}$ is at unit distance from the other vertices $\mathbf{a}_i^{n+1}$ for $i \leqslant n+1$. We prove it by induction on n; the case $n = 1$ is clear. Now, using the formulas in the theorem, we have

$$d^2\left(\mathbf{a}_{n+2}^{n+1}, \mathbf{a}_i^{n+1}\right) = \sum_{t=1}^{n-1} \left(a_t^{n,n+1} - a_t^{n,i}\right)^2 + \left(a_n^{n,n+1} \cdot \alpha_{n+1} - a_n^{n,i}\right)^2 + \left(a_n^{n,n+1} \cdot \beta_{n+1} - 0\right)^2. \tag{5}$$

In case $1 \lneqq n+1$, the sum of the last two terms is equal to

$$\left(a_n^{n,n+1} \cdot \alpha_{n+1} - 0\right)^2 + \left(a_n^{n,n+1} \cdot \beta_{n+1} - 0\right)^2 = \left(a_n^{n,n+1}\right)^2 \cdot \left(\alpha_{n+1}^2 + \beta_{n+1}^2\right) = \left(a_n^{n,n+1}\right),$$

using the fact that the last *two co-ordinates of* $\mathbf{a}_i^{n+1}$ are equal to 0: $a_n^{n,i} = 0$ for $i \lneqq n$.[2] So the distance $d(\mathbf{a}_{n+2}^{n+1}, \mathbf{a}_i^{n+1})$ becomes

$$\sum_{t=1}^{n-1} \left(a_t^{n,n+1} - a_t^{n,i}\right)^2 + \left(a_n^{n,n+1}\right)^2 = d^2\left(\mathbf{a}_{n+1}^n, \mathbf{a}_i^n\right) = 1$$

by the induction hypothesis.

In case $i = n+1$, we have to compute $d(\mathbf{a}_{n+2}^{n+1}, \mathbf{a}_{n+1}^{n+1})$, so all the terms in the $\sum$ in (5) become 0. This means that we have

$$\begin{aligned} d^2\left(\mathbf{a}_{n+2}^{n+1}, \mathbf{a}_{n+1}^{n+1}\right) &= \left(a_n^{n,n+1} \cdot \alpha_{n+1} - a_n^{n,n+1}\right)^2 + \left(a_n^{n,n+1} \cdot \beta_{n+1} - 0\right)^2 \\ &= \left(a_n^{n,n+1}\right)^2 \cdot \left((\alpha_{n+1} - 1)^2 + \beta_{n+1}^2\right) \\ &= \left(a_n^{n,n+1}\right)^2 \cdot \left((1 - \alpha_{n+1})^2 + \left(1 - \alpha_{n+1}^2\right)\right) \\ &= \left(a_n^{n,n+1}\right)^2 \cdot 2 \cdot (1 - \alpha_{n+1}) = 1. \end{aligned}$$

For the last equality it can be seen, by a trivial induction on n, that

$$a_n^{n,n+1} = \beta_2 \beta_3 \cdots \beta_n$$

and that

$$\beta_2^2 \beta_3^2 \cdots \beta_n^2 \cdot 2 \cdot (1 - \alpha_{n+1}) = 1. \qquad \square$$

P. Fekete [1], our student, gave recursive and explicite formulas for the co-ordinates of the vertices of the above simplexes.

Theorem 2 ([1]). For any fixed dimension $n \in \mathbb{N}$, we have $\mathbf{a}_1^n = 0$, and

$$a_j^{n,i} = \begin{cases} \frac{1}{\sqrt{2j(j+1)}} & \text{if } j < i-1, \\ \sqrt{\frac{j+1}{2j}} & \text{if } j = i-1, \\ 0 & \text{if } j > i-1, \end{cases} \quad \text{for } 2 \leqslant i \leqslant n \text{ and } 1 \leqslant j \leqslant n. \tag{6}$$

The proof runs by an easy induction, using the results of the statement and the proof of theorem 1. $\square$

These co-ordinates are shown in table 2, in dimensions at most 10.

The above result shows that the last but one co-ordinate of $\mathbf{a}_{n+2}^{n+1}$ (the crucial new vector) is the arithmetic average of the same co-ordinates of the previous vectors $\mathbf{a}_1^{n+1}, \mathbf{a}_2^{n+1}, \ldots \mathbf{a}_{n+1}^{n+1}$, which quantity is identical to the average of the corresponding

[2] *At least two last co-ordinates of* $\mathbf{a}_i^{n+1}$ *are* 0, we had to say. To be much more precise, exactly the last $(n-i-1)$ co-ordinates of $\mathbf{a}_i^n$ are equal to 0 for all $1 \leqslant i \leqslant n+1$. This is because of the inductive definition of the vectors $\mathbf{a}_i^n$.

(last) co-ordinates of the vectors $\mathbf{a}_1^n, \mathbf{a}_2^n, \ldots, \mathbf{a}_{n+1}^n$.[3] Similarly, the jth co-ordinates of the vectors $\mathbf{a}_i^n$ for $j+2 \leqslant i \leqslant n+1$ are the same. In formulae this reads as

$$a_n^{n+1,n+2} = \frac{1}{n+1}\sum_{i=1}^{n+1} a_n^{n+1,i} = \frac{1}{n+1}\sum_{i=1}^{n+1} a_n^{n,i} = \frac{1}{n+1} a_n^{n,n+1}$$

and

$$a_j^{n,i} = a_j^{n,k} \quad \text{for } j+2 \leqslant i \leqslant k \leqslant n+1,\ 1 \leqslant j \leqslant n.$$

Fekete in [1] described also other geometric properties of the above simplexes; for example, he determined the number of their (lower dimensional) hyper-faces, areas and volumes, the in- and outer radii of them.

1.2. Co-ordinate transformations

1.2.1. Barycentric and Cartesian co-ordinates

We start this subsection with the problem of converting barycentric and (rectangular) Cartesian co-ordinates in both directions. The base of these calculations is (4), so let us repeate that equality here again:[4]

$$\mathbf{p} := \alpha_1 \cdot \mathbf{a}_1 + \alpha_2 \cdot \mathbf{a}_2 + \cdots + \alpha_n \cdot \mathbf{a}_n + \alpha_{n+1} \cdot \mathbf{a}_{n+1}. \tag{7}$$

(Recall that $\alpha_1 + \alpha_2 + \cdots + \alpha_n + \alpha_{n+1} = 1$.)

This equality shows that $\mathbf{p}$ is a linear combination of the vectors $\mathbf{a}_1, \mathbf{a}_2, \ldots, \mathbf{a}_{n+1}$, where the coefficients are the barycentric co-ordinates themselves. So the Cartesian co-ordinates of $\mathbf{p}$ are easy to determine, since theorem 1 above gives all the co-ordinates of $\mathbf{a}_1, \mathbf{a}_2, \ldots, \mathbf{a}_{n+1}$. In other words, we have to multiply the vector of the barycentric co-ordinates with the matrix A_n to obtain the Cartesian co-ordinates:

$$\mathbf{p} = A_n \cdot [\alpha_2, \ldots, \alpha_{n+1}]^{\mathrm{T}}. \tag{8}$$

Here we made use of that $\mathbf{a}_1 = \mathbf{0}$ always. Of course, α_1 is determined by the remaining co-ordinates $\alpha_2, \ldots, \alpha_{n+1}$. (Recall that n refers to the dimension of $\mathbb{R}^n$.)

Conversely, if the Cartesian co-ordinates of $\mathbf{p}$ are given, the barycentric co-ordinates are the solutions of the system of linear equalities in (7) or, equivalently, in (8). The columns of the system matrix A_n contain the co-ordinates of the vectors $\mathbf{a}_2, \ldots, \mathbf{a}_{n+1}$, which implies that A_n is an upper-triangle matrix. Moreover, the inverse of A_n (which is a lower-triangle matrix) can be determined from (6) as the following result shows:

[3] This can also be directly seen from theorem 1 and the value of α_{n+1}.

[4] In the remaining part of the present section we fix n (the dimension we are in), so mainly we omit the superscript referring to n.

Theorem 3 ([1]). For any fixed dimension $n \in \mathbb{N}$, if $B_n = [b_{i,j}]$ denotes the inverse of A_n, we have

$$b_{i,j} = \begin{cases} \sqrt{\frac{2}{j(j+1)}} & \text{if } i < j, \\ \sqrt{\frac{2j}{j+1}} & \text{if } i = j, \\ 0 & \text{if } i > j, \end{cases} \quad \text{for } 1 \leqslant i, j \leqslant n. \tag{9}$$

In other words, the desired co-ordinates can be obtained again by a single multiplication with matrix B_n as

$$[\alpha_2, \ldots, \alpha_{n+1}]^{\mathrm{T}} = B_n \cdot \mathbf{p} \tag{10}$$

and $\alpha_1 = 1 - (\alpha_2 + \cdots + \alpha_{n+1})$.

1.2.2. Prisms and simplexes

We conclude this subsection with the discussion of another type of diagrams about mixtures. In many cases one (or several) quantitative properties of mixtures are exhibited, depending on a measured physical quantity, say, temperature. (A typical diagram for a ternary system and temperature is shown in figure 3(a).[5]) Though the approximation methods described in the next section can be used directly for these full-dimension diagrams, it would be useful (e.g., for using directly the computer software developed by us) to develop the transformation method between the inner points of these higher dimension prisms (with a base of a lower dimension simplex) and a simplex with this higher dimension.

We displayed n-ary mixtures in the previous section using an $(n-1)$-dimensional simplex of vertices $\{\mathbf{a}_1, \mathbf{a}_2, \ldots, \mathbf{a}_n\} \subset \mathbb{R}^{n-1}$. Adding the temperature axis, we form an n-dimensional prism Π with the base of the previous simplex. Denote the vertices of this prism in $\mathbb{R}^n$ by

$$\{\mathbf{a}_1, \mathbf{a}_2, \ldots, \mathbf{a}_n, \mathbf{b}_1, \mathbf{b}_2, \ldots, \mathbf{b}_n\}.$$

(The last co-ordinates of $\mathbf{a}_1, \mathbf{a}_2, \ldots, \mathbf{a}_n$ are 0, while the last co-ordinates of $\mathbf{b}_1$, $\mathbf{b}_2, \ldots, \mathbf{b}_n$ are $T_{\max}$, the maximum temperature, which we set to 1 now.)

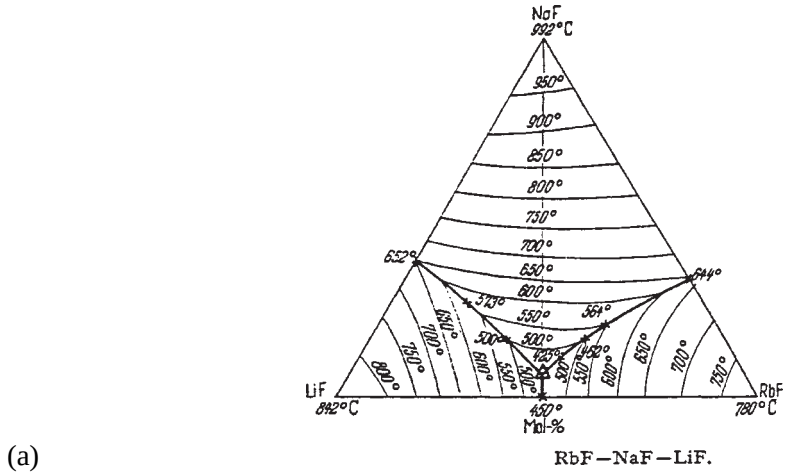
First, the transformation ξ (from $\mathbb{R}^n$ to $\mathbb{R}^n$),

$$\xi : [x_1, x_2, \ldots, x_n] \mapsto \big[\mu(x_n) \cdot x_1, \mu(x_n) \cdot x_2, \ldots, \mu(x_n) \cdot x_{n-1}, x_n/(T_{\max} + \varepsilon)\big],$$

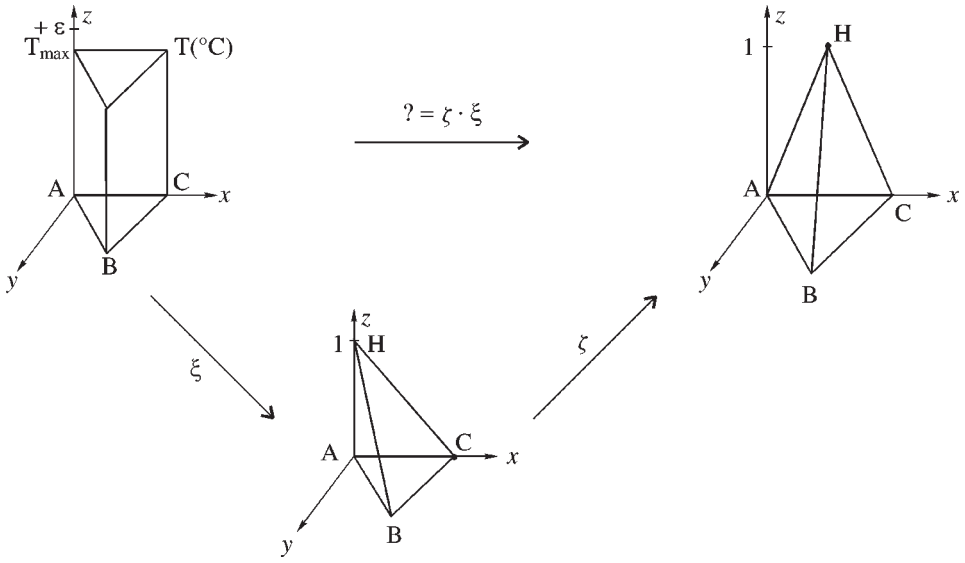
maps Π into the simplex S of vertices $\{\mathbf{a}_1, \mathbf{a}_2, \ldots, \mathbf{a}_n, \mathbf{z}_H\}$, where $\mathbf{z}_H = [0, 0, \ldots, 0, 1]$ and $\mu(z) = 1 - z/(T_{\max} + \varepsilon)$ for real numbers $z \in \mathbb{R}$ and ε is any nonnegative number. (We must set ε to be positive if we want to develop the inverse of ξ.) Second, the transformation ζ (from $\mathbb{R}^n$ to $\mathbb{R}^n$ again),

$$\zeta : [x_1, x_2, \ldots, x_n] \mapsto [x_1, x_2, \ldots, x_n] + x_n \cdot [c_1, c_2, \ldots, c_{n-1}, 0],$$

[5] The 2-dimensional level sections for fixed temperatures can also be useful for explanations, but for approximating the surfaces, we need full-dimension pictures, at least in our mind.



(a) RbF—NaF—LiF.



(b)

Figure 3. (a) A typical diagram of a ternary system with equitemperature curves. Reproduced from [5]. (b) The transformations ξ and ζ in dimension $n = 3$.

maps S into the simplex Σ_n (with property (L)), discussed in the previous section, of vertices $\{\mathbf{a}_1, \mathbf{a}_2, \ldots, \mathbf{a}_n, \mathbf{a}_{n+1}\} \subset \mathbb{R}^n$. Here c_j denotes the jth co-ordinate of

$$\mathbf{a}_{n+1} = \mathbf{a}^n_{n+1} = \left[x_1^{n,n+1}, x_2^{n,n+1}, \ldots, x_n^{n,n+1}\right] = [c_1, c_2, \ldots, c_n] \in \mathbb{R}^n$$

calculated in theorem 1. This means, that the required transformation is the composition $\zeta \circ \xi : \Pi \mapsto \Sigma_n$. ($\zeta \circ \xi(\mathbf{x}) := \zeta(\xi(\mathbf{x}))$ we mean.) The effect of the above transformations for $n = 3$ is illustrated in figure 3(b).

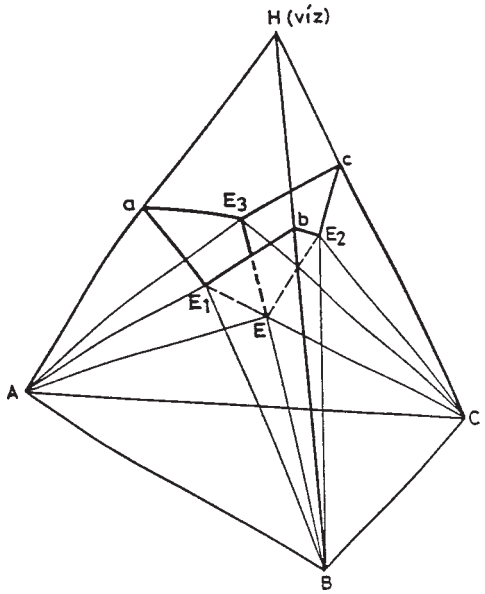


Figure 4. Typical eutectic surfaces in ternary systems. Reproduced from [6].

The inverse of the above transformation is clearly $\xi^{-1} \circ \zeta^{-1} : \Sigma_n \mapsto \Pi$ (i.e., $\xi^{-1}(\zeta^{-1}(\mathbf{x}))$ for $\mathbf{x} \in \Sigma_n$), where clearly

$$\zeta^{-1} : [x_1, x_2, \ldots, x_n] \mapsto [x_1, x_2, \ldots, x_n] - x_n \cdot [c_1, c_2, \ldots, c_{n-1}, 0]$$

and

$$\xi^{-1} : [x_1, x_2, \ldots, x_n] \mapsto \left[x_1/\nu(x_n), x_2/\nu(x_n), \ldots, x_{n-1}/\nu(x_n), x_n \cdot (T_{\max} + \varepsilon)\right]$$

defined for the points $[x_1, x_2, \ldots, x_n] \in S$ such that $x_n \leqslant T_{\max}/(T_{\max} + \varepsilon)$, where $\nu(z) = \mu(z \cdot (T_{\max} + \varepsilon)) = 1 - z$ for real numbers $z \in \mathbb{R}$.

The above easy transformations can be used to use *directly* the features of the software developed in [8].

1.3. Surfaces and approximation

It is fairly well known that the important special points, which separate points of $\mathbb{R}^n$ representing different phases of the mixtures of the components, form *smooth* surfaces in our diagram. (A typical diagram of crystallization and "eutectic surfaces" for ternary systems is shown in figure 4.)

Moreover, if we investigate these surfaces (placed into the simplexes of section 1.1) in the usual rectangular Cartesian co-ordinate system in $\mathbb{R}^n$, it could be assumed that the last co-ordinate is a *function* of the other ones:

$$x_n = f(x_1, x_2, \ldots, x_{n-1}).$$

On top of all, this function f could be assumed to be *continuous*. This empirical observation is widely used (see, e.g., [3], [7], or [11]).

The main difficulty while approximating this more variable function is that any dataset may not be regular, because of the transformation of the barycentric co-ordinates into rectangular Cartesian ones. The only possibility that remains is the *scattered data interpolation*! We suggest, e.g., the relevant chapter of [4] to the reader for an excellent introduction to the theory of this kind of approximation.

In our computer software we used the fairly widely known method of D. Shepard, which is explained in detail, e.g., in [2], [4], and [8]. Below we give only a short introduction to this method.

Shepard's method

Let the dataset $P_1, P_2, \ldots, P_N \in \mathbb{R}^m$ be given with the measured values $F_1, F_2, \ldots, F_N \in \mathbb{R}$ also given. We give a *continuous* function $U : \mathbb{R}^m \to \mathbb{R}$ which gives an exact approximation for the dataset above (that is, $U(P_i) = F_i$ for $i \leqslant N$) by the expression

$$U(P) = \frac{\sum_{i=1}^{N} F_i \cdot \sigma(d(P, P_i))}{\sum_{i=1}^{N} \sigma(d(P, P_i))}, \tag{11}$$

where $d(P, Q)$ denotes the (usual) Euclid distance of the points $P, Q \in \mathbb{R}^m$, and

$$\sigma(x) = \mathrm{e}^{-x^\beta} \cdot x^{-\alpha} \tag{12}$$

for nonnegative real numbers $x \geqslant 0$ and for any exponents $\alpha > 0,\ \beta \geqslant 0$.

Though $U(P)$ is continuous on the whole $\mathbb{R}^m$ for *any* possible α and β, it has definite limit $\overline{U} = \lim_{P \to \infty} U(P)$ and approximates the dataset F_i exactly: $U(P_i) = F_i$ for $i \leqslant N$; on the other hand, it has some inconvenient properties for *some* α and β (e.g., U strongly tends to its limit $\overline{U}$ *inside* the convex hull of the dataset). These inconvenient and other properties of Shepard's original and modified function will be discussed in more detail in [10], even for various decreasing functions σ. However, for the values $\alpha = 1$ and $\beta = 2$ we found this simple method good enough for computer runs, as in [9] can easily be checked.

After having approximated these surfaces, their intersection points and lines with each other and with the sides of the simplex can also be determined. The simplest way is to pass along all the points of a suitably fine grid of the domain of the functions describing the surfaces. During this walk on grid points, we simply must check which surface (or the function approximating it) goes above the other surface or the side of the simplex we want to intersect. We report an intersection point if the order of these surfaces *changes*: the lower becomes higher, in passing from the previous grid point to the next one. Of course, we have to walk on all the grid points in suitable order, and to store the information which surface is lower than the other at the grid points, some of which neighbours will be investigated later. A picture made by our computer software using these ideas in 3 dimensions is shown in [9]. (Let us emphasize that our method works in any dimension, only the computer program is for $\mathbb{R}^3$ only.)

The functions describing the sides of the simplex can be obtained from the well known equality of the $(n-1)$-dimensional hyperplane incident to a given set of n points in $\mathbb{R}^n$, briefly recalled in the theorem below:

Theorem 4. The $(n-1)$-dimensional hyperplane $\mathcal{S} \subseteq \mathbb{R}^n$, which meets the (arbitrary) given points $P_1, P_2, \ldots, P_n \in \mathbb{R}^n$ ($P_i = [p_1^{(i)}, p_2^{(i)}, \ldots, p_n^{(i)}]$ for $i \leqslant n$), has the equality

$$A_1 \cdot \left(x_1 - p_1^{(1)}\right) + A_2 \cdot \left(x_2 - p_2^{(1)}\right) + \cdots + A_n \cdot \left(x_n - p_n^{(1)}\right) = 0,$$

where the coefficients A_i are determined as the $(1,i)$th subdeterminant of the matrix below:

$$\begin{vmatrix} \ldots & \ldots & \ldots & \ldots \\ q_1^{(2)} & q_2^{(2)} & \ldots & q_n^{(2)} \\ \vdots & \vdots & \vdots & \vdots \\ q_1^{(n)} & q_2^{(n)} & \ldots & q_n^{(n)} \end{vmatrix}$$

(i.e., delete the 1st row and the ith column of the matrix, and take A_i to be the determinant of this smaller matrix), where

$$q_j^{(i)} = p_j^{(1)} - p_j^{(i)} \quad \text{for } 2 \leqslant i \leqslant n,\ 1 \leqslant j \leqslant n \text{ (i.e., } Q_i = \overrightarrow{P_1 P_i}\text{).} \qquad \square$$

The vector $\mathbf{n} := [A_1, A_2, \ldots, A_n]$ is called the *normal vector* of the hyperplane $\mathcal{S}$, which is clearly orthogonal to all vectors lying in $\mathcal{S}$.

Lower dimensional hyperplanes in $\mathbb{R}^n$ can be expressed by a *vector-equality* (i.e., a *system* of equalities) only, the well-known result is included below for the reader's convenience.

Theorem 5. For any $k \leqslant n-1$, the k-dimensional subspace $\mathcal{R} \subseteq \mathbb{R}^n$ which meets the (arbitrary) given points $P_1, P_2, \ldots, P_{k+1} \in \mathbb{R}^n$ has the vector-equality

$$\mathbf{x} = P_1 + \sum_{i=2}^{k+1} \lambda_i \cdot \overrightarrow{P_1 P_i},$$

where each $\lambda_i \in \mathbb{R}$ runs through all the real numbers independently of each other. $\square$

In the special cases $k = 1$ and $k = n-1$, we get the well-known equalities of lines and 2-dimensional hyperplanes.

When we want to make intersections or projections with/to lower dimensional (say 2D or 3D) subspaces in $\mathbb{R}^n$, for the necessary grid (see section 1.6) we simply have to give all λ_i some discrete values, depending on the fine resolution we want to achieve.

1.4. In which region is P located?

The surfaces described in the previous subsection divide the space $\mathbb{R}^n$ into regions corresponding to different states of the chemical system. In figure 4, these regions are

$HaE_1bE_2cE_3$, AaE_1EE_3, BbE_2EE_1, CcE_3EE_2, ABCE, AE_1EB, BE_2EC and CE_3EA for quaternary systems in the 3-dimensional space. These intersection points can be calculated by the method described in the previous section, even in any dimension. In higher dimensions, however, the number and border points of the regions the simplex is divided into may be determined by the knowledge of the concrete dataset of intersection points of the surfaces and can be done in a similar way!

Now our (theoretical and computational) task is to determine which is the region of the above mentioned ones, in which *any* given point $P = [p_1, p_2, \ldots, p_n] \in \mathbb{R}^n$ falls into. Our method is as follows:

(1) Determine whether P is *under* or *above* each surface, using their approximations. This sets P *inside* or *outside* the region $HaE_1bE_2cE_3$.

(2) If P is under *all* of them, determine whether P is a *convex* linear combination of the vector set $\{\overrightarrow{AE}, \overrightarrow{AB}, \overrightarrow{AC}\}$. This requires to solve a system of linear equations and settles the region ABCE.

(3) If under one of the surfaces (say aE_1EE_3), determine whether P is a *positive* linear combination of the corresponding vector set ($\{\overrightarrow{AE_1}, \overrightarrow{AE}, \overrightarrow{AE_3}, \overrightarrow{Aa}\}$ in our case).

These rules are general ones for *any* higher dimension, modifying the list of the vectors according to the actual set of intersection points and the vertices of the simplex.

1.5. Modifying the system

In this general overwiew we consider only one of the methods for modifying the content of the mixture – gradually adding *one* of the compounds. Well, starting from the state in $\mathbb{R}^n$,

$$P_0 = \alpha_1\mathbf{a}_1 + \alpha_2\mathbf{a}_2 + \cdots + \alpha_{n+1}\mathbf{a}_{n+1},$$

and adding $\Delta\alpha_k$ many quantity of the compound a_k ($k \leqslant n$ is fixed), we get the system

$$P' = \alpha'_1\mathbf{a}_1 + \alpha'_2\mathbf{a}_2 + \cdots + \alpha'_{n+1}\mathbf{a}_{n+1},$$

where

$$\alpha'_i = \frac{\alpha_i}{1 + \Delta\alpha_k} \quad \text{for } i \neq k$$

and

$$\alpha'_k = \frac{\alpha_i + \Delta\alpha_k}{1 + \Delta\alpha_k}.$$

(Here we made of use of the facts that $\sum_{i=1}^{n+1} \alpha_i = 1$ and $\sum_{i=1}^{n+1} \alpha'_i = 1$ must hold.)

Using the method of the previous section, we can describe the new phase of the system where P' must fall into. However, an easy computation helps us to draw the geometrical orbit of the points P' in $\mathbb{R}^n$ whenever $\Delta\alpha_k \in \mathbb{R}^+$ runs through all the positive real numbers.

Theorem 6. Adding gradually (infinitely many) the kth compound to the mixture, the points $P' \in \mathbb{R}^n$ move through the *straight line segment* connecting P_0 and $\mathbf{a}_k$ (= the vertex of the simplex representing the pure mixture containing 100% of the kth compound and nothing else).

Proof. Clearly, we may deal with the case $k = 1$ and may shorten $\Delta\alpha_k$ as ε. Now we calculate the vector $\overrightarrow{PP'}$ (where $P_0 = [\alpha_1\mathbf{a}_1 + \alpha_2\mathbf{a}_2 + \cdots + \alpha_{n+1}\mathbf{a}_{n+1}]$) as

$$\begin{aligned}\overrightarrow{PP'} = P' - P &= \left[\frac{\alpha_1+\varepsilon}{1+\varepsilon} - \alpha_1, \frac{\alpha_2}{1+\varepsilon} - \alpha_2, \ldots, \frac{\alpha_{n+1}}{1+\varepsilon} - \alpha_{n+1}\right] \\ &= \frac{\varepsilon}{1+\varepsilon} \cdot [1-\alpha_1, -\alpha_2, \ldots, -\alpha_{n+1}] = \frac{\varepsilon}{1+\varepsilon} \cdot \overrightarrow{Pa_1},\end{aligned}$$

that is, the vector $\overrightarrow{PP'}$ is a scalar-multiple of the vector $\overrightarrow{Pa_1}$. Finally, $\varepsilon/(1+\varepsilon)$ goes to 1 as ε tends to positive infinity, so the points P' represent *all* the points of the straight line segment Pa_1. □

Let us mention that the above computation is OK, though it is made in barycentric co-ordinates, since $P_0 = [\alpha_1, \alpha_2, \ldots, \alpha_{n+1}]$ means $P_0 = \alpha_1\mathbf{a}_1 + \alpha_2\mathbf{a}_2 + \cdots + \alpha_{n+1}\mathbf{a}_{n+1}$.

1.6. Other questions

Here we list only some other problems which might be useful in chemistry and can be easily computed in any dimension. We do not think, however, that the simplest methods for these problems must be described here in full mathematical detail.

Making intersections of the full diagram with *any* lower dimensional hyperplanes in any dimension could be resolved as the problem of finding intersections of surfaces with the sides of the simplex, described in the previous section.

Orthogonal and central projecting of the full diagram can be calculated using the well-known equality systems of lines incident to a given point $P_0(p_1, p_2, \ldots, p_n)$ with direction vector $\mathbf{v}(v_1, v_2, \ldots, v_n)$ as

$$\begin{cases} x_1 = p_1 + v_1 \cdot t, & \\ \quad\vdots & t \in \mathbb{R}, \\ x_n = p_n + v_n \cdot t, & \end{cases}$$

or, if two points P_0 and Q_0 of the line are given, clearly $\mathbf{v} = \overrightarrow{P_0Q_0} = Q_0 - P_0$. The equality and the normal (orthogonal) vector of hyperplanes are given in theorem 4. The process clearly must proceed along a sufficiently fine grid on the hyperplane. Perhaps intersections with hyperplanes parallel to the sides of the simplex are most interesting: they represent mixtures when one chosen fixed compound has a fixed prescribed percentage. The easiest projections are the ones to the hyperplanes spanned by the co-ordinate axes: we simply have to forget the appropriate co-ordinate!

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