

## Introduction of boundary conditions in the Pelton–Flengas Gibbs–Duhem integration for ternary solutions

ISHAK KARAKAYA AND WILLIAM T. THOMPSON

Department of Chemistry and Chemical Engineering, Royal Military College of Canada, Kingston, Ont., Canada K7L 2W3

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A multiple linear regression technique to represent partial excess property data for one component (A) in a ternary A–B–C system is presented. The procedure, following the methodology of Pelton and Flengas, recognizes the need to satisfy Henry's law for components B and C in solutions rich in component A as well as independent experimental knowledge which may be available for the B–C binary.

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On présente une technique de régression linéaire multiple qui permet de représenter les données relatives aux propriétés partielles en excès pour un composant (A) dans un système ternaire A–B–C. Cette technique, qui suit la méthodologie de Pelton et Flengas, reconnaît d'une part le besoin de satisfaire à la loi de Henry pour les composants B et C dans des solutions qui sont riches en A et d'autre part les connaissances expérimentales indépendantes qui peuvent être disponibles pour le mélange binaire B–C.

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For a ternary system A–B–C, Pelton and Flengas (1) proposed an analytical method to perform the Gibbs–Duhem integration. This is particularly well suited for use in phase diagram computations (2).

Let  $f_A$ ,  $f_B$ , and  $f_C$  represent isothermal partial molar excess thermodynamic functions for components A, B, and C. The composition variation for these properties are defined by the coefficients  $a_{jk}$ ,  $b_{jk}$ , and  $c_{jk}$  in the following expressions

$$[1] \quad f_A = \sum_{j=2} \sum_{k=0} a_{jk} y^j t^k$$

$$[2] \quad f_B = \sum_{j=0} \sum_{k=0} b_{jk} y^j t^k$$

$$[3] \quad f_C = \sum_{j=0} \sum_{k=0} c_{jk} y^j t^k$$

where the composition variables  $y$  and  $t$  are defined by

$$y = 1 - X_A$$

and

$$t = \frac{X_C}{X_B + X_C}$$

This choice of composition variables is particularly convenient for experimental purposes (3, 4), where concentrations of A may be altered in solutions of fixed B-to-C ratios. Coefficients  $a_{jk}$ ,  $b_{jk}$ , and  $c_{jk}$  are related by the following recursion formulae (1):

$$[4] \quad b_{jk} = a_{jk} - \left( \frac{j+1-k}{j} \right) a_{(j+1)k} \text{ for } j \geq 1$$

$$[5] \quad c_{jk} = b_{jk} - \left( \frac{k+1}{j} \right) a_{(j+1)(k+1)} \text{ for } j \geq 1$$

The suggested method of applying these equations is to establish the coefficients  $a_{jk}$  for one of the components, say A, from experimental data using multiple linear regression methods (7). An example is given in ref. 1 for Cd–Bi–Sn system. It is suggested that the boundary conditions to give the complete expressions for  $f_B$  and  $f_C$  be obtained from an independent knowledge of the thermodynamic properties of the B–C binary system. However, this procedure always leads to slight thermodynamic inconsistencies in the behaviour of the partial properties of components B and C near concentrations very rich in component A (1, 4–6). In particular, the limiting properties for  $f_B$  and  $f_C$  for  $X_A = 1$  are multivalued due to the indeterminacy of the variable  $t$  at this composition. This communication shows how this problem may be circumvented.

When for a given temperature, the expansion of the power series given by eq. [1] is written as

$$[6] \quad f_A = (a_{20} + a_{21}t + a_{22}t^2 + \dots + a_{2n}t^n)y^2 \\ + (a_{30} + a_{31}t + a_{32}t^2 + \dots + a_{3n}t^n)y^3 \\ \cdot \\ \cdot \\ + (a_{m0} + a_{m1}t + a_{m2}t^2 + \dots + a_{mn}t^n)y^m$$

it follows that the series expansion of eq. [2] for the partial excess property of B must (to satisfy the Gibbs–Duhem equation) be given (1) by

$$[7] \quad f_B = [(b_{00}) \quad + (b_{01})t \quad + (b_{02})t^2 \quad + \dots + (b_{0n})t^n] \\ + \left[ (-2a_{20}) \quad + (-a_{21})t \quad + 0 \quad + \dots + \left( -\frac{2-n}{1}a_{2n} \right) t^n \right] y \\ + \left[ \left( a_{20} - \frac{3}{2}a_{30} \right) + (a_{21} - a_{31})t + \left( a_{22} - \frac{1}{2}a_{32} \right) t^2 + \dots + \left( a_{2n} - \frac{3-n}{2}a_{3n} \right) t^n \right] y^2 \\ + \left[ \left( a_{30} - \frac{4}{3}a_{40} \right) + (a_{31} - a_{41})t + \left( a_{32} - \frac{2}{3}a_{42} \right) t^2 + \dots + \left( a_{3n} - \frac{4-n}{3}a_{4n} \right) t^n \right] y^3 \\ \cdot \\ \cdot \\ + \left[ (a_{m0}) \quad + (a_{m1})t \quad + (a_{m2})t^2 \quad + \dots + (a_{mn})t^n \right] y^m$$

In eq. [7], coefficients  $b_{0k}$  are zero for  $k \geq 1$ . This simply recognizes that  $f_B$  has a fixed value in solutions approaching pure A in composition and is therefore necessarily independent of the value of the variable  $t$  which becomes indeterminate at  $y = 0$  (pure A). In principle, the constant  $b_{00}$  can be determined from a knowledge of  $f_B$  at any composition (1). However, when this is done, it fixes the variation of  $f_B$  in the B-C binary where  $y = 1$ . Such a data treatment gives excess partial molar properties for B that are almost always inconsistent with independent experimental measurements of  $f_B$  in the B-C binary. The heart of this dilemma is the very sensitive nature of the coefficients in parentheses (eg.  $(a_{21} - a_{31})$ ) in eq. [7] to the constants involved in eq. [6]. In other words, differences in the regression of  $f_A$  (due to very small experimental error, different number of data points etc.) which yield the coefficients  $a_{jk}$  can result in substantially different coefficients in eq. [7]. These in turn have a large effect on the calculated partial excess properties of B in the B-C binary. This difficulty may be overcome by introducing appropriate constraints into the statistical evaluation of coefficients  $a_{jk}$  so as to require behaviour in the B-C binary that is in agreement with direct experimental studies of this system.

If independently established integral excess properties in the B-C binary,  $f$ , are expressed in the form

$$[8] \quad f = p_1 t + p_2 t^2 + \dots + p_n t^n$$

the partial excess thermodynamic property of B in this binary must be given by

$$[9] \quad f_B = -p_2 t^2 - 2p_3 t^3 + \dots + (1 - n)p_n t^n$$

Equation [9] is eq. [7] for the case where  $y = 1$ . Noting that the parameter  $b_{01}$  automatically becomes zero by virtue of the Pelton-Flengas recursion relationships (1), it follows that

$$[10] \quad \begin{aligned} a_{22} &= -p_2 - \frac{1}{2}a_{32} - \frac{1}{3}a_{42} - \dots - \frac{1}{m-1}a_{m2} \\ &\vdots \\ &\vdots \\ a_{2n} &= -(n-1)p_n - \frac{1}{2}a_{3n} - \frac{1}{3}a_{4n} - \dots - \frac{1}{m-1}a_{mn} \end{aligned}$$

Incorporation of these relationships into eq. [6] gives, upon rearrangement,

$$[11] \quad \begin{aligned} &[f_A + p_2 t^2 + 2p_3 t^3 + \dots + (n-1)p_n t^n] \\ &= [a_{20} y^2 + a_{21} y^2 t \\ &+ [a_{30} y^3 + a_{31} y^3 t + a_{32} t^2 (y^3 - \frac{1}{2} y^2) + \dots + a_{3n} t^n (y^3 - \frac{1}{2} y^2)] \\ &\vdots \\ &\vdots \\ &+ [a_{m0} y^m + a_{m1} y^m t + a_{m2} t^2 (y^m - \frac{1}{m-1} y^2) + \dots + a_{mn} t^n (y^m - \frac{1}{m-1} y^2)] \end{aligned}$$

Since  $f_A$  is regarded as the measured partial excess property of A in the ternary system and the parameters  $p_i$ , we are supposing, can be obtained from an independent study of the B-C binary, the left hand side of the eq. [11] is known. The coefficients  $a_{jk}$  (other than  $a_{2k}$  for  $k > 1$ ) can now be established by multiple linear regression in which the left hand side of eq. [11] is the dependent variable and the functions of  $t$  and  $y$  next to each coefficient are the independent variables. The procedure is completed by using eq. [10] to establish the coefficients  $a_{2k}$  for  $k > 1$ . In this way, it is possible to observe the constancy of the activity coefficient of B (and C at the same time) at virtually pure A as well as to incorporate independently established thermodynamic properties for the B-C binary.

The foregoing procedure has been applied to ternary salt systems investigated in this laboratory. It has been found that placing the suggested interrelationships on the coefficients does

not reduce the quality of the analytical representation of the excess partial molar properties of component A.

1. A. D. PELTON and S. N. FLENGAS. *Can. J. Chem.* **47**, 2283 (1969).
2. P.-L. LIN, A. D. PELTON, C. W. BALE, and W. T. THOMPSON. *Calphad*, **4**, 47 (1980).
3. T. OSTVOLD. *Acta Chem. Scand.* **26**, 1751 (1972).
4. W. T. THOMPSON, A. LEUNG, and D. G. HURKOT. *Can. Met. Quart.* **12**, 421 (1973).
5. A. D. PELTON and W. T. THOMPSON. *Prog. Solid State Chem.* **10**, 119 (1975).
6. A. D. PELTON and C. W. BALE. *Calphad*, **1**, 253 (1977).
7. C. A. BENNETT and N. L. FRANKLIN. *Statistical analysis in chemistry and chemical industries*. John Wiley and Sons Inc. 1961.