On the physical validity of the proposed separation potentials for multicomponent mixtures

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Abstract. The object of the study is the "generalized" separation potential for multicomponent mixtures. A critical assessment of its validity from the point of view of thermodynamics is given and the assumptions made in its derivation are analyzed. The work is of a debatable nature and aims to develop a unified point of view on such a problematic topic of the theory of separation of multicomponent molecular and isotopic mixtures as the separation potential and separating capacity.

1. Introduction

One of the open questions of the modern theory of separation of multicomponent isotope and molecular mixtures is the search for a universal separation potential (value function), which would become a complete analogue of the corresponding potential widely used in the case of separation of binary mixtures. The basic idea of using the separation potential in the binary case is that this function allows, based only on the external parameters of the separation facility (concentration at the product and waste), to characterize the "separation forces" associated with obtaining the desired product (for example, the mixture of enriched uranium). In practice, this makes it possible to introduce a single scale of separation efficiency, not taking into account the features of the specific method used to solve the problem of obtaining a product with specified characteristics, which turned out to be extremely convenient for carrying out practical, including economic, calculations [1].

However, despite the active development in recent decades in the theory of separation of multicomponent mixtures, it has not yet been possible to introduce a separation potential that would allow us, without calculating the parameters of separation devices, to estimate the complexity and cost of the separation process only at specified concentrations of the target isotope in the ingoing and outgoing flows. Nevertheless, until the moment several variants of separation potentials have been proposed [2-15]. At the same time, in some works, an attempt was made not only to introduce the separation potential but also to relate it to the thermodynamics of the process [2, 3].

The object to study within the framework of the present paper is the potential for separating a multicomponent mixture of a kind \( \Phi(\vec{x}) = \Phi(x_1, ..., x_m) = \sum_{j=1}^{m} x_j \ln\left(\frac{x_j}{1-x_j}\right) \) (adhering to the author's notation \( x_j \) - the concentration of the \( j \)th component, \( m \) is the number of components of the mixture) considered in [2, 3] and originally proposed by P.G. Kuznetsov and others in 1963 [4] without
derivation and physical justification. The choice of this type of separation potential is largely
determined by the fact that it is most often used in the works of other authors [4-15].
The authors of [2, 3] attempted to derive and interpret this relation, based on the following
assumptions:

- the separation work that characterizes the "efforts" made by the cascade in the separation
  of a mixture \( W_k \) can be represented as a sum
  \[
  W_k = \sum_{i,j} W_{k,ij},
  \]
  where - refers to each, in the terminology of the authors, the "selected" pair of
  components that make up the multicomponent mixture;
- the efficiency of the cascade is determined by the "symmetry" of the operation of its
  stages, the authors suggest the possibility of non-mixing at the entrance to each stage by
  several relative concentrations from the selected pairs of components.

In view of the fact that the assumptions and statements made by the authors seem, in our opinion,
to be insufficiently correct, and also in order to develop a concept coordinated with the authors [2, 3],
within the framework of this article, we give our remarks and point of view on the principal problems
touched upon in [2, 3].

2. An analysis of the problem

Let us consider in more detail the results of [2, 3] for the purpose of carrying out a critical analysis.
Below are some comments on the essence of these works.

1. The formula \( \sum W_{k,ij} \) implies, obviously, that the separation of a multicomponent
   mixture occurs as an independent binary separation of a mixture of vapor-containing
   components. Since each component of the mixture "interacts" with each of the other
   (m-1) components, the work of separating the 4-component mixture (A, B, C, D-
   components of the mixture) [2, 3]
   \[
   W_k = W_{k,AB} + W_{k,AC} + W_{k,AD} + W_{k,BC} + W_{k,BD} + W_{k,CD},
   \]
   \[
   W_k = \sum_{j=1}^{m} W_{k,ij},
   \]
   However, in [3], \( \sum W_{k,ij} \) they speak of the sum of the "selected" pairs of components of the
   mixture, without giving the principle that the "choice" of these pairs is made. In this case, the work
   of separating the 4-component mixture is represented as:
   \[
   W_k = W_{k,AB} + W_{k,CD},
   \]
   those "selected" are two pairs (AB, CD) of 6 possible. As a result, it remains unclear the criterion for
   choosing such pairs and the validity of this assumption in principle.

2. It is logical to assume that in [2, 3] the authors arrange the components of the 4-
   component mixture in the series: A (1) - B (2) - C (3) - D (4) according to the increase
   (or decrease) of "activity" components. This means, for example, that
   \( \alpha_j > 1, \alpha_j = \alpha_j^{-1} \), when \( i < j \) and \( \alpha_i = 1 \). Taking into account the obvious relation
   \( \alpha_j = \alpha_j \cdot \alpha_i \), it can be stated that the equations given in [3] \( \alpha_{BD} = \alpha_{CA} (\alpha_{24} = \alpha_{31}) \)
   and \( \alpha_{AD} = \alpha_{CB} (\alpha_{14} = \alpha_{32}) \) can not be fulfilled.

3. During the past decades has been introduced many different variants of separation
   potential for multicomponent mixtures based on axiomatic assumptions (in particular,
a new treatment Peierls-Dirac axioms different interpretation representation of the
   separation process in the form of an independent separation binary mixtures consisting
   of pairs of components or aggregates and etc. [4-11]). Detailed information can be
   found in [15]. The results of numerical experiments on the optimization stages show
that all the known potential for multicomponent mixtures corresponds to particular cases depending on the type of mixture to be separated, which does not allow to determine which one is best for a particular purpose. The latter circumstance leaves open the question of the expediency of using them in practical calculations.

What is the reason for the absence of a single consistent theory of the potential for separation of multicomponent mixtures? Let us consider the analytical form of the separation potential for the case of binary mixtures:

$$\Phi(x) = (2x-1)\ln\left(\frac{x}{1-x}\right),$$

where \(x\) is the concentration of the "target" component.

This type of potential was obtained in the classical Peierls-Dirac theory on the basis of the following axioms:

- the separation potential \(\Phi(x)\) is only a function of the concentration of the mixture;
- separating capacity of an individual element \(\delta U = \sum_{j=1}^{n} q^j \Phi(x^j) - q^j \Phi(x^0)\), (\(n\) - number of species of mixture obtained as a result of the process of separation of the initial mixture of components, indices 0 and \(j\) determine, respectively, the parameters of the initial and enriched mixtures: \(q^0\) and \(q^j\) - the quantitative fluxes of the initial and enriched mixtures per unit time) is independent of the mixture concentration [16,17].

Expression (5) strictly justifies the theory of the "non-mixing" (ideal) cascade which, under certain conditions (small or large symmetrical separation on the steps), corresponds to the optimal separation conditions - the minimum number of separating elements (minimum of the total flow) to fulfill the given program of separation [16-18]. The function \(\Phi(x) = (2x-1)\ln\left(\frac{x}{1-x}\right)\), can be considered as a universal and generally accepted characteristic of the process of separation of a binary mixture. In particular, it is one of the basic concepts of the theory and practice of separating uranium isotopes [19].

In the case of separation of multicomponent mixtures, the mathematical model of mass transfer of components in the cascade is a system of differential equations (for "weak" enrichment) [20], or a system of difference equations (for the case values of separation coefficients \(\alpha_{ij}\) which are not close to unity) [9, 21,22] the impossibility of constructing an ordinary multicomponent cascade, which, like the ideal cascade for a binary mixture, would have "non-mixing" all concentrations at the entrances to the separation stages simultaneously. In other words, the impossibility of introducing a universal separation potential for a multicomponent mixture is a consequence of the absence in this case of a "reference" cascade, whose role in the separation of binary mixtures is played by an ideal cascade. At the same time, the multiplicity of possible boundary conditions in the optimization problem (the minimum of the total flow), whose solution is possible in the general case only by numerical methods [23]) also indicates the absence of a universal characteristic for an arbitrary separation process. Therefore, the use of physically unreasonable relationships derived from formal considerations (for the potential of P.G. Kuznetsov and others) in calculating and interpreting such characteristics as the thermodynamic work of separation, in our opinion, the total flow of the "best" cascade is inappropriate.

The procedure for calculating the total cascade flow with constant relative separation coefficients \(\alpha_{ij}\) is presented in [3], with the subsequent use of the result obtained to justify the relation determining the separation forces performed during processing of the multicomponent mixture. During the calculation, the condition was used that the "symmetry" of the separation at the stages of the cascade is possible for more than one pair of components in the separated mixture.

In this connection, it should be noted that in the case of constancy of the separation coefficients \(\alpha_{ij}\), the system of transport equations has an analytical solution connecting "external" and "internal"
parameters (since the "quasi-ideal" cascade) [9, 22, 24]. In other words, there is no need to calculate such a cascade by using the appropriate recurrence relations, as was done in [3]. In a particular case, this solution allows the construction of a cascade with no mixing of one (and only one) pair of selected "key" components \( R_{nk} = \frac{x_n}{x_k} \), (n, k are the key component numbers) at the entrance to the steps [8, 9, 22, 25, 26].

The impossibility of simultaneously mixing at several relative concentrations (for example \( R_{AB} \) and \( R_{CD} \) in [3]) follows both from a rigorous analysis of the system of transport equations, so from the next consideration: when the m-component mixture is divided (the number of independent equations describing the transfer of components (m-1)) the only parameter that ensures the "symmetry" of the separation on the stage is the function of the distribution of the power flow of the stages \( L(s) \) (s - stage number), which for each pair of "key" components will have its own individual character.

3. Conclusion
The paper gives a critical assessment of the physical validity of the separation potential described in [2, 3]. Inaccuracies in the determination of the separation work by the authors [2, 3] were found using the analyzed potential. It is shown that the considered potential, as well as the other variants of separation potentials proposed so far, can not act as a full-fledged analog of the corresponding function widely used in the case of binary mixtures separation.

The work is of a debatable nature and aims to develop a unified point of view on such a problematic topic of the theory of separation of multicomponent molecular and isotopic mixtures as a separation potential and separating ability.

4. References
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