Legendre Polynomial Expansions of Thermodynamic Properties of Binary Solutions

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The advantages of orthogonal Legendre polynomials for representing the excess thermodynamic properties of binary solutions are presented. It is shown by means of examples that, in searching for empirical correlations among the coefficients of series expansions of several solutions, it is essential to start with a set of coefficients of an orthogonal series. Simple relationships are derived which permit the partial excess properties of each component to be expressed in terms of the same set of Legendre coefficients used for expressing the corresponding integral excess property. The Legendre polynomials are reformulated and the most accurate and convenient means of calculating them *via* a simple recursion relationship is described. Explicit conversion formulae from the coefficients of simple power series or Redlich-Kister polynomials to Legendre coefficients are given.

I. INTRODUCTION

SEVERAL years ago, in this journal we proposed the use of orthogonal Legendre polynomials for the representation of excess thermodynamic properties of binary solutions.[1] Although Legendre series have since been adopted by a number of authors, their widespread use has been hindered by the fact that some of the mathematical relationships given in the original article were unnecessarily complex. In particular, it was not shown how partial excess properties could easily be expressed with the same set of coefficients as was used for the integral excess property. In the present article, the advantages of Legendre series are reiterated. In particular, it is shown how the use of Legendre series can aid in the search for empirical correlations among the thermodynamic properties of groups of similar systems. The Legendre series are reformulated, and simple relationships permitting partial and integral properties to be calculated from one single set of coefficients are presented. The calculation of Legendre polynomials *via* a simple recursion relationship is also described in detail. Finally, explicit relationships permitting conversion from simple power series or Redlich-Kister series to Legendre series are given.

II. ADVANTAGES OF LEGENDRE POLYNOMIALS

In a binary system with components A and B, let ω^E be any integral excess thermodynamic property (such as excess Gibbs energy, G^E, excess enthalpy, H^E, or excess entropy, S^E). It is customary to express ω^E as a simple empirical power series expansion in the mole fractions X_A and X_B:

A. *Simple Power Series*

$$\omega^E = X_A X_B(q_0 + q_1 X_B + q_2 X_B^2 + \ldots) \quad [1]$$

The disadvantage of a simple power series representation is the interdependence (correlation) of the coefficients q_n. In Eq. [1], all the terms $q_n X_B^n$ have a maximum absolute value at $X_B = 1.0$ and all are zero at $X_B = 0$. Therefore, as n becomes progressively larger, the terms $q_n X_B^n$ become very small near $X_B = 0$, but are many orders of magnitude larger in absolute value near $X_B = 1.0$. The result is that, as n increases, the absolute value of q_n must become very large in order that this term can contribute to the total summation when X_B is close to zero. As the total number of coefficients is increased, the absolute values of q_n increase dramatically. This necessitates the storage and manipulation of variables to a large number of significant digits, since the total summation involves taking small differences between very large numbers.

It is also clear that no significance, either mathematical or physical, can be attached to the numerical values of the coefficients. Because of the high interdependence (correlation) between coefficients, simply adding one more term to the series will completely change the numerical values of all the previous coefficients.

Hence, if ω^E has been represented by, say, a 5-coefficient series and we wish to obtain an approximate expression by reducing the number of coefficients to three, we cannot simply truncate the last two terms.

Furthermore, with a simple power series representation, one is limited in practice to about 8 terms. Beyond this, the coefficients become so huge and the number of significant digits which must be maintained becomes so large as to be completely unwieldy.

The correlation among coefficients can be reduced if ω^E is expressed as a Redlich-Kister expansion:[2,3]

B. *Redlich-Kister Expansion*

$$\omega^E = X_A X_B(k_0 + k_1 z_B + k_2 z_B^2 + k_3 z_B^3 + \ldots) \quad [2]$$

where:

$$z_B = X_B - X_A = 2X_B - 1 \quad [3]$$

(Alternatively, the expansion could be in terms of the variable z_A:

$$z_A = X_A - X_B \quad [4]$$

In this case, the coefficients k_n remain unchanged if n is even and simply change sign if n is odd. By contrast, converting a simple power series in X_B as in Eq. [1] to a series in X_A is not so trivial.)

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Manuscript submitted October 2, 1985.

The use of the Redlich-Lister expansion decreases the correlation among coefficients since now the terms z^n are all zero at $X_A = X_B = 0.5$ and the terms do not all have their maximum absolute values at the same composition. Hence, with a Redlich-Kister expansion, the coefficients do not become so large so rapidly and the values are less dependent upon the total number of terms used in the series.

However, in order for the coefficients to be completely uncorrelated, ω^E should be expanded in terms of a set of orthogonal functions such as the Legendre polynomials:

C. *Legendre Expansion*

$$\begin{aligned}\omega^E &= X_A X_B[p_0 P_0(X_B) + p_1 P_1(X_B) + p_2 P_2(X_B) \\ &\quad + p_3 P_3(X_B) + \ldots] \\ &= X_A X_B[p_0 + p_1(2X_B - 1) \\ &\quad + p_2(6X_B^2 - 6X_B + 1) \\ &\quad + p_3(20X_B^3 - 30X_B^2 + 12X_B - 1) \\ &\quad + \ldots]\end{aligned} \qquad [5]$$

where the $P_n(X_B)$ are the Legendre polynomials which form a complete orthogonal set of functions in the interval $0 \leq X_B \leq 1$. That is:

$$\int_{X_B=0}^{1} P_n(X_B) \cdot P_m(X_B)\, dX_B = 0 \qquad (n \neq m) \qquad [6]$$

This orthogonality condition ensures that the coefficients p_n are uncorrelated. The first few Legendre polynomials $P_n(X_B)$ are listed in Table I.

As a first example to illustrate the advantages of an orthogonal series representation, consider the excess enthalpies of molten CsBr-CaBr$_2$ solutions measured calorimetrically at 810 °C. These were fitted by Østvold[4] to a four-membered simple power series of the form of Eq. [1]. The coefficients are listed in Table II, and the four-coefficient fit is compared to the experimental points in Figure 1(a). Since the Redlich-Kister and Legendre series are also polynomial expansions, the simple power series can be rearranged into a four-coefficient Redlich-Kister or a four-coefficient Legendre expansion. Explicit relationships for the coefficient conversions will be given in a later section. The Redlich-Kister and Legendre coefficients obtained by such rearrangement are also listed in Table II. All three representations, of course, give identical curves when all four coefficients are used as in Figures 1(a) through (c).

Table II. Coefficients (kcal/mol)* of Series Expansions for the Excess Enthalpy of Molten CsBr-CaBr$_2$ (A-B) Solutions at 810 °C[4]

Simple power series: $H^E = X_A X_B(q_0 + q_1 X_B + q_2 X_B^2 + q_3 X_B^3)$

$q_0 = -\ 9.143$

$q_1 = -16.757$

$q_2 = \ 29.082$

$q_3 = -14.426$

Redlich-Kister series: $H^E = X_A X_B(k_0 + k_1 Z_B + k_2 Z_B^2 + k_3 Z_B^3)$

$k_0 = -12.054$

$k_1 = \ 0.753$

$k_2 = \ 1.861$

$k_3 = -\ 1.803$

Legendre series:

$H^E = X_A X_B[p_0 + p_1 P_1(X_B) + p_2 P_2(X_B) + p_3 P_3(X_B)]$

$= X_A X_B[p_0 + p_1 P_1(Z_B) + p_2 P_2(Z_B) + p_3 P_3(Z_B)]$

$p_0 = -11.436$

$p_1 = -\ 0.331$

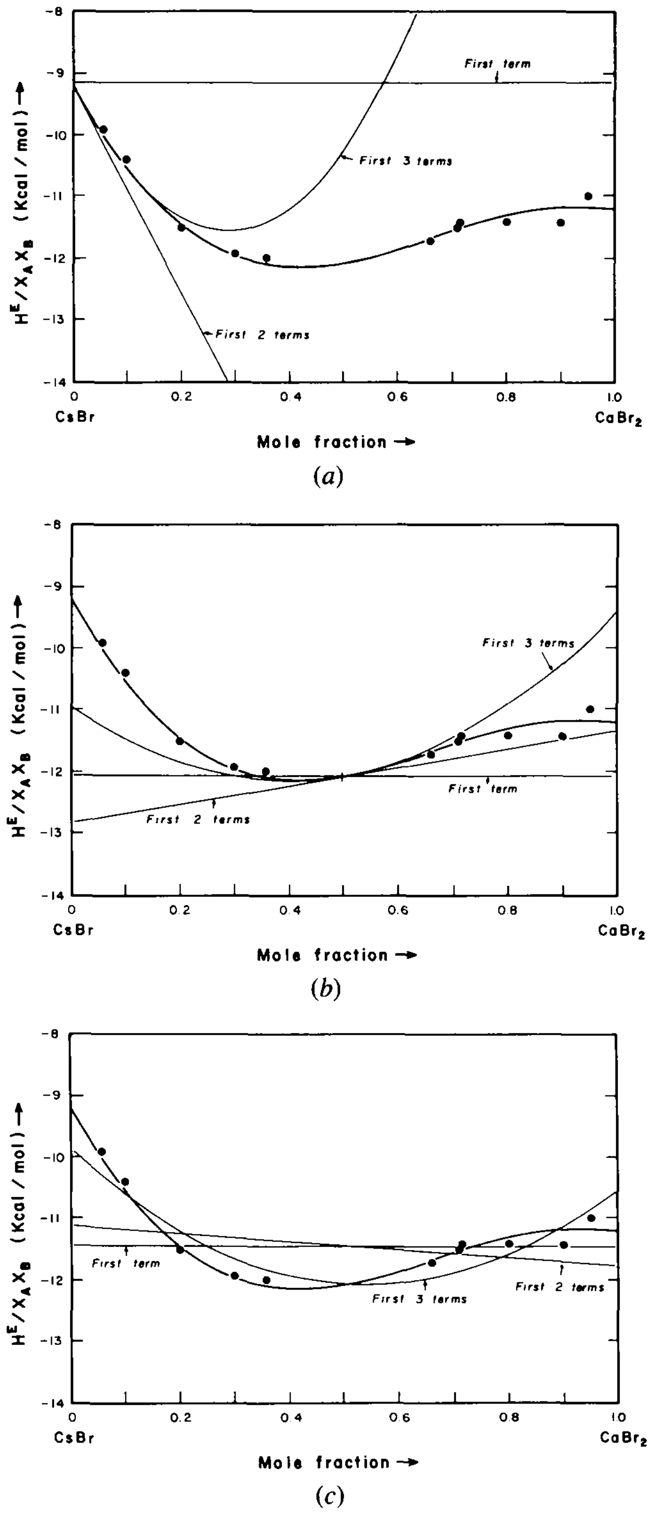
$p_2 = \ 1.241$

$p_3 = -\ 0.721$

*1 kcal = 4184 joules

Table I. The First Few Legendre Polynomials $P_n(X_B)$ and $P_n(Z_B)$ Where $Z_B = X_B - X_A$ and the Polynomials for the Expansions of the Partial Properties in Equations [12] and [13]

n	Legendre Polynomial $P_n(X_B)$	Legendre Polynomial $P_n(Z_B)$	$P_n(Z_B) + (Z_B - 1)P'_n(Z_B)$ (Polynomials for ω_A^E Expansion from Eq. [11])	$P_n(Z_B) + (Z_B + 1)P'_n(Z_B)$ (Polynomials for ω_B^E Expansion from Eq. [12])
0	1	1	1	1
1	$2X_B - 1$	Z_B	$2Z_B - 1$	$2Z_B + 1$
2	$6X_B^2 - 6X_B + 1$	$1/2(3Z_B^2 - 1)$	$1/2(9Z_B^2 - 6Z_B - 1)$	$1/2(9Z_B^2 + 6Z_B - 1)$
3	$20X_B^3 - 30X_B^2 + 12X_B - 1$	$1/2(5Z_B^3 - 3Z_B)$	$1/2(20Z_B^3 - 15Z_B^2 - 6Z_B + 3)$	$1/2(20Z_B^3 + 15Z_B^2 - 6Z_B - 3)$
4	$70X_B^4 - 140X_B^3 + 90X_B^2 - 20X_B + 1$	$1/8(35Z_B^4 - 30Z_B^2 + 3)$	$1/8(175Z_B^4 - 140Z_B^3 - 90Z_B^2 + 60Z_B + 3)$	$1/8(175Z_B^4 + 140Z_B^3 - 90Z_B^2 - 60Z_B + 3$
5	$252X_B^5 - 630X_B^4 + 560X_B^3 - 210X_B^2 + 30X_B - 1$	$1/8(63Z_B^5 - 70Z_B^3 + 15Z_B)$	$1/8(378Z_B^5 - 315Z_B^4 - 280Z_B^3 + 210Z_B^2 + 30Z_B - 15)$	$1/8(378Z_B^5 + 315Z_B^4 - 280Z_B^3 - 210Z_B^2 + 30Z_B + 15)$
6	$924X_B^6 - 2772X_B^5 + 3150X_B^4 - 1680X_B^3 + 420X_B^2 - 42X_B + 1$	$1/16(231Z_B^6 - 315Z_B^4 + 105Z_B^2 - 5)$	$1/16(1617Z_B^6 - 1386Z_B^5 - 1575Z_B^4 + 1260Z_B^3 + 315Z_B^2 - 210Z_B - 5)$	$1/16(1617Z_B^6 + 1386Z_B^5 - 1575Z_B^4 - 1260Z_B^3 + 315Z_B^2 + 210Z_B - 5)$
7	$3432X_B^7 - 12012X_B^6 + 16632X_B^5 - 11550X_B^4 + 4200X_B^3 - 756X_B^2 + 56X_B - 1$	$1/16(429Z_B^7 - 693Z_B^5 + 315Z_B^3 - 35Z_B)$	$1/16(3432Z_B^7 - 3003Z_B^6 - 4158Z_B^5 + 3465Z_B^4 + 1260Z_B^3 - 945Z_B^2 - 70Z_B + 35)$	$1/16(3432Z_B^7 + 3003Z_B^6 - 4158Z_B^5 - 3465Z_B^4 + 1260Z_B^3 + 945Z_B^2 - 70Z_B - 35)$



(*a*)

(*b*)

(*c*)

Fig. 1—(*a*) Excess enthalpy parameter, $H^E/X_{CsBr}X_{CaBr_2}$, for CsBr-CaBr$_2$ solutions at 810 °C. Points are experimental.[4] Heavy line is 4-coefficient simple power series expansion from Table II. Light lines are functions obtained by successively truncating terms of this expansion (1 kcal = 4184 joules). (*b*) Excess enthalpy parameter, $H^E/X_{CsBr}X_{CaBr_2}$, for CsBr-CaBr$_2$ solutions at 810 °C. Points are experimental.[4] Heavy line is 4-coefficient Redlich-Kister expansion from Table II. Light lines are functions obtained by successively truncating terms of this expansion. (1 kcal = 4184 joules). (*c*) Excess enthalpy parameter, $H^E/X_{CsBr}X_{CaBr_2}$, for CsBr-CaBr$_2$ solutions at 810 °C. Points are experimental.[4] Heavy line is 4-coefficient Legendre expansion from Table II. Light lines are functions obtained by successively truncating terms of this expansion (1 kcal = 4184 joules).

However, if terms are truncated from these series the situation is very different. In Figure 1(a) is shown the result of successive truncations of the final terms of the simple power series. Clearly, one cannot truncate such a series. In Figure 1(b) is shown the result of successive truncations of the final terms of the Redlich-Kister series. Acceptable approximations are obtained. However, the best approximations result from truncating the orthogonal Legendre expansion as can be seen from Figure 1(c).

As a second example to illustrate the advantages of an orthogonal series representation, we consider the eight binary molten salt solutions listed in Table III. Calorimetrically measured excess enthalpies have been fitted by Østvold[4] to simple power series expansions of the form of Eq. [1]. The coefficients q_n are listed in Table III. Most systems were well fitted with three coefficients. The two systems with cesium halides required four coefficients. A general tendency for the first coefficient, q_0, to become more negative as one descends in each group from the sodium halide to the cesium halide is observed. However, no obvious trends are observed in the other coefficients. Furthermore, we see that the higher coefficients can assume large numerical values. For CsBr-SrBr$_2$, q_2 and q_3 are as large as q_0.

These simple power series have been rearranged to the form of Legendre series as in Eq. [5] by means of the coefficient conversion relationships of Table IV which are discussed in a later section. The Legendre coefficients p_n are listed in Table III. It is evident that for any binary system the absolute value of the coefficients p_n tends to decrease as n increases. Also, a general tendency for p_1 to increase as one descends in each group from the Na halide to the Cs halide is evident. Although such a simple trend in the values of p_2 is not observed, all p_2 values are of the same sign and approximately of the same magnitude. It has been pointed out[4,5] that the change in Coulomb repulsion energy of next nearest neighbor cations for the mixing of an alkali halide MeX and an alkaline earth halide MX should vary approximatley as:

$$\delta = \frac{1}{2d_{MeX}} - \frac{2(d_{MeX} - d_{MX})}{d_{MX}(d_{MX} + d_{MeX})} \qquad [7]$$

where d_{MeX} and d_{MX} are the interionic distances. In Figure 2 are plotted the Legendre coefficients p_0 and p_1 from Table III *vs* δ calculated from Pauling's[6] ionic radii.

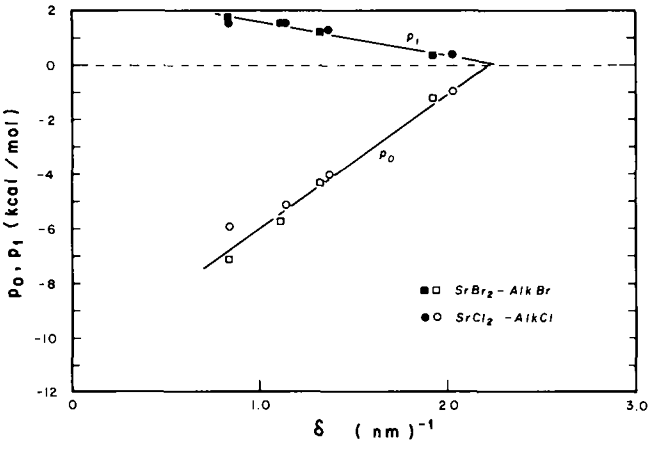


Fig. 2—Coefficients p_0 and p_1 of the Legendre expansions for the excess enthalpies of the molten salt solutions in Table III plotted *vs* the ionic size parameter δ defined in Eq. [7] (1 kcal = 4184 joules).

Table III. Coefficients q_n of Simple Power Series Expansions in X_B, Equation [1], and of Legendre Expansions in $P_n(X_B)$ or $P_n(Z_B)$, Equations [5] or [8], for the Excess Enthalpy of Some Molten Salt Solutions*

	Simple Power Series Coefficients (kcal/mol)[†4]				Legendre Coefficients (kcal/mol)[†]			
System A-B	q_0	q_1	q_2	q_3	p_0	p_1	p_2	p_3
$NaBr-SrBr_2$	−1.599	1.480	−0.790		−1.122	0.345	−0.132	
$KBr-SrBr_2$	−5.969	5.125	−2.719		−4.313	1.203	−0.453	
$RbBr-SrBr_2$	−7.718	5.641	−2.536		−5.743	1.553	−0.423	
$CsBr-SrBr_2$	−8.730	0.115	10.389	−7.701	−7.135	1.786	−0.194	−0.385
$NaCl-SrCl_2$	−1.505	1.554	−0.792		−0.992	0.381	−0.132	
$KCl-SrCl_2$	−5.716	5.066	−2.499		−4.016	1.284	−0.417	
$RbCl-SrCl_2$	−7.045	5.281	−2.198		−5.138	1.542	−0.366	
$CsCl-SrCl_2$	−7.463	1.939	4.471	−3.721	−5.934	1.530	−0.185	−0.186

*Bromide systems at 760 °C
Chloride systems at 894 °C
[†] 1 kcal = 4184 joules

Table IV. Conversion Formulae to Calculate Legendre Coefficients p_n of Equations [5] or [8] from Redlich-Kister Coefficients k_n of Equation [2] or from Simple Power Series Coefficients q_n of Equation [1]

$$\begin{aligned}
p_7 &= 16/429\ k_7 \\
p_6 &= 16/231\ k_6 \\
p_5 &= 8/63\ k_5 + 8/39\ k_7 \\
p_4 &= 8/35\ k_4 + 24/77\ k_6 \\
p_3 &= 2/5\ k_3 + 4/9\ k_5 + 14/33\ k_7 \\
p_2 &= 2/3\ k_2 + 4/7\ k_4 + 10/21\ k_6 \\
p_1 &= k_1 + 3/5\ k_3 + 3/7\ k_5 + 1/3\ k_7 \\
p_0 &= k_0 + 1/3\ k_2 + 1/5\ k_4 + 1/7\ k_6
\end{aligned}$$

$$\begin{aligned}
p_7 &= 1/3432\ q_7 \\
p_6 &= 1/924\ q_6 + 1/264\ q_7 \\
p_5 &= 1/252\ q_5 + 1/84\ q_6 + 7/312\ q_7 \\
p_4 &= 1/70\ q_4 + 1/28\ q_5 + 9/154\ q_6 + 7/88\ q_7 \\
p_3 &= 1/20\ q_3 + 1/10\ q_4 + 5/36\ q_5 + 1/6\ q_6 + 49/264\ q_7 \\
p_2 &= 1/6\ q_2 + 1/4\ q_3 + 2/7\ q_4 + 25/84\ q_5 + 25/84\ q_6 \\
&\quad + 7/24\ q_7 \\
p_1 &= 1/2\ q_1 + 1/2\ q_2 + 9/20\ q_3 + 2/5\ q_4 + 5/14\ q_5 \\
&\quad + 9/28\ q_6 + 7/24\ q_7 \\
p_0 &= q_0 + 1/2\ q_1 + 1/3\ q_2 + 1/4\ q_3 + 1/5\ q_4 + 1/6\ q_5 \\
&\quad + 1/7\ q_6 + 1/8\ q_7
\end{aligned}$$

Approximately linear correlations are observed. (The two lines also pass through zero at approximately the same value of δ.) Such correlations are, of course, purely empirical, and not all groups of systems yield such satisfying correlations. Nevertheless, in searching for such empirical correlations it is essential to start with a set of coefficients of an orthogonal series.

Another advantage of the Legendre expression was pointed out by Hillert.[7] When the coefficients are evaluated from experimental information they can, in principle, be determined one after the other due to the orthogonality. That is, the data could be first fitted to a one-coefficient series, then to a two-coefficient series, *etc*. In this way, the standard deviation for each parameter could be calculated and judged separately.

Finally, with Legendre expansions the number of terms which can be employed in practice is unlimited since round-off errors never arise because the coefficients never become large. In our previous article[1] it was shown that 50-coefficient expansions can be performed *via* least-squares regression with only eight-significant digit precision (FORTRAN "single-precision").

III. LEGENDRE EXPANSION IN $z_B = X_B - X_A$

A simplification may be effected by replacing X_B in the Legendre polynomials $P_n(X_B)$ in Table I by $(z_B + 1)/2$ (taken from Eq. [3]). Doing this, we obtain the (identical) Legendre polynomials $P_n(z_B)$ which are now orthogonal over the interval $-1 \leq z_B \leq 1$. These are also listed in Table I. We may now write:

$$\begin{aligned}
\omega^E &= X_A X_B[p_0 P_0(z_B) + p_1 P_1(z_B) + p_2 P_2(z_B) + \ldots] \\
&= X_A X_B[p_0 + p_1 z_B + p_2(3z_B^2 - 1)/2 \\
&\qquad + p_2(5z_B^3 - 3z_B)/2 + \ldots] \qquad [8]
\end{aligned}$$

Eq. [8] is identical to Eq. [5], and the coefficients p_n of the two series are identical. For example, for the $CsBr-CaBr_2$ system given in Table II we may write:

$$\begin{aligned}
H^E = X_A X_B[&-11.436 - 0.331\,(2X_B - 1) \\
&+ 1.241(6X_B^2 - 6X_B + 1) \\
&- 0.721(20X_B^3 - 30X_B^2 + 12X_B - 1)] \qquad [9]
\end{aligned}$$

or alternatively:

$$\begin{aligned}
H^E = X_A X_B[&-11.436 - 0.331 z_B \\
&+ 1.241(3z_B^2 - 1)/2 - 0.721(5z_B^3 - 3z_B)/2] \qquad [10]
\end{aligned}$$

where $X_B = X_{CaBr_2}$ and $z_B = X_B - X_A$. Eqs. [9] and [10] are completely identical and the use of Legendre polynomials in X_B, $P_n(X_B)$, or in z_B, $P_n(z_B)$, is a matter of choice. However, the use of $P_n(z_B)$ yields some simplification because, as can be seen in Table I, the Legendre polynomials $P_n(z_B)$ contain only odd powers of z_B when n is odd and only even powers when z_B is even. The polynomials $P_n(z_B)$ thus contain fewer terms than the polynomials $P_n(X_B)$. It is also now evident that replacing z_B by $z_A = -z_B$ leaves the coefficient p_n unchanged when n is even and changes the sign of P_n when n is odd. Hence, just as in the case of the Redlich-Kister expansion, we can convert a Legendre expansion in $P_n(z_B)$

to an expansion in $P_n(z_A)$ simply by changing the signs of the odd-numbered coefficients p_n. (Similarly, of course, a series in $P_n(X_B)$ as in Eq. [6] can be converted to a series in $P_n(X_A)$ in the same way.)

It is also now immediately clear from Table I that a two-coefficient Legendre expansion and a two-coefficient Redlich-Kister expansion are identical.

Another advantage to the use of $P_n(z_B)$ over that of $P_n(X_B)$ was pointed out by Rand[8] and Hillert.[7] Although Legendre series in $P_n(X_B)$ and $P_n(z_B)$ are identical in the binary system A-B, they are no longer identical in a ternary system A-B-C where $(X_A + X_B) \neq 1$. The expansion in terms of $P_n(z_B)$ has been shown[7,8] to be preferable in certain cases for purposes of estimating thermodynamic properties of ternary solutions from properties of the constituent binary subsystems.

IV. EXPRESSIONS FOR PARTIAL PROPERTIES

In the original article,[1] expressions for the partial excess properties of components A and B, ω_A^E and ω_B^E, were introduced which were unnecessarily complex and which were criticized by Howald and Eliezer[3] for this reason. See also References 9 and 10. A new and simpler set of expressions will now be derived.

The integral and partial properties are related by the expression:

$$\omega_A^E = \omega^E - X_B \frac{d\omega^E}{dX_B} = \omega^E - (z_B + 1)\frac{d\omega^E}{dz_B} \qquad [11]$$

Substituting Eq. [8] into Eq. [11] and collecting terms yields:

$$\begin{aligned}\omega_A^E &= X_B^2 \sum_{n=0} p_n[P_n(z_B) + (z_B - 1)P_n'(z_B)] \\ &= X_B^2[p_0 + p_1(2z_B - 1) \\ &\quad + p_2(9z_B^2 - 6z_B - 1)/2 + \cdots]\end{aligned} \qquad [12]$$

where $P_n'(z_B) = dP_n(z_B)/dz_B$.

Similarly:

$$\begin{aligned}\omega_B^E &= X_A^2 \sum_{n=0} p_n[P_n(z_B) + (z_B + 1)P_n'(z_B)] \\ &= X_A^2[p_0 + p_1(2z_B + 1) \\ &\quad + p_2(9z_B^2 + 6z_B - 1)/2 + \cdots]\end{aligned} \qquad [13]$$

The first few terms of these series are listed in Table I. General recursion relationships are presented in a later section.

For example, consider the CsBr-CaBr$_2$ system. Legendre coefficients for the integral excess enthalpy were listed in Table II, and the series was written out explicitly in Eq. [10]. The partial excess enthalpies of the components are given by Eqs. [12, 13] as:

$$\begin{aligned}H_{\mathrm{CsBr}}^E &= X_{\mathrm{CaBr_2}}^2[-11.436 - 0.331(2z_B - 1) \\ &\quad + 1.241(9z_B^2 - 6z_B - 1)/2 \\ &\quad - 0.721(20z_B^3 - 15z_B^2 - 6z_B + 3)/2]\end{aligned} \qquad [14]$$

$$\begin{aligned}H_{\mathrm{CaBr_2}}^E &= X_{\mathrm{CsBr}}^2[-11.436 - 0.331(2z_B + 1) \\ &\quad + 1.241(9z_B^2 - 6z_B - 1)/2 \\ &\quad - 0.721(20z_B^3 + 15z_B^2 - 6z_B - 3)/2]\end{aligned} \qquad [15]$$

where $z_B = X_{\mathrm{CaBr_2}} - X_{\mathrm{CsBr}}$.

The series for the integral property, Eq. [8], and the series for the partial properties, Eqs. [12, 13], are all expressed in terms of the one single set of coefficients, p_n, thereby responding to Howald and Eliezer's[3] principal objection to the earlier[1] formulation.

Since the integral and partial properties are now expressed in terms of one single set of coefficients, Legendre expansions may be used directly in least-squares optimization procedures[11,12] for the simultaneous optimization of experimental data for integral and partial thermodynamic properties.

V. CALCULATION OF LEGENDRE POLYNOMIALS

The general recursion relationship for the calculation of Legendre polynomials is:

$$P_n(z) = \frac{(2n-1)z}{n} P_{n-1}(z) - \frac{(n-1)}{n} \cdot P_{n-2}(z) \qquad [16]$$

where $z = z_B$ or z_A. Given that $P_0(z) = 1$ and $P_1(z) = z$, Eq. [16] can be used to calculate $P_n(z)$ for any n. It is from this relationship that the polynomials $P_n(z)$ in Table I were calculated.

In order now to calculate a numerical value of $P_n(z)$ for a given n and a given z, one can substitute the value of z into the appropriate polynomial expression in Table I. However, such a procedure is neither necessary nor desirable. It is simpler and more precise to perform the calculation directly from Eq. [16] each time. In Appendix 1 is a short FORTRAN subroutine to calculate $P_n(z)$ for any n and z *via* Eq. [16]. Besides the fact that this method of calculation is completely general and does not require the storage of a large number of polynomials in the computer memory, it is also faster and more precise when n is large. Substituting z directly into a polynomial in Table I involves evaluating z^n, z^{n-2}, z^{n-4}, *etc.* and then taking sums and differences of several terms. When n is large, round-off errors can accumulate. Calculation directly *via* Eq. [16] minimizes round-off errors.

The recursion relationship for $P_n'(z)$ is obtained by differentiating Eq. [16]:

$$\begin{aligned}P_n'(z) &= \frac{(2n-1)z}{n} P_{n-1}'(z) \\ &\quad - \frac{(n-1)}{n} P_{n-2}'(z) + \frac{(2n-1)}{n} P_{n-1}(z)\end{aligned} \qquad [17]$$

A short FORTRAN subroutine to calculate $P_n'(z)$ for any n and z is given in Appendix 2. The subroutines of Appendices 1 and 2 may be combined to calculate the polynomials $[P_n(z_B) + (z_B - 1)P_n'(z_B)]$ and $[P_n(z_B) + (z_B + 1)P_n'(z_B)]$ of Eqs. [12, 13] for the partial properties.

VI. CONVERTING SIMPLE POWER SERIES AND REDLICH-KISTER SERIES TO LEGENDRE SERIES

If data have already been fitted to a simple power series as in Eq. [1], or to a Redlich-Kister series as in Eq. [2], then it is clearly possible to convert the series into a Legendre expansion with the same number of coefficients, since all three types of series are polynomial expansions. The relationships permitting the Legendre coefficients p_n to be calculated from the coefficients q_n of a simple power series or from the coefficients k_n of a Redlich-Kister series are given for the first few terms in Table IV. The relationships for the conversion between the Redlich-Kister and Legendre coefficients were given previously by Hillert.[7]

The use of the relationships in Table IV can be illustrated by converting from the q_n or k_n coefficients to the p_n coefficients for the CsBr-CaBr$_2$ system in Table II.

VII. CONCLUSIONS

Orthogonal Legendre polynomials present several advantages over simple nonorthogonal power series for representing excess binary solution properties as functions of composition. Because the series is orthogonal, the terms are independent (uncorrelated). As a result, terms may be truncated from such a series in order to yield acceptable approximations. An example has been given. Also, since the value of any given coefficient is essentially independent of the number of terms used in the representation, coefficients of Legendre expansions of the properties of different solutions may be compared directly in searches for empirical correlations among solutions. An example has been given for the binary SrBr$_2$-alkali bromide and SrCl$_2$-alkali chloride systems. Furthermore, with Legendre expansions the number of terms which can be employed in practice is unlimited since the number of significant digits which must be retained in each coefficient does not increase as the number of coefficients increases.

Equations have been derived which permit the partial excess properties of each component in a binary solution to be expressed in terms of the same set of Legendre coefficients which are used for expressing the corresponding integral property. This represents a significant simplification over the earlier[1] formulation, and responds to the principal criticism of this earlier formulation.

The Legendre polynomials have been reformulated in terms of the composition variable $z_B = X_B - X_A$. This results in a reduction in the number of terms in each polynomial without affecting the numerical values of the Legendre coefficients.

The general recursion relationships for calculating Legendre polynomials as well as the functions for expressing the corresponding partial properties have been presented, and computer subroutines have been given for each case. The advantages of computing Legendre polynomials directly from these recursion relationships rather than by substitution into the explicit Legendre polynomial expressions have been discussed.

Sets of coefficient relationships up to the eighth term permitting conversion from simple power series or Redlich-Kister coefficients to Legendre coefficients have been given.

APPENDIX 1

FORTRAN subroutine to calculate
the Legendre polynomial $P_n(z)$

```
      FUNCTION P(N,Z)
      REAL*8 P,Z,PDUM,PHOLD
      INTEGER K,N
      P=1
      IF(N.EQ.0)RETURN
      P=Z
      IF(N.EQ.1)RETURN
      PDUM=1
      DO 10 K=2,N
        PHOLD=P
        P=(2*K-1)*Z*P/K-(K-1)*PDUM/K
        PDUM=PHOLD
   10 CONTINUE
      RETURN
      END
```

APPENDIX 2

FORTRAN subroutine to calculate the
derivative $P_n'(z)$ of a Legendre polynomial

```
      FUNCTION DP(N,Z)
      REAL*8 DP,Z,DPHOLD, DPDUM,P
      INTEGER K,N
      DP=0
      IF(N.EQ.0)RETURN
      DP=1
      IF(N.EQ.1)RETURN
      DPDUM=0
      DO 20 K=2,N
        DPHOLD=DP
        DP=(2*K-1)*Z*DP/K-(K-1)*DPDUM/K
     *       +(2*K-1)*P(K-1,Z)/K
        DPDUM=DPHOLD
   20 CONTINUE
      RETURN
      END
```

NOTE: This subroutine calls the subroutine of Appendix 1.

ACKNOWLEDGMENT

Financial support was provided by the Natural Sciences and Engineering Research Council of Canada.

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