Proof of the Equivalence of the Hillert Analytical Method and the Method of Orthogonal Projection

Dmitry N. Saulov *,[a],

[a] *School of Engineering, The University of Queensland, AUSTRALIA*

Abstract

In this short paper, the equivalence of the Hillert analytical method with the method of orthogonal projection (or the Muggianu method) is rigorously proven.

Key words: Orthogonal projection, The Muggianu method, The Hillert analytical method

Consider a multicomponent system $A_1 - \ldots - A_n - \ldots - A_r$, where $(r > n > 1)$. Let $(x_1, \ldots, x_n, \ldots, x_r)$ be molar fractions in r-component system. Recalling the equality $x_1 + \cdots + x_r = 1$ and omitting x_r, one verifies that a composition of the r-component system $A_1 - \ldots - A_n - \ldots - A_r$ is represented by a point of the $(r-1)$-dimensional equilateral simplex. The faces and edges of the simplex represent the corresponding sub-systems. An example of such a simplex for 4-component system (Gibbs tetrahedron) is given in Figure 1. Each point of the simplex is described by the compositional vector

$$\mathbf{x} = x_1\mathbf{u}_1 + \cdots + x_{r-1}\mathbf{u}_{r-1} \ . \qquad (1)$$

where $\mathbf{u}_i$ are the spanning vectors of the simplex (see Figure 1).

Now assume that a compositionally dependent n-component interaction parameter $\alpha(y_1, \ldots, y_n)$ is defined for the n-component sub-system $A_1 - \ldots - A_n$. Here, $(y_1, \ldots, y_n)$ are the molar fractions in the n-component system $A_1 - \ldots - A_n$ so that $y_1 + \cdots + y_n = 1$. The parameter α can be extrapolated into the r-component system $A_1, \ldots, A_n, \ldots, A_r$ $(r > n)$ by the orthogonal projection of the point in $(r-1)$-dimensional simplex to the $(n-1)$-dimensional sub-simplex, which represents the sub-system $A_1, \ldots, A_n$ (see, for example, Figure 1).

Hillert [1] suggested the analytical method for the extrapolation of interaction parameters. In the Hillert analytical method (see, for example, the work by Ansara [2]), the extrapolation of the parameter α into r-component system is carried out by substituting the values v_i $(i = 1, \ldots, n)$ for the corresponding molar fractions y_i. The values v_i are given by

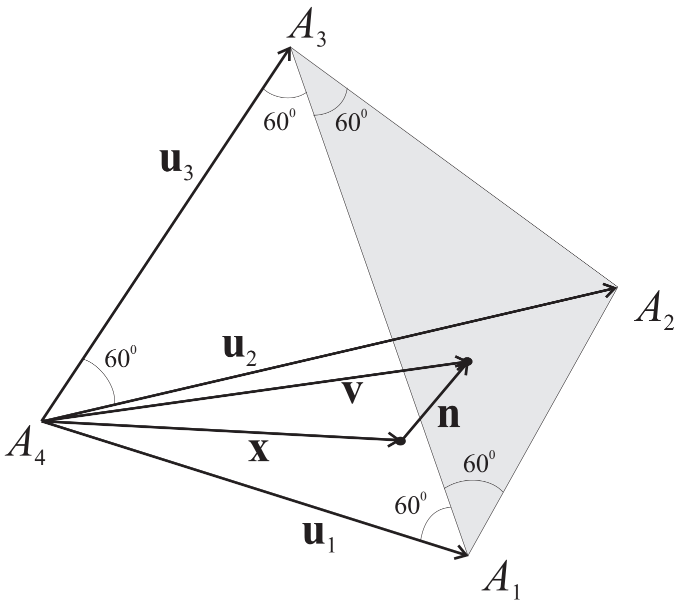

Fig. 1. The orthogonal projection of the four-component composition $\mathbf{x}$ to the three-component system (the plane $x_1 + x_2 + x_3 = 1$) when the system is represented by the Gibbs simplex

$$v_i = \frac{1}{n}\left(1 + nx_i - \sum_{j=1}^{n} x_j\right) \qquad i = 1, \ldots, n, \qquad (2)$$

where x_i $(i = 1, \ldots, n)$ are the molar fractions in the r-component system.

The case of extrapolating binary interaction parameters into multicomponent systems has been discussed by Cheng and Ganguly [3]. As pointed out by the authors, the quantities v_1 and v_2 define a point on the $A_1 - A_2$ binary join that is obtained

* Corresponding author: School of Engineering, The University of Queensland, St. Lucia, QLD 4072, Australia. Phone: (07)3365-6072

Email address: d.saulov@uq.edu.au (Dmitry N. Saulov).

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by the normal projection of a multicomponent composition (x_1, x_2,..., x_r). Cheng and Ganguly indicated that there exists a rigorous proof of this statement. According to the authors, however, the proof of the statement is too lengthy to be presented in Ref. [3]. Note also that the statement does not involve extrapolation of ternary and higher order interaction parameters, while dealing with binary parameters only.

More generally, the equivalence of the Hillert analytical method with the method of orthogonal projection (or the Muggianu method) can be formulated as the following lemma.

Lemma

The values v_i defined by Eqs. (2) determine the point, which is obtained by the orthogonal projection of the composition $\mathbf{x}$ defined by Eq. (1) in the r-component system $A_1 - \ldots - A_n - \ldots - A_r$ to the face of the simplex that represent the sub-system $A_1 - \ldots - A_n$.

Proof

Consider the vector $\mathbf{v} = v_1\mathbf{u}_1 + \cdots + v_{r-1}\mathbf{u}_{r-1}$ (see Figure 1) obtained by the orthogonal projection of vector $\mathbf{x}$ to the corresponding face. Note that $v_1 + v_2 + \ldots + v_n = 1$, since the vector $\mathbf{v}$ represents a composition in the sub-system $A_1 - \ldots - A_n$. The orthogonality of the vector $\mathbf{n} = \mathbf{v} - \mathbf{x}$ to the face implies that the inner products of the vector $\mathbf{n}$ and the vectors $(\mathbf{u}_1 - \mathbf{u}_2), \ldots, (\mathbf{u}_1 - \mathbf{u}_n)$ are equal to zero. That is

$$\begin{cases} (\mathbf{u}_1 - \mathbf{u}_2) \cdot (\mathbf{v} - \mathbf{x}) = 0 \\ \vdots \\ (\mathbf{u}_1 - \mathbf{u}_n) \cdot (\mathbf{v} - \mathbf{x}) = 0 \ . \end{cases} \tag{3}$$

In terms of the basis vectors $\mathbf{u}_1, \ldots, \mathbf{u}_{r-1}$, Eqs. 3 read

$$\begin{cases} (\mathbf{u}_1 - \mathbf{u}_2) \cdot \sum_{i=1}^{r-1} (v_i - x_i)\ \mathbf{u}_i = 0 \\ \vdots \\ (\mathbf{u}_1 - \mathbf{u}_n) \cdot \sum_{i=1}^{r-1} (v_i - x_i)\ \mathbf{u}_i = 0 \ . \end{cases} \tag{4}$$

One verifies that in equilateral simplex

$$\mathbf{u}_i \cdot \mathbf{u}_j = \frac{1 + \delta_{ij}}{2} \ , \tag{5}$$

where δ_{ij} is Kronecker's delta. Substitution of Eq. (5) into Eqs. (4) and the addition of the equality $v_1 + v_2 + \ldots + v_n = 1$ lead to the following system of linear equations:

$$\begin{cases} v_1 - x_1 - v_2 + x_2 = 0 \\ v_1 - x_1 - v_3 + x_3 = 0 \\ \qquad \vdots \\ v_1 - x_1 - v_n + x_n = 0 \\ v_1 + v_2 + \ldots + v_n = 1 \end{cases} \tag{6}$$

Summation of Eqs. (6) and rearrangement give

$$v_1 = \frac{1}{n} \left(1 + n x_1 - \sum_{j=1}^{n} x_j \right) \ . \tag{7}$$

Eq. (7) is equivalent to Eqs. (2) for $i = 1$. Substitution of Eq. (7) into Eqs. (6) gives Eqs. (2) for $i = 2, \ldots, n$. ■

The proven lemma also holds when the system is represented by a simplex in Cartesian coordinates as shown in Figure 2. Indeed, in the case of Cartesian coordinates, Eq. (5) reads

$$\mathbf{u}_i \cdot \mathbf{u}_j = \delta_{ij} \ . \tag{8}$$

All other equations remain unchanged.

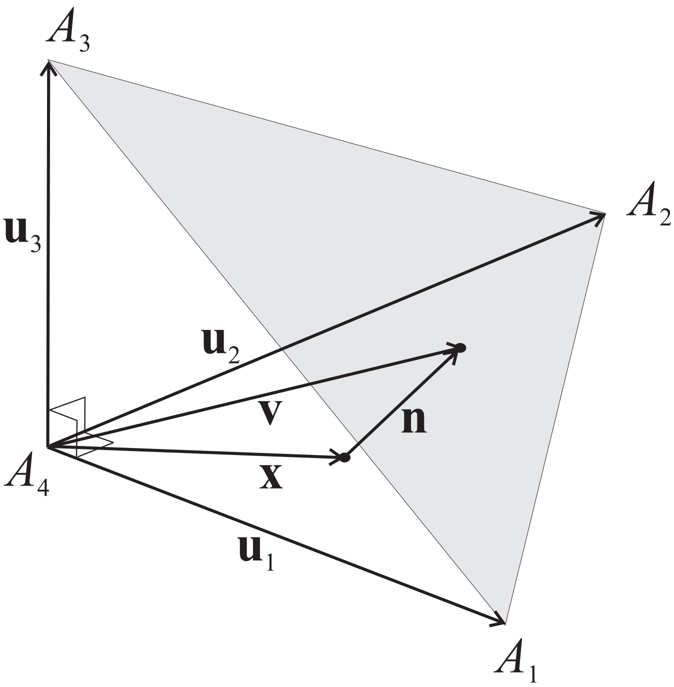

Fig. 2. The orthogonal projection of the four-component composition $\mathbf{x}$ to the three-component system (the plane $x_1 + x_2 + x_3 = 1$) when the system is represented by a simplex in the Cartesian coordinates

The presented proof is an important result. The proven equivalence implies that all the results obtained for the Hillert analytical method also hold for the method of orthogonal projection and vice versa.

Acknowledgments

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