Rational Interpolation Formulae for the Excess Functions of Binary Mixtures

H. Brodowsky
Institut für Physikalische Chemie der Universität Kiel, Olshausenstr. 40, D-24098 Kiel

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Dedicated to Professor Dr. E. Wicke on occasion of his 80th birthday

A variation of the commonly used polynomial interpolation formulae for the excess functions of binary mixtures is proposed, in which the cross-calculation of the coefficients of partial and integral molar functions is greatly facilitated.

Introduction

It has become common practice to evaluate measurements of the activity coefficients or enthalpies of mixing of binary liquids or of terminal solid solutions in terms of interpolation formulae. The representation of experimental results in terms of parameters is often a prerequisite step in such applications as phase diagram calculations. If properly chosen, the set of all related integral and partial molar functions can be derived from one of them. In addition, the functions expressed in these formulae are mutually consistent and automatically obey Raoult's law and the Gibbs-Duhem relations.

There is no need, in continuous systems, to carry out the integration of the Gibbs-Duhem equation to obtain one partial molar function from the other. However, the interpolation schemes most widely used for partial and for integral functions are such, that it is tedious to bridge the gap between the two kinds, if more than two parameters are used in any formula. A variation of the method in which the parameters of the whole set of functions can be more readily obtained from the multi-parameter description of one them is therefore of great practical interest.

Historical Overview

As far back as 1895, Margules showed that the two partial molar relative functions of a binary system can be expressed as polynomials of the mole fraction of the other component, with the square of the mole fraction as the leading term [1]. This description assures adherence to Raoult's law of the solvent in the limit of an almost pure component. E.g., the partial molar excess Gibbs energies can be expressed in the following manner:

$$\Delta\bar{G}_1^{\mathrm{E}} = \sum_{i=2}^{k} \frac{1}{i} a_i x^i , \tag{1}$$

$$\Delta\bar{G}_2^{\mathrm{E}} = \sum_{j=2}^{k} \frac{1}{j} b_j (1-x)^j \tag{2}$$

if x is the mole fraction of the second component [2].

Of course, the two functions are not independent of each other; e.g., the coefficients b_j can be obtained from the a_i's by an integration of the Gibbs-Duhem relation of (1), such that

$$b_2 = \sum_{i=2}^{k} a_i , \tag{3}$$

$$b_3 = -\sum_{i=3}^{k} (i-2)\, a_i , \tag{4}$$

$$b_4 = \sum_{i=4}^{k} \binom{i-2}{2} a_i , \tag{5}$$

$$b_5 = -\sum_{i=5}^{k} \binom{i-2}{3} a_i , \tag{6}$$

$$b_k = (-1)^k a_k . \tag{7}$$

More general

$$b_j = (-1)^j \sum_{i=j}^{k} \binom{i-2}{j-2} a_i \tag{8}$$

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where the expression in front of the coefficient a_i is the binomial coefficient of the "j minus second" term of a difference $(1 - a_i)$, raised to the power of $(i - 2)$.

Similarly, the coefficients a_i can be calculated from the values of b_j.

A widely used interpolation formula for integral relative excess functions was first proposed by Guggenheim [3] and later propagated by Redlich and Kister [4], e.g. for the Gibbs energy of mixing,

$$\Delta G^{\mathrm{E}} = x(1-x) \sum_{i=0}^{k} c_i (1-2x)^i . \tag{9}$$

The symmetrical function $x(1-x)$ assures, that the expression vanishes at $x=1$ and at $x=0$, as called for in a proper "relative" function.

The variable $(1-2x)$ of the polynomial in the parentheses has the appealing property of being symmetrical with respect to $x=0.5$. The even and odd powers of this variable contribute in a lucid way to the overall value of the excess function.

However, the choice of this variable does not come without a price. It is rather laborious to calculate the values of a_i or b_j from the c_i's and vice versa [5, 6], if more than two coefficients of a kind are involved.

In wide-ranging investigations, Tomiska studied classes of interpolation formulae for the excess functions of binary and multicomponent systems, which fulfill the basic thermodynamic requirements, so-called "thermodynamically adapted power series" [7]. The commonly-used approaches of Margules, (1) and (2), and of Guggenheim, (9), appear as special cases of his general treatment. The particular types of polynomials singled out for consideration in this paper are also covered by his general approach.

It goes without saying that all polynomials conforming to the Gibbs-Duhem relations and to Raoult's law for dilute solutions, i.e. which belong to the class of "thermodynamically adapted power series", are not only fundamentally equivalent, but also share varying degrees of common features. The purpose here is to point out the convenience of one particular approach and to present the algorithm of the cross-calculations between various sets of polynomial coefficients.

Present Approach

For the purpose of a more tractable cross-calculation, (1), (2), and (9) are factorized into general parts x^2, $(1-x)^2$, and $x(1-x)$, respectively, and specific parts, to be called polynomials of the mole fraction x, $P_1(x)$, $P_2(x)$, and $P(x)$, respectively. This device will assure adherence to Raoult's limiting law of the partial molar function and to vanishing values of the relative integral functions at $x=0$ and $x=1$.

If coefficients A_i, B_i, and C_i are chosen to represent

$$P_1(x) = \sum_{i=0}^{k} A_i x^i ; \qquad \Delta\bar{G}_1^{\mathrm{E}} = x^2 P_1(x), \tag{10}$$

$$P_2(x) = \sum_{i=0}^{k} B_i x^i ; \qquad \Delta\bar{G}_2^{\mathrm{E}} = (1-x)^2 P_2(x), \tag{11}$$

and

$$P(x) = \sum_{i=0}^{k} C_i x^i ; \qquad \Delta G^{\mathrm{E}} = x(1-x) P(x), \tag{12}$$

application of the equation

$$\Delta\bar{G}_2^{\mathrm{E}} = \Delta G^{\mathrm{E}} + (1-x)\frac{\partial \Delta G^{\mathrm{E}}}{\partial x} \tag{13}$$

leads to the relationship between the coefficients B_i and C_i:

$$B_i = C_i (i+1) . \tag{14}$$

This follows from (12) and (13):

$$\frac{\partial \Delta G^{\mathrm{E}}}{\partial x} = \sum_{i=0}^{k} C_i [(i+1)x^i - (i+2)x^{i+1}], \tag{15}$$

$$\Delta\bar{G}_2^{\mathrm{E}} = \sum_{i=0}^{k} C_i (i+1) x^i [1 - 2x + x^2], \tag{16}$$

$$= (1-x)^2 \sum_{i=0}^{k} C_i (i+1) x^i . \tag{17}$$

Similarly, using the complementary expression of (13)

$$\Delta\bar{G}_1^{\mathrm{E}} = \Delta G^{\mathrm{E}} - x\frac{\partial \Delta G^{\mathrm{E}}}{\partial x} , \tag{18}$$

the relationship between the other coefficients is eventually obtained. Including the reverse operations, the set of all six relationships between the coefficients of the polynomials P_1, P_2, and P is

$$\begin{aligned} A_i &= B_i - B_{i+1}\frac{i+1}{i+2} = (C_i - C_{i+1})(i+1), \\ B_i &= \sum_{j=i}^{k} A_j \frac{i+1}{j+1} = C_i (i+1), \\ C_i &= \sum_{j=i}^{k} A_j \frac{1}{j+1} = B_i \frac{1}{i+1} \end{aligned} \tag{19}$$

with $A_{k+1} = B_{k+1} = C_{k+1} = 0$.

A change of the variable x, the mole fraction of the second component, to that of the first component $(1-x)$ affects only the polynomials $P_1(x)$, $P_2(x)$, and $P(x)$, which are replaced by $P_1'(1-x)$, $P_2'(1-x)$, and $P'(1-x)$, respectively, the prepolynomial factors in (10)–(12) remaining the same. The algorithm for the calculation of the new coefficients C_j', appropriate for the variable $(1-x)$, from the old coefficients C_i, e.g. for

$$P'(1-x) = \sum_{j=0}^{k} C_j'(1-x)^j , \tag{20}$$

$$C_j' = (-1)^j \sum_{i=j}^{k} \binom{i}{j} C_i \tag{21}$$

is identical for each of the three polynomials.

Another function of practical interest, the difference of the partial molar quantities, can also be expressed as a polynomial in x, the coefficients D_i being related to each of the other coefficients A_i, B_i, or C_i:

$$\Delta\overline{G}_2^{\mathrm{E}} - \Delta\overline{G}_1^{\mathrm{E}} = \frac{\partial \Delta G^{\mathrm{E}}}{\partial x} = \sum_{i=0}^{k+1} D_i x^i . \tag{22}$$

There is no prepolynomial factor in this case, and the degree of the polynomial is raised by one to $k+1$. Application of (15) leads to

$$D_i = (C_i - C_{i-1})(i+1) = B_i - B_{i-1}\frac{i+1}{i} \tag{23}$$

with $C_{-1} = B_{-1} = C_{k+1} = B_{k+1} = 0$.

The reverse relationships for these coefficients are

$$C_i = \sum_{j=0}^{i} D_j \frac{1}{j+1} \tag{24}$$

and

$$B_i = \sum_{j=0}^{i} D_j \frac{i+1}{j+1} . \tag{25}$$

The difference of the chemical potentials of the two components, (22), is sometimes directly obtained from such experiments as the vapor pressure ratio [8] or the chemical equilibration between halide solid solutions and the corresponding gaseous hydrogen halides [6]. In addition, it is often theoretically more easily tractable than the individual partial excees functions, being sometimes more directly interpreted in terms of the properties of the components than its single constituent partial molar excess Gibbs energies [9–13].

As it happens, (10) is practically identical with (1), the coefficients being related by

$$a_i = i \cdot A_{i-2} ; \quad 2 \le i \le k . \tag{26}$$

This similarity, or almost-identity, does not carry over to the pairs of equations (2) and (11) or (9) and (12), since the polynomials in these latter pairs are completely differently defined.

Another similarity, or virtual indentity, is observed between (8) and (21), particularly if the different starting numbers of the indices zero and two, respectively, are taken into account. In both cases, the change of the variable from x to $(1-x)$ is involved. Nevertheless, this similarity comes as a surprise, since different partial molar excess functions are tied together by (8), while equal polynomials $P(x) = P'(1-x)$ are tied together by (21), aside from the denominators i or j in (1) and (2).

Discussion

It is obvious that the coefficients A_i, B_i, C_i, and D_i can be more easily computed from each other than the coefficients a_i, b_i, and c_i, if the number of coefficients is larger than 2.

There is another reason for preferring the representation of polynomials according to (12) rather than to (9): If experimental points of an integral function, e.g. $\Delta H(x)$, are to be evaluated, the polynomial $P(x)$ of (12) is more directly obtained from a least squares fit to the data points of $\Delta H/(x-x^2)$ than the polynomial in terms of the variable $(1-2x)$ of (9). A similar though less pronounced advantage holds for the determination of the coefficients B_i of $P_2(x)$ in (11) rather than the coefficients b_i in (2) from a least squares fit to the data points of $\Delta\overline{G}_2^{\mathrm{E}}/(1-x)^2$.

There is, of course, no difference in the convenience of determining the parameters A_i in (10) and a_i in (1).

The relations between the interpolation formulae of integral and partial molar relative excess functions of binary solutions were illustrated for the excess Gibbs energies. The same set of rules applies, of course, to the excess part of all extensive thermodynamic functions, in particular to the excess volume, to the enthalpy of mixing, and to the excess entropy.

There is no fundamental difference in the presentation of the excess functions according to (1), (2), and (9) and according to (10), (11), and (12). However, since time and effort may be saved in applying the latter ones, it is, perhaps, worthwhile to share this approach with colleagues who wish to express their experimental results in terms of analytical interpolation formulae of excess functions.

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