



# Relationship between the partial molar and molar quantity of a thermodynamic state function in a multicomponent mixture – revisited

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## ABSTRACT

As far as a multicomponent mixture is concerned, different versions exist in the literature for the relationship between the partial molar and molar quantity of a thermodynamic state function with the most prominent example of the two quantities being the activity coefficient of an arbitrary component and the excess Gibbs free energy of a mixture comprising this component. Since the relationships published so far have to a large degree been derived independently of each other and result from apparently conflicting approaches, they are still considered as separate subjects in the literature. It is demonstrated that despite this curious situation all relationships are equivalent to each other from a mathematical point of view.

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## 1. Introduction

The relationship between the partial molar and the respective molar quantity of a thermodynamic state function belongs to the fundamentals of chemical thermodynamics. In combination with the Gibbs–Duhem relation it is a key issue of every thermodynamics textbook, at least as far as a binary system is concerned. At first glance, the transfer of the considerations from a binary to a multicomponent mixture appears to be a formality. The reality shows, however, that this is not true.

From a practical point of view, one of the most relevant pair of molar and related partial molar quantity is the excess Gibbs free energy of a mixture and the activity coefficients of the components being the constituents of it. In a binary solution, for instance, the relationship in question allows to determine the activity coefficient of the solute from experimental data on the activity coefficient of the solvent, and vice versa. Thus, the relationship is the prerequisite for reducing experimental effort or, if both sets of data are known, it serves to accomplish a consistency test of the data. Because of the practical relevance, a similar recursive approach for a multicomponent system has long been in the focus of interest. As a result, various relations have become known in the literature up to the present. Altogether they can be sorted into four groups. Interestingly, the representatives of these groups have never or only partially referred to the work of the representatives of another group. Therefore and due to the fact that the relationships belonging to these groups differ from each other in terms of mathematical

appearance and in terms of the conditions taken into account, the question arises as to how they are related to each other. This question will be answered hereinafter.

## 2. General relations

Suppose  $z$  is an extensive state function of a thermodynamic system which depends on the pressure,  $p$ , the temperature,  $T$ , and the composition of that system expressed by all mole numbers  $n_i$  of the components with  $i$  ranging from 1 to  $N$ . Then  $z$  is related to its molar quantity,  $Z$ , and its partial molar quantity,  $Z_k$ , by the following definitions:

$$Z = \frac{z}{\sum_{i=1}^N n_i}, \quad (1)$$

$$Z_k = \left( \frac{\partial z}{\partial n_k} \right)_{p,T,n_j}. \quad (2)$$

Here and in the following the index  $j$  covers all components ranging from 1 to  $N$  except the one component that refers to the quantity with respect to which the differentiation is carried out. If, upon differentiation, the quantities of less components than covered by the spectrum of  $j$  are kept constant, the exclusion of the questionable components will explicitly be stated, e.g., by  $j \neq m$  with  $m$  being one of the components of the mixture.

Mathematically, the extensive character of  $z$  means that  $z$  is a homogeneous function of first degree with respect to the numbers of moles. Then Euler's theorem is applicable according to which it holds that:

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$$z = \sum_{i=1}^N n_i Z_i. \quad (3)$$

The introduction of the mole fraction  $x_k$  of the  $k$ th component:

$$x_k = \frac{n_k}{\sum_{i=1}^N n_i} \quad (4)$$

allows equation (3) to be alternatively represented. By invoking equations (1) and (4), relationship (3) can be rewritten as:

$$Z = \sum_{i=1}^N x_i Z_i. \quad (5)$$

Moreover, in view of equation (4), it follows that:

$$x_N = 1 - \sum_{i=1}^{N-1} x_i. \quad (6)$$

The real behaviour of the partial molar property  $Z_k$  may be split into two contributions. One of them is attributed to the supposed ideal mixture with the respective partial molar property being denoted by  $Z_k^{id}$ . The second contribution covers the deviation of the real behaviour from ideality. This deviation is called the excess property or excess function which is indicated by the superscript  $E$ :  $Z_k = Z_k^{id} + Z_k^E$ . (7)

Via the definition of the excess partial molar quantity, the pertaining excess molar quantity  $Z^E$  can be introduced by means of which equation (5) can be reformulated:

$$Z^E = \sum_{i=1}^N x_i Z_i^E. \quad (8)$$

By differentiating equation (8) and by taking the Gibbs-Duhem relation for isobaric ( $p = \text{const.}$ ) and isothermal conditions ( $T = \text{const.}$ ) into account, one obtains:

$$(dZ^E)_{p,T} = \sum_{i=1}^N Z_i^E dx_i. \quad (9)$$

Let the state function  $z$  be equal to the Gibbs free energy  $g$ . Then the partial molar quantity  $G_i$  of the  $i$ th component is identical with the chemical potential  $\mu_i$ , and equations (8) and (9) take the form:

$$G^E = \sum_{i=1}^N x_i \mu_i^E, \quad (10)$$

$$(dG^E)_{p,T} = \sum_{i=1}^N \mu_i^E dx_i. \quad (11)$$

In view of the definition of the chemical potential of the  $k$ th component and by taking into account that the respective component is considered to behave ideal if its Raoultian activity is equal to the mole fraction, it follows from equation (7) for the excess chemical potential of the same component:

$$\mu_k^E = RT \ln f_k, \quad (12)$$

where  $f_k$  is the Raoultian activity coefficient of  $k$  in the mixture under consideration.

In the following, four different versions of the relationship between  $Z_k$  and  $Z$  for the most prominent example, i.e.,  $\mu_k^E$  and  $G^E$ , are scrutinized, in each case with regard to a multicomponent system. They are treated in the order in which they have become public. For the sake of completeness, it should be noted that aside from these four groups further relationships are under discussion in the literature, which, however, are excluded here from consideration. They either concentrate on the partial molar quantities alone as

it is true for the treatments of Wagner [1], McKay [2], Schuhmann [3], Gokcen [4], Arita and St. Pierre [5] as well as Anderson and Record [6], or they concentrate on quantities that are not exactly equivalent to each other in the sense of  $Z_k$  and  $Z$ . The latter applies to the efforts recently made in order to adapt the known relation between the Raoultian activity coefficient and the excess Gibbs free energy to a relation between the Henrian activity coefficient and the excess Gibbs free energy (see e.g., Ghosh [7]). Note that the Henrian activity coefficient, as a partial molar quantity, is not the equivalent to the molar quantity of the excess Gibbs free energy of a mixture and, moreover, note that there is already a well-defined thermodynamic relationship between the Raoultian and the Henrian activity coefficient [8] which is why the one problem can be readily reduced to the other.

### 3. Relationship by Redlich and Kister

The relationship between  $\mu_k^E$  and  $G^E$  that Redlich and Kister [9] published in 1948 has been overlooked in the literature for some time. This might have been due to the fact that Redlich and Kister did not waste a single word of explanation about how they ended up with their equation. The only association of thoughts in their work with respect to the starting point of their approach is even misleading, insofar as the authors merely referred to the definition of equation (10). Thus, the impression is created as if the authors'  $\mu_k^E$ - $G^E$  relationship had not required any comment or had even been pre-published which is, however, not true as a survey of the preceding literature shows. The truth is that for quite a long time a discussion had taken place in the community about how to transfer a partial molar quantity with respect to the numbers of moles into a quantity with respect to the mole fractions. The fundamental problem inherent to the discussion was the question as to whether, in general, a partial derivative with respect to the mole fraction is defined as this definition requires the variation of the mole fraction of one of the components of the system upon holding constant the mole fractions of all other components. At first glance, this appeared impossible from both a practical and a mathematical point of view due to the interrelationship of the mole fractions of all components as expressed in the equality of equation (6). The discussion had partially been echoed in the textbook of Lewis and Randall [10] (see also Young and Vogel [11]) and since Otto Redlich had translated this book into German, he might have considered the way of derivation to be obvious to the informed reader and, thus, refrained from giving further details.

There seems to be still another reason why Redlich and Kister only stated the final result of their relationship rather than the derivation of it. The main stimuli of their work were due to the fundamental publication of Benedict *et al.* [12] and due to the, of that time, most profound analysis in the field of evaluation of solution-thermodynamic data by Wohl [13]. Both Benedict *et al.* and Wohl had introduced and tested various forms of power-series expressions for the excess Gibbs free energy in terms of the mole fractions of all components and had calculated the respective activity coefficients from this quantity on the basis of the definition of the excess chemical potential, which is the implication of equations (1), (2), and (7):

$$\mu_k^E = \left( \frac{\partial \left( \sum_{i=1}^N n_i \cdot G^E \right)}{\partial n_k} \right)_{p,T,n_j}. \quad (13)$$

As a result, Benedict *et al.* [12] and Wohl [13] had made use of the same mathematical operation that underlay the derivation of Redlich and Kister's relationship. While Benedict *et al.* first of all

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