Mathematical Representation of Thermodynamic Properties in Binary Systems and Solution of Gibbs-Duhem Equation

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The storage, retrieval, and manipulation of thermodynamic data with the aid of a computer requires accurate analytical representation of thermodynamic properties of solutions. In the present paper, a critical assessment is made of simple power series expansions and their limitations in representing thermodynamic properties over the entire composition range of a binary system. The advantages of certain orthogonal series as an alternative method of representation is also discussed. Particular emphasis is placed upon series representations which use Legendre polynomials due to their simplicity and the fact that their functional form is consistent with empirical observations of solution behavior. Since the coefficients of orthogonal series are independent of each other when the entire composition range of a binary system is represented, any thermodynamic property can be fitted to any desired degree of accuracy by a finite number of terms without the necessity of storing a large number of significant digits. Also, because the coefficients are uncorrelated, they are amenable to mathematical interpolation and extrapolation as well as to physical interpretation. The relationships between coefficients of series expansions of all partial and integral properties for the general case have been derived using the Gibbs-Duhem equation.

MODERN advances in computer technology have created an increasing necessity to have an analytical representation of the thermodynamic properties of binary systems for purposes of: i) data storage and retrieval, and ii) data manipulation, as for example in phase diagram, Gibbs-Duhem, and chemical equilibrium calculations.

Until now, simple power series expansions in terms of mole fractions have been used almost exclusively for these purposes. The fact that the coefficients of a power series expansion are highly interdependent means that a large number of significant digits must be retained in storage and in the calculations for all but the simplest systems. Furthermore, for many systems in which the thermodynamic properties vary in a more complicated way with composition it is impossible to adequately represent the properties by a simple power series at all. This problem may be partially rectified by data storage and retrieval using "spline functions." That is, a number of isolated data points are stored, and these are connected by a series of interpolating functions. However, this makes the task of data extrapolation, comparison, and manipulation arduous.

Through the use of orthogonal series expansions, one can retain the advantages of expressing properties by one simple equation, while avoiding the need to store and manipulate large numbers of significant digits, for even the most complicated of systems. Furthermore, since the coefficients of orthogonal expansions are completely uncorrelated with one another, they provide an easy method of comparison between systems, and they are more amenable to physical interpretation. The particular orthogonal series chosen should have a functional form similar to that of the thermodynamic properties being fitted, and should be easy to manipulate mathematically. In the present work, several orthogonal series representations are examined, and particular emphasis is placed upon the advantages of the Legendre series of orthogonal polynomials.

SIMPLE POWER SERIES EXPANSION

Any integral excess thermodynamic property, ω^E, or any partial excess property of component A, ω_A^E, or of component B, ω_B^E, in the binary system A-B, may be expressed as a simple power series expansion of the mole fraction:[1]

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

$$\omega_A^E = X_B^2 (a_0 + a_1 X_B + a_2 X_B^2 + \ldots\ldots) \qquad [2]$$

$$\omega_B^E = X_A^2 (b_0 + b_1 X_B + b_2 X_B^2 + \ldots\ldots) \qquad [3]$$

where X_A and X_B are the mole fractions, and ω is any thermodynamic property such as G, H, S, and so forth. Excess properties are preferable in such series expansions, since they remain finite in the dilute regions.

The simple power series expansions in the form shown above are well-behaved in the dilute regions. For example, $\omega_A^E = 0$ when $X_B = 0$, and Raoult's Law, $d\omega_A^E/dX_B \to 0$ as $X_B \to 0$, is obeyed. The thermodynamic relationships between the coefficients of Eqs. [1] to [3] are derived in Appendix 1 by differentiation of Eq. [1]. These are:

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$$b_n = (n+1)q_n \qquad [4]$$

$$a_n = (n+1)(q_n - q_{n+1}) \qquad [5]$$

$$a_n = b_n - \frac{n+1}{n+2} \cdot b_{n+1} \qquad [6]$$

Thus, if values of any one of the properties ω^E, ω_A^E, or ω_B^E are known at various compositions, then a least squares regression analysis to obtain the coefficients a_n, b_n, or q_n of the measured property, followed by application of the above relationships, will generate the functional behavior of all three thermodynamic properties over the composition range in question.

For example, for a system where one coefficient is sufficient to describe the measured property, then, from Eqs. [4] to [6]:

$$a_0 = b_0 = q_0 \qquad [7]$$

If the relative molar enthalpy can be described by one coefficient, then we speak of a "regular solution":

$$\Delta h = q_0 X_A X_B \qquad [8]$$

$$\Delta h_A = q_0 X_B^2 \qquad [9]$$

$$\Delta h_B = q_0 X_A^2 \qquad [10]$$

Or, in a "sub-regular" solution where Δh is adequately described by two coefficients:

$$\Delta h = X_A X_B (q_0 + q_1 X_B) \qquad [11]$$

and so, from Eqs. (4-5):

$$\Delta h_A = X_B^2 (q_0 + 2q_1 X_B) \qquad [12]$$

$$\Delta h_B = X_A^2 ((q_0 - q_1) + 2q_1 X_B) \qquad [13]$$

In an actual system, we fit the experimental data to as many coefficients as are necessary to give an adequate representation. For example, in the AgCl-RbCl system[2] a least squares fit to the experimentally measured values of the excess molar free energy g_{AgCl}^E at 800°C gives (in units of cal mol^{-1}):

$$g_{\text{AgCl}}^E = X_{\text{RbCl}}^2(-1497 - 3549 X_{\text{RbCl}} + 2759 X_{\text{RbCl}}^2) \qquad [14]$$

From Eq. [6], with AgCl as component A:

$$g_{\text{RbCl}}^E = X_{\text{AgCl}}^2(-2334 - 1710 X_{\text{RbCl}} + 2759 X_{\text{RbCl}}^2) + C \qquad [15]$$

where C is a constant of integration obtained from a known end-point value of g_{RbCl}^E at some value of X_{RbCl} somewhere in the composition range studied. Generally, the end-point composition will be that of the pure component or of a phase boundary. In the present case, the measured composition range extends up to $X_{\text{RbCl}} = 1$ where $g_{\text{RbCl}}^E = 0$. Hence, from Eq. [15], $C = 0$ in this particular case.*

Thermodynamic properties in relatively simple systems which do not deviate too far from sub-regular solution behavior can be adequately described by simple power series expansions with only a few coefficients (5 coefficients or less). However, a great many systems require a much larger number of coefficients. In such cases, the fact that the coefficients are interdependent becomes a real problem. For example, suppose that ω_A^E in a certain system is described by a ten-coefficient power series. All the terms $a_n X_B^n$ have a maximum absolute value at $X_B = 1.0$, and are all zero at $X_B = 0$. The higher terms such as $a_9 X_B^9$ are extremely small near $X_B = 0.0$, but are many orders of magnitude larger in absolute values near $X_B = 1.0$. The result is that, as n increases, the absolute value of a_n must become very large in order that this term can contribute to the total summation when X_B is close to 0.0. As the total number of coefficients is increased, the absolute values of a_n increase dramatically. This necessitates the storage and manipulation of variables in the computer to a large number of significant digits (DOUBLE PRECISION—16 significant digits, or higher) since the total summation involves taking small differences between very large numbers, particularly for larger values of X_B. In many complicated systems, particularly those in which the thermodynamic properties change rapidly over a narrow composition range, this problem becomes so acute that the properties cannot be adequately represented by simple power series expansions at all, as will be illustrated later.

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. Thus, one requirement of any proposed new series is that there be no interdependence between coefficients. Before proposing such a series, let us examine some other important considerations in the analytical representation of thermodynamic properties in binary systems.

GENERAL CONSIDERATIONS IN USE OF SERIES REPRESENTATIONS IN BINARY SYSTEMS

It must be recognized that in fitting thermodynamic data to any series representation, one is usually not attempting to obtain a statistical averaging of the data, since there is no real physical significance to the terms in the series (except possibly to the first and second "regular" and "sub-regular" terms of a power series.) One is simply trying to obtain an analytical expression which adequately describes the property by a smooth curve. Since there is no known analytical expression to which data must conform over the entire composition range of a binary system, the "best" curve which one can draw through the data points is the one which one draws "by eye," using experience and common sense as one's guide. Consequently, when analytically representing thermodynamic data, one is better off plotting up the data points, drawing the best curve by eye, and then fitting an analytical series to this curve rather than performing a least squares analysis directly to the experimental data points. Hence, in complex systems it is possible that one may end up using an analytical series with more coefficients than there were original experimental data points.

In the dilute regions ($X_B \to 0.0$ and $X_B \to 1.0$), there are certain criteria to which any analytical representation should conform. Specifically, the "α" functions" should be well-behaved (*i.e.*, continuous and finite)

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*The calculation of the integration constant C is discussed for the general case in the summary of equations (Table V).

in the dilute regions. The α functions are defined as follows:

$$\alpha_{\text{int}} = \omega^E/X_AX_B \qquad [16]$$

$$\alpha_A = \omega_A^E/X_B^2 \qquad [17]$$

$$\alpha_B = \omega_B^E/X_A^2 \qquad [18]$$

(where the subscript "int" refers to the integral excess property). For example, as $X_B \to 0.0$ (and $g_A^E \to 0.0$), it is necessary that the ratio $\alpha_A = g_A^E/X_B^2$ remain finite. This is based upon empirical observations of solution behavior as well as upon theoretical considerations as discussed, for example, by Darken.[3] Consequently, when fitting data to any series representation, we should note that: i) The series expansion should be fitted to the best curve which has been drawn "by eye" through the experimental α *function* points (rather than through the experimental ω^E points) in order to ensure that one is extrapolating properly in the limiting regions; ii) The analytical series employed to represent the system must give finite and otherwise well-behaved α functions in the limiting regions.

ORTHOGONAL SERIES

Orthogonal series appear attractive for representation of thermodynamic properties since the coefficients of such series are uncorrelated. That is, the value of any one coefficient in independent of the total number of terms used in the series expansion. Before we look at specific orthogonal series, we shall first consider the general properties of orthogonal sets of functions.

Consider an infinite sequence of functions of the independent variable x: $\phi_0(x)$, $\phi_1(x)$, $\phi_2(x)$, ... These functions are said to form an orthogonal set of functions over the interval $a \le x \le b$ if, for all $m \neq n$:

$$\int_a^b \phi_n(x)\cdot\phi_m(x)\,dx = 0 \qquad [19]$$

For example, the set of functions defined by $\phi_n(x) = \cos(nx)$ are orthogonal over the interval $0 \le x \le \pi$ since

$$\int_0^\pi \cos(mx)\cdot\cos(nx)\,dx = 0 \qquad [20]$$

for all $m \neq n$. However, the functions used in the simple power series of Eq. [1], $\phi_n(x) = x^n$, are not orthogonal over any interval.

An arbitrary function $f(x)$ can be expressed as an infinite series of the orthogonal functions $\phi_n(x)$:

$$f(x) = \sum_{n=0}^{\infty} c_n\phi_n(x) \qquad [21]$$

where the c_n are called the coefficients of $f(x)$ relative to the orthogonal functions $\phi_n(x)$. For example, $f(x)$ can be expressed over the interval $0 \le x \le \pi$ as a "Fourier cosine series":

$$f(x) = \sum_{n=0}^{\infty} c_n \cos(nx) \qquad [22]$$

where the c_n are the "Fourier cosine coefficients" of $f(x)$.

By multiplying both sides of Eq. [21] by $\phi_m(x)$ and integrating over the interval $a \le x \le b$, we see that:

$$c_m = \frac{\int_a^b f(x)\cdot\phi_m(x)\,dx}{W(m)} \qquad [23]$$

where

$$W(m) = \int_a^b [\phi_m(x)]^2\,dx \qquad [24]$$

$W(m)$ is a normalization factor which can be seen to be a function only of m. Consequently, each of the coefficients c_n can be obtained by taking the area under the curve of the product $f(x)\cdot\phi_m(x)$ over the interval $a \le x \le b$, and so the coefficients c_n are uncorrelated with each other. That is, the coefficient c_4, for example, has the same numerical value whether we terminate the expansion after 4, 10, or 100 terms. Furthermore, there is no tendency for the coefficients to become progressively larger as n increases, and in general, all coefficients tend to be of the same order or less than the first few coefficients.

The complete theory of orthogonal functions can be found in standard texts.[4] It can be shown that if the set $\{\phi_n(x)\}$ is a "complete" orthogonal set, then any function $f(x)$ can be expressed to any desired degree of precision by a finite number of terms in the expansion Eq. [21].

If a graphical plot of a function $f(x)$ is known, and we wish to represent this curve by an orthogonal series, then we can determine as many coefficients c_n as are necessary to give the desired precision of fit by taking the areas as in Eq. [23]. This could easily be done by numerical integration on a computer. Alternatively, it may often be simpler to determine the coefficients by a least squares regression analysis. First, we note that if a function $f(x)$ is approximated by n' terms of an orthogonal series, then the coefficients c_n are such as to minimize the integral

$$\int_a^b [f(x) - \sum_{n=0}^{n'} c_n\cdot\phi_n(x)]^2\,dx \qquad [25]$$

This may be shown from the general theory of orthogonal series.[4] Now, if we take our graphical plot of $f(x)$ which was drawn "by eye," and from this curve we read off a large number of dummy "data points" which are evenly spaced along the x-axis, and which cover the complete interval $a \le x \le b$, then a least squares regression analysis using these dummy data points will generate the coefficients ξ_n of the series $f(x) = \sum_{n=0}^{n'} \xi_n\phi_n(x)$, where the ξ_n will approximate the coefficients c_n. The approximation will be better the greater is the number of dummy data points. In effect, we are approximating the integral [25] by a large number of rectangles, and then minimizing the area of these rectangles. Hence, it can be appreciated why the dummy data points should be evenly spaced along the x-axis (so that all the rectangles are of the same width), and also why the entire interval $a \le x \le b$ must be covered (since the series is only orthogonal over the entire interval.) If we do not wish to draw the function $f(x)$ "by eye," but instead we wish to use the original experimental data points in the least squares approximation of $f(x) = \sum_{n=0}^{n'} \xi_n \phi_n(x)$, then the coefficients ξ_n which we generate will not, in general, equal the orthogonal coefficients c_n, although the approximation will become better the more data points there are and the more evenly spaced these points are along the x-axis. Even in this case, because of the nature of orthogonal series, the coefficients ξ_n will, in general, not be high interdependent, and will all tend to be of the same order of magnitude or to decrease as n increases.

We shall now consider some of the orthogonal or nearly orthogonal series which may be utilized to give series representations of thermodynamic properties in binary systems.

LEGENDRE POLYNOMIALS

Although many orthogonal series of functions could, in principle, be used to represent thermodynamic functions in binary systems, the number of coefficients required to give a representation of a desired precision can be greatly reduced by choosing an orthogonal series which approximates the functional form of the thermodynamic properties being represented. Since quasi-chemical theory predicts that excess thermodynamic functions are generally algebraic functions of composition (rather than trigonometric or other transcendental functions), an orthogonal series based upon algebraic functions is preferable. Furthermore, the series chosen should be such as to obey Raoult's Law and to give finite and well-behaved α functions in the dilute regions, as discussed previously. It should also be easily differentiated and integrated for manipulation in the Gibbs-Duhem equation, etc. It would also be desirable that the first and second terms correspond to the "regular" and "sub-regular" solution terms. These criteria are all satisfied if we expand the α functions as orthogonal series of the orthogonal functions $P_n(x)$:

$$\alpha_{\text{int}} = \omega^E/X_A X_B = \sum_{n=0}^{n'} q_n P_n(X_B) \qquad [26]$$

$$\alpha_A = \omega_A^E/X_B^2 = \sum_{n=0}^{n'} a_n P_n(X_B) \qquad [27]$$

$$\alpha_B = \omega_B^E/X_A^2 = \sum_{n=0}^{n'} b_n P_n(X_B) \qquad [28]$$

where the $P_n(x)$ are the Legendre polynomials which form a complete orthogonal set of functions in the interval $0 \le x \le 1.0$. The first few Legendre functions over this interval are:

$$P_0(x) = 1 \qquad [29]$$

$$P_1(x) = 2x - 1 \qquad [30]$$

$$P_2(x) = 6x^2 - 6x + 1 \qquad [31]$$

$$P_3(x) = 20x^3 - 30x^2 + 12x - 1 \qquad [32]$$

$$P_4(x) = 70x^4 - 140x^3 + 90x^2 - 20x + 1 \qquad [33]$$

For example the Legendre series of α_A is:

$$\alpha_A = \omega_A^E/X_B^2 = a_0\cdot(1) + a_1\cdot(2X_B - 1) + a_2\cdot(6X_B^2 - 6X_B + 1) + \ldots\ldots \qquad [34]$$

The first term ($n = 0$) is simply the "regular solution" term, and the second ($n = 1$) is the "sub-regular solution" term. The series obeys Raoult's Law (and hence also Henry's Law) and gives finite and otherwise well-behaved α functions in the dilute regions. Each Legendre polynomial $P_n(x)$ is merely a grouping of powers of x. Thus, all the physical advantages of a power series representation are maintained, but because the series is now orthogonal, the disadvantages are avoided.

The general recursion relationship for the terms $P_n(x)$ is:

$$P_n(x) = \frac{(2n-1)(2x-1)}{n}\cdot P_{n-1}(x) - \frac{(n-1)}{n}\cdot P_{n-2}(x) \qquad [35]$$

The series is orthogonal over the interval $0 \le x \le 1$. That is:

$$\int_0^1 P_n(x)\cdot P_m(x)\,dx = 0 \qquad (n \ne m) \qquad [36]$$

and the normalization factor (Eq. [24]) is:

$$W(n) = \int_0^1 [P_n(x)]^2\,dx = 1/(2n+1) \qquad [37]$$

Usually, in standard texts, the Legendre polynomials are given as functions $P_n(z)$ orthogonal over the interval $-1 \le z \le 1$. In the present case, a substitution $z = 2x - 1$ has been made to make the functions orthogonal over the interval $0 \le x \le 1$.

A graph of the first few Legendre functions is shown in Fig. 1. All functions are equal to +1.0 at $x = 1.0$, and to ± 1.0 at $x = 0$. In the interval $0 \le x \le 1.0$, all functions are bounded by ± 1.0. Unlike the simple power series functions (x, x^2, x^3, ...) which all have maxima at $x = 1.0$ and which are all zero at $x = 0.0$, the Legendre functions all have maxima and minima

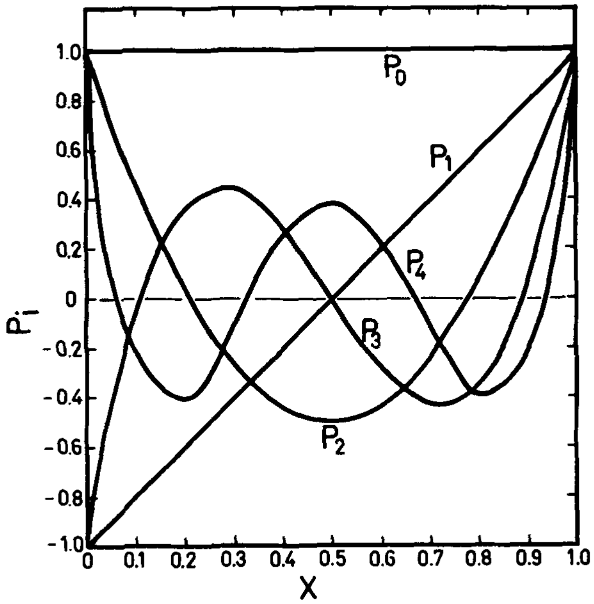

Fig. 1—The first 5 Legendre polynomials orthogonal over the interval $0 \le x \le 1$.

at different values of x. Also, each function after the second one has one more extremum in the interval $0 \leq x \leq 1$ that did the previous function, and so the error in fit is not concentrated near $x = 1.0$ as in the case of simple power series. We can thus appreciate qualitatively why the coefficients of Legendre series expansions (as in Eqs. [26] to [28]) are uncorrelated. Each term $P_n(x)$ represents a different functional "character" than any of the other terms. This is, of course, the meaning of the orthogonality criterion of Eq. [19].

Differentiation of Eq. [26] (see Appendix 2) generates the following relationships between the coefficients of Eqs. [26] to [28]:

$$a_n = (n+1)q_n + (2n+1) \cdot \sum_{k=1}^{(n+k)=n'} q_{n+k}(-1)^k \qquad [38]$$

$$b_n = (n+1)q_n + (2n+1) \cdot \sum_{k=1}^{(n+k)=n'} q_{n+k} \qquad [39]$$

$$q_n = a_n/(n+1) + (2n+1) \cdot \sum_{k=1}^{(n+k)=n'} \frac{1}{(n+k)(n+k+1)} \cdot a_{n+k} \qquad [40]$$

$$q_n = b_n/(n+1) + (2n+1) \cdot \sum_{k=1}^{(n+k)=n'} \frac{(-1)^k}{(n+k)(n+k+1)} \cdot b_{n+k} \qquad [41]$$

$$b_n = a_n + (2n+1) \cdot \sum_{k=1}^{(n+k)=n'} \frac{k\,(2n+k+1)}{(n+k)(n+k+1)} \cdot a_{n+k} \qquad [42]$$

Thus, knowing numerical values of the coefficients of any one of ω^E, ω_A^E, or ω_B^E expressed as an α function Legendre series, we can calculate the coefficients of the corresponding Legendre series for the other two properties. For example, if the coefficients q_n of the expansion Eq. [26], expressed as a 6-member series ($n' = 5$) are known, then the coefficients a_n of α_A in Eq. [27] are given by Eq. [38] as:

$$\begin{aligned} a_5 &= 6q_5 \\ a_4 &= 5q_4 - 9q_5 \\ a_3 &= 4q_3 - 7q_4 + 7q_5 \\ a_2 &= 3q_2 - 5q_3 + 5q_4 - 5q_5 \\ a_1 &= 2q_1 - 3q_2 + 3q_3 - 3q_4 + 3q_5 \\ a_0 &= q_0 - q_1 + q_2 - q_3 + q_4 - q_5 \end{aligned} \qquad [43]$$

Legendre Series Representation in Complicated Systems

(a) Integral properties: We shall first demonstrate the use of Legendre series in obtaining analytical representations of integral thermodynamic properties of relatively complex binary systems.

In Fig. 2(a) are shown experimental relative integral enthalpies Δh in the liquid system LiF-BeF$_2$ at 862°C.[5] The corresponding integral α function, $\alpha_{\text{int}} = \Delta h/X_{\text{LiF}}X_{\text{BeF}_2}$ is plotted in Fig. 2(b). The smooth curve in Fig. 2(b) was drawn by eye through the points in Fig. 2(b), thus ensuring that the α function remains well-behaved in the dilute regions. Fifty equally space values were read off the smoothed curve of Fig. 2(b) every 2 mole pct, and these points were then used as the input dummy "data points" for the least squares curve-fitting.

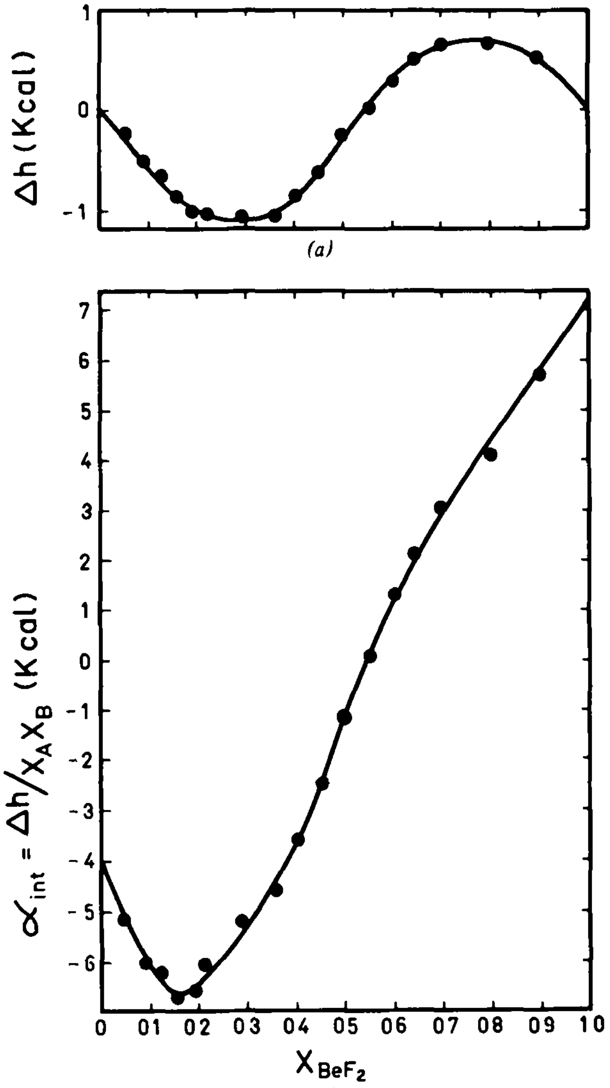

Fig. 2—Relative integral molar enthalpy and corresponding α function in the LiF-BeF$_2$ liquid system at 862°C.[5]

In Table Ia are the generated least squares coefficients q_n of the Legendre expansion of Eq. [26]. That is:

$$\alpha_{\text{int}} = q_0 P_0(X_{\text{BeF}_2}) + q_1 P_1(X_{\text{BeF}_2}) + q_2 P_2(X_{\text{BeF}_2}) + \cdot \qquad [44]$$

Values are listed for the cases when the total number of coefficients used in the series was 4, 7, and 13. Root-mean-square deviations $\bar{\rho}$ are also listed.

(It should be pointed out that although each term of the series $P_n(X_{\text{BeF}_2})$ could be calculated from the corresponding polynomial expansion as in Eqs. [29] to [33] the simple recursion relationship of Eq. [35] was alway used to give $P_n(x)$ at any value of x in this and all subsequent calculations. Thus, it is never necessary to ac tually calculate values of x^n for large n, and so we avoi the "round-off" error typical of polynomial expansions when n is large which results from taking the differenc

Table I. Coefficients of Legendre and Simple Power Series Expansions for $\alpha_{\text{int}} = \Delta h/X_A X_B$ (kcal) in the LiF-BeF$_2$ System ($\bar{\rho}$ = r.m.s. deviation)

(a) Legendre Expansion

4 Coefficients $\bar{\rho} = 0.316$ kcal	7 Coefficients $\bar{\rho} = 0.091$ kcal	13 Coefficients $\bar{\rho} = 0.022$ kcal
$q_0 = -0.718$	$q_0 = -0.732$	$q_0 = -0.731$
$q_1 = 7.743$	$q_1 = 7.730$	$q_1 = 7.730$
$q_2 = 1.662$	$q_2 = 1.586$	$q_2 = 1.595$
$q_3 = -2.345$	$q_3 = -2.376$	$q_3 = -2.376$
	$q_4 = 0.821$	$q_4 = 0.837$
	$q_5 = 0.234$	$q_5 = 0.235$
	$q_6 = -0.035$	$q_6 = -0.011$
		$q_7 = -0.157$
		$q_8 = -0.166$
		$q_9 = 0.262$
		$q_{10} = -0.041$
		$q_{11} = -0.113$
		$q_{12} = 0.081$

(b) Simple Power Series

4 Coefficients $\bar{\rho} = 0.316$ kcal	7 Coefficients $\bar{\rho} = 0.091$ kcal	13 Coefficients $\bar{\rho} = 0.031$ kcal
$q_0 = -4.452$	$q_0 = -3.948$	$q_0 = -4.046$
$q_1 = -22.632$	$q_1 = -30.476$	$q_1 = -16.735$
$q_2 = 80.335$	$q_2 = 90.592$	$q_2 = -167.517$
$q_3 = -46.908$	$q_3 = 28.366$	$q_3 = 1147.277$
	$q_4 = -201.955$	$q_4 = 5765.667$
	$q_5 = 157.455$	$q_5 = -70909.856$
	$q_6 = -32.807$	$q_6 = 278574.173$
		$q_7 = -576629.573$
		$q_8 = 672556.393$
		$q_9 = -405454.563$
		$q_{10} = 64075.408$
		$q_{11} = 51639.989$
		$q_{12} = -20564.477$

between large numbers. It is more efficient to utilize the recursion relationship Eq. [35], and we also note that for all n, $P_n(x) > P_{n+1}(x)$, and hence a round-off error is impossible.)

In Table Ib are the corresponding least squares coefficients q_n of the simple power series expansion (Eq. [1]):

$$\alpha_{\text{int}} = q_0 + q_1 X_{\text{BeF}_2} + q_2 X^2_{\text{BeF}_2} + \cdots\cdots \qquad [45]$$

The least squares fit was performed on the same 50 dummy data points. For both the Legendre and the simple power series, the 13 coefficient fit gave a generated curve with a maximum deviation from the curve which was drawn by eye of approximately 60 cal. This is about the width of the line drawn in Fig. 2(*b*).

From Table I, the following observations can be made: (1) The coefficients of the Legendre series are uncorrelated. That is, the value of any Legendre coefficient q_n is virtually independent of the total number of coefficients used in the series. The fact that in this example the coefficients do not remain exactly constant is due to the use of the least squares approximation to the true orthogonal coefficients. Clearly, increasing the number of dummy "data points" to ∞, or calculating coefficients by the area method (Eq. [23]) would completely eliminate this slight variation. In the simple power series expression, on the other hand, we see that the coefficients are highly correlated. For example, $q_5 = 157.455$ when a 7-coefficient fit is used, but $q_5 = -70909.856$ in a 13-coefficient series. (2) From the 13-coefficient fit it can be seen that the Legendre coefficients tend, in general, to become smaller as one progresses down the list from q_0 to q_{12}. The coefficients of the power series, on the other hand, tend to become larger. For example, q_{12} is some 5000 times larger than q_0. If we desire to generate the curve in Fig. 2(*b*) to about ±10 cal, it is necessary to store all coefficients to 3 decimal places. Clearly, the Legendre coefficients in this example need be stored to a maximum of only 4 significant digits, whereas the simple power series coefficients require up to 9 significant digits when a 13-coefficient series is used. In practice, we generally need more than the 4 or 9 significant figure storage, respectively, in the computer in order to eliminate round-off error. Thus, a 13-coefficient power series fit actually requires at least 16 significant digit (DOUBLE PRECISION) computing programs, whereas it has been found that for even the most complicated systems, where far more than 13 coefficients are required, the Legendre expansion can always be calculated with 8 significant digit (SINGLE PRECISION) computer programs. (3) For the 4 and 7 coefficient fits, the r.m.s. deviations are exactly the same for the Legendre and the simple power series expansions. This is to be expected, since the Legendre series can obviously be reduced to the simple power series expansion by a rearrangement of terms. For 13 coefficients, the r.m.s. deviation for a simple power series is slightly greater than for the Legendre expansion. This is the result of the round-off error involved in carrying so many significant digits. For systems requiring more than 13 coefficients, this error soon becomes so acute that thermodynamic properties in many complicated systems cannot be adequately represented by a simple power series expansion at all. An example will be given shortly.

From the coefficients q_n in Table I, the coefficients a_n and b_n of the Legendre expansions for α_{LiF} and α_{BeF_2} (LiF = A; BeF$_2$ = B) as in Eqs. [27] and [28] were calculated by use of the relationships in Eqs. [38] and [39]. These are listed in Table IIa. We see that the calculated coefficients change only slightly as the number of coefficients is changed. Furthermore, the higher coefficients are of the same order of magnitude or smaller than the first few coefficients. We note that these coefficients a_n and b_n are the true orthogonal coefficients of the calculated series expansions for α_{LiF} and α_{BeF_2}, but since the fits to the smoothed α_{int} curve improves somewhat as the number of coefficients is increased, the calculated curves of α_{LiF} and α_{BeF_2} also change somewhat, and so the values of a_n and b_n also vary.

The coefficients a_n and b_n of the simple power series expansions (Eqs. [2] and [3]) for α_{LiF} and α_{BeF_2} were calculated from the coefficients q_n in Table Ib by use of Eqs. [4] and [5]. These are listed in Table IIb. As expected, these coefficients are highly correlated and require the storage of a large number of significant digits.

Plots of the relative partial molar enthalpies Δh_{LiF} and Δh_{BeF_2} as calculated from the 13 coefficient expansions are drawn in Fig. 3. As mentioned previously, for this particular example, the fits obtained using the Legendre and the simple power series are virtually the same.

Table II. Coefficients of Legendre and Simple Power Series Expansions of the Enthalpy α Functions α_{LiF} (Coefficients a_n), and α_{BeF_2} (Coefficients b_n) (kcal) as Calculated from the Coefficients for α_{int} in Table I.

4 Coefficients		7 Coefficients		13 Coefficients	
		(a) Legendre Expansion			
$a_0 = -4.453$	$b_0 = 6.342$	$a_0 = -3.948$	$b_0 = 7.228$	$a_0 = -4.018$	$b_0 = 7.147$
$a_1 = 3.463$	$b_1 = 13.436$	$a_1 = 1.918$	$b_1 = 16.150$	$a_1 = 2.132$	$b_1 = 15.904$
$a_2 = 16.713$	$b_2 = -6.740$	$a_2 = 19.397$	$b_2 = -2.023$	$a_2 = 19.024$	$b_2 = -2.452$
$a_3 = -9.382$	$b_3 = -9.382$	$a_3 = -13.364$	$b_3 = -2.366$	$a_3 = -12.808$	$b_3 = -3.005$
		$a_4 = 1.677$	$b_4 = 5.894$	$a_4 = 0.902$	$b_4 = 5.005$
		$a_5 = 1.796$	$b_5 = 1.015$	$a_5 = 2.836$	$b_5 = 0.176$
		$a_6 = -0.248$	$b_6 = -0.248$	$a_6 = -1.617$	$b_6 = -1.812$
				$a_7 = 2.877$	$b_7 = -0.905$
				$a_8 = -3.356$	$b_8 = 1.723$
				$a_9 = -0.278$	$b_9 = 1.233$
				$a_{10} = 3.618$	$b_{10} = -1.124$
				$a_{11} = -3.218$	$b_{11} = 0.508$
				$a_{12} = 1.053$	$b_{12} = 1.053$
		(b) Simple Power Series			
$a_0 = 18.179$	$b_0 = -4.453$	$a_0 = 26.527$	$b_0 = -3.948$	$a_0 = 12.688$	$b_0 = -4.046$
$a_1 = -205.934$	$b_1 = -45.264$	$a_1 = -242.136$	$b_1 = -60.951$	$a_1 = 301.565$	$b_1 = -33.469$
$a_2 = 381.728$	$b_2 = 241.004$	$a_2 = 186.680$	$b_2 = 271.777$	$a_2 = -3929.355$	$b_2 = -502.551$
$a_3 = -187.632$	$b_3 = -187.632$	$a_3 = 921.281$	$b_3 = 113.463$	$a_3 = -18493.597$	$b_3 = 4569.071$
		$a_4 = -1797.046$	$b_4 = -1009.773$	$a_4 = 383377.623$	$b_4 = 28828.335$
		$a_5 = 1141.566$	$b_5 = 944.727$	$a_5 = -2096904.130$	$b_5 = -425459.143$
		$a_6 = -229.645$	$b_6 = -299.645$	$a_6 = 5986426.125$	$b_6 = 1950019.215$
				$a_7 = -9993487.720$	$b_7 = -4613036.628$
				$a_8 = 9702098.510$	$b_8 = 6053007.519$
				$a_9 = -4695299.644$	$b_9 = -4054545.645$
				$a_{10} = 136789.621$	$b_{10} = 704829.493$
				$a_{11} = 866453.594$	$b_{11} = 619679.864$
				$a_{12} = -267338.202$	$b_{12} = -267338.200$

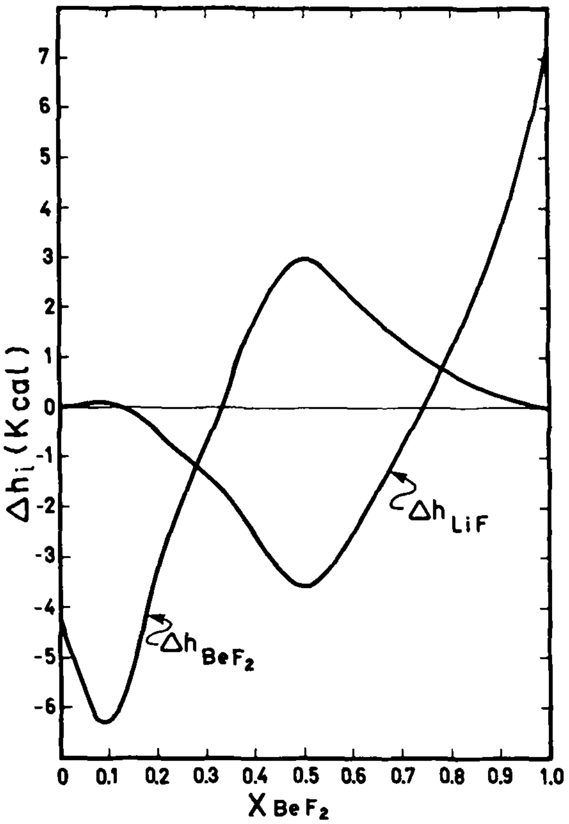

Fig. 3—Relative partial molar enthalpies in LiF-BeF$_2$ system calculated analytically.

(b) Partial properties: We shall now consider the use of Legendre expansions for representing excess partial molar properties. In Fig. 4(a) are plotted the excess partial molar free energies of Mg, g^E_{Mg}, in the Mg-Bi binary system at 700°C.[6] The calculated corresponding values of $\alpha_{Mg} = g^E_{Mg}/X^2_{Bi}$ are shown in Fig. 4(b). The points shown in Fig. 4 are not experimental values, but are the smoothed values as tabulated by Hultgren *et al.*[6] We note that this system has a strong stability at $X_{Bi} \approx 0.4$ (the point of inflection in Fig. 4(a)), which may be associated with a "tendency to ordering" at this composition. The plotted curve in Fig. 4(b) was drawn by eye through the α function points. Fifty evenly space dummy data points were read off the curve in Fig. 4(b) every 2 mole pct, and a least squares regression analysis was performed on these points. The coefficients of the Legendre expansion

$$\alpha_{Mg} = a_0P_0(X_{Bi}) + a_1P_1(X_{Bi}) + a_2P_2(X_{Bi}) + \dots \qquad [46]$$

for expansions with a total of 4, 10, and 16 coefficients are listed in Table III. The curve generated by the 16 coefficient series had a maximum deviation of 0.7 kcal from the curve which was drawn by eye. This is about the thickness of the line drawn in Fig. 4(b). Again we see that the coefficients are uncorrelated and that a_n tends to become smaller as n increases.

The coefficients of the simple power series expansion

$$\alpha_{Mg} = a_0 + a_1X_{Bi} + a_2X^2_{Bi} + \dots \qquad [47]$$

are also listed for a 16 coefficient expansion in Table

III. The r.m.s. deviation of this fit is now about twice that of the Legendre expansion for the same number of coefficients. As before, a large number of significant digits must be stored in order to retain significance.

Integration of Eq. [46] (essentially a Gibbs-Duhem integration) yields the corresponding Legendre expansions for α_{Bi} and α_{int}:

$$\alpha_{\text{Bi}} = g^E_{\text{Bi}}/X^2_{\text{Mg}} = \sum_{n=0}^{n'} b_n P_n(X_{\text{Bi}}) + C/X^2_{\text{Mg}} \qquad [48]$$

$$\alpha_{\text{int}} = g^E/X_{\text{Mg}} X_{\text{Bi}} = \sum_{n=0}^{n'} q_n P_n(X_{\text{Bi}}) + C/X_{\text{Mg}} \qquad [49]$$

where C is a constant of integration. The coefficients b_n and q_n can be calculated from Eqs. [40] and [42]. The constant C must, in general, be calculated from a known end point value of g^E_{Bi} or of g^E at some point within the composition range over which α_{Mg} has been measured. In the present example, the entire composition range of the Mg-Bi system has been covered, and since $g^E_{\text{Bi}} = g^E = 0.0$ when $X_{\text{Mg}} = 0.0$, it follows from Eqs. [48] to [49] that $C = 0.0$ for this particular case.

The calculated coefficients q_n and b_n for the 16 coefficient series are listed in Table III, and the generated curves of g^E_{Bi} and of g^E are shown in Fig. 5. The calculation of the integration constant C is discussed for the general case in the summary of equations (Table VI).

A useful thermodynamic quantity is the "stability function,"[3,7] ψ, which, for a binary system is defined by:[7]

$$\psi = 1 + \frac{X_A X_B}{RT} \cdot \frac{d^2 g^E}{dX_B^2} \qquad [50]$$

It is often difficult to calculate stability functions graphically, since such calculations involve the graphical determination of the second derivative. Analytically, however, this is an easy matter. If we expand ψ as a Legendre series:

$$\psi = 1 + \frac{X_A X_B}{RT} \cdot \sum_{n=0}^{n'} \theta_n P_n(X_B) \qquad [51]$$

then the following relationship exists between the coefficients θ_n and the coefficients q_n of the expansion Eq. [26] (See Appendix 2):

$$\theta_n = -(n+1)(n+2)q_n - 2(2n+1) \sum_{k=1}^{(n+k)=n'} q_{n+2k} \qquad [52]$$

The calculated curve of ψ over the range of interest in the Mg-Bi system is plotted in Fig. 5. The solution of maximum "stability" occurs at $X_{\text{Bi}} \approx 0.42$.

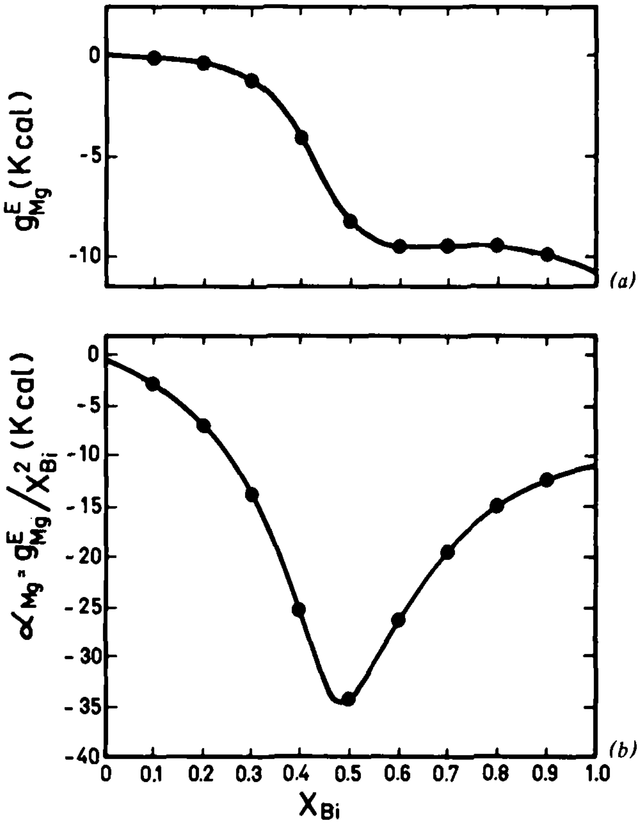

Fig. 4—Partial molar excess free energy of Mg and corresponding α function in the Mg-Bi liquid system[6] at 700°C.

Table III. Coefficients of the α Functions (kcal) for the Excess Molar Free Energies in the Mg-Bi System at 700°C (A = Mg; B = Bi)
($\bar{\rho}$ = r.m.s. deviation)

(a) Legendre Expansion					(b) Simple Power Series
4 Coefficients $\bar{\rho}$ = 4.498 kcal	10 Coefficients $\bar{\rho}$ = 0.994 kcal	16 Coefficients $\bar{\rho}$ = 0.290 kcal			16 Coefficients $\bar{\rho}$ = 0.548 kcal
$a_0 = -16.41$	$a_0 = -16.25$	$a_0 = -16.28$	$q_0 = -16.76$	$b_0 = -11.38$	$a_0 = -0.51$
$a_1 = -5.97$	$a_1 = -5.99$	$a_1 = -5.96$	$q_1 = 4.54$	$b_1 = 11.59$	$a_1 = -92.56$
$a_2 = 16.73$	$a_2 = 17.53$	$a_2 = 17.38$	$q_2 = 3.85$	$b_2 = -3.52$	$a_2 = 2822.66$
$a_3 = 0.62$	$a_3 = 0.57$	$a_3 = 0.64$	$q_3 = -2.94$	$b_3 = -12.24$	$a_3 = -37075.75$
	$a_4 = -10.97$	$a_4 = -11.24$	$q_4 = -1.18$	$b_4 = 4.14$	$a_4 = 204207.76$
	$a_5 = 0.20$	$a_5 = 0.32$	$q_5 = 1.24$	$b_5 = 6.11$	$a_5 = -431517.16$
	$a_6 = 7.00$	$a_6 = 6.61$	$q_6 = 0.30$	$b_6 = -3.33$	$a_6 = -393529.30$
	$a_7 = -0.76$	$a_7 = -0.61$	$q_7 = -0.66$	$b_7 = -1.64$	$a_7 = 3557834.32$
	$a_8 = -4.16$	$a_8 = -4.69$	$q_8 = -0.07$	$b_8 = 4.69$	$a_8 = -6072116.28$
	$a_9 = 0.85$	$a_9 = 1.04$	$q_9 = 0.38$	$b_9 = 2.53$	$a_9 = 2279811.64$
		$a_{10} = 3.09$	$q_{10} = 0.00$	$b_{10} = -1.45$	$a_{10} = 4798141.33$
		$a_{11} = -1.05$	$q_{11} = -0.21$	$b_{11} = 0.75$	$a_{11} = -5786413.80$
		$a_{12} = -2.28$	$q_{12} = 0.05$	$b_{12} = 2.94$	$a_{12} = 1439827.04$
		$a_{13} = 1.16$	$q_{13} = 0.16$	$b_{13} = 0.35$	$a_{13} = 698122.29$
		$a_{14} = 1.35$	$q_{14} = -0.01$	$b_{14} = -1.80$	$a_{14} = -177380.52$
		$a_{15} = -0.87$	$q_{15} = -0.05$	$b_{15} = -0.87$	$a_{15} = -82652.58$

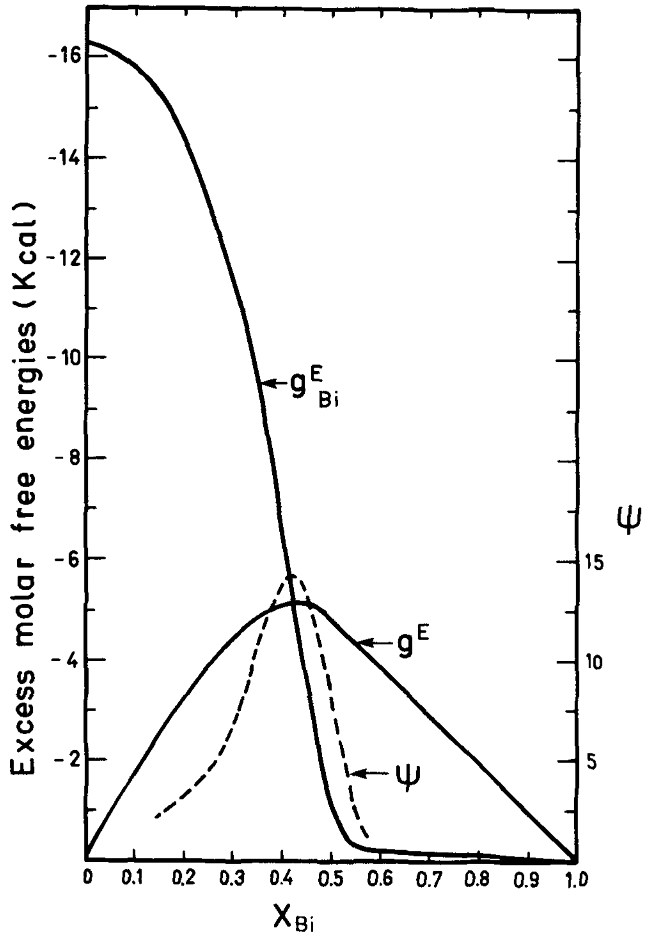

Fig. 5—Partial molar excess free energy of Bi, integral molar excess free energy, and stability function in Mg-Bi system at 700°C, calculated analytically.

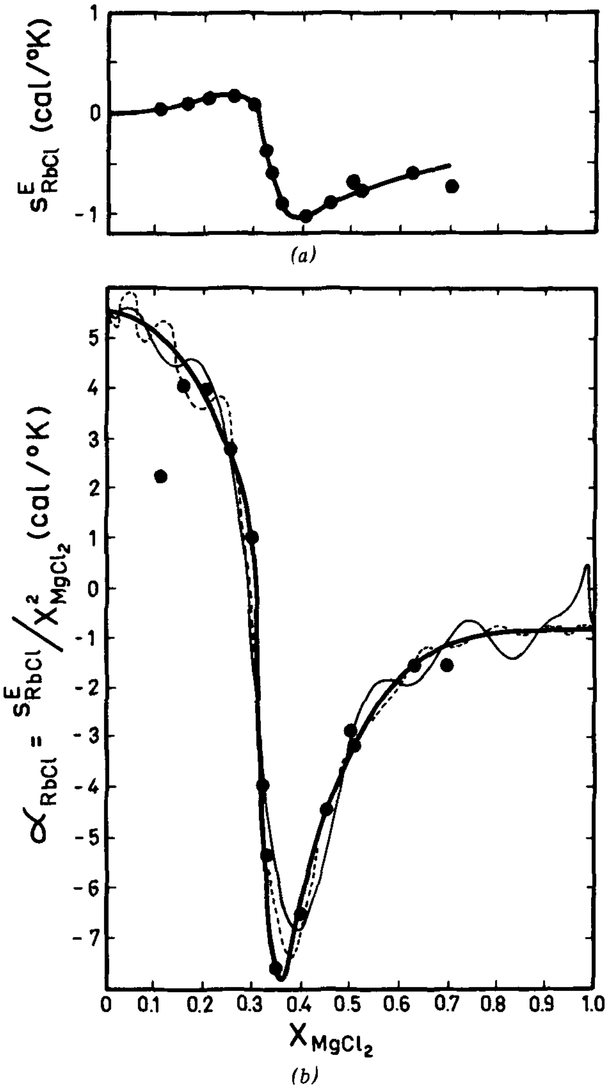

Fig. 6—Partial molar excess entropy of RbCl and corresponding α function in RbCl-$MgCl_2$ system[8] at 717°C. ——— Curv drawn "by eye" and 50 coefficient Legendre representation (2 curves coincidental). - - - - - 19 coefficient Legendre representation. ——— 19 coefficient simple power series represer tation.

ψ could also be expanded in terms of a simple power series, and an analogous coefficient relationship to Eq. [52] can be derived. (See Appendix 1). These equations are all listed in the summary.

One of the more difficult excess properties to represent analytically is the partial molar excess entropy for a system which exhibits a strong tendency to "ordering." For example, experimental values of the excess molar entropy of RbCl, s^E_{RbCl} and its corresponding α function, $\alpha_{RbCl} = s^E_{RbCl}/X^2_{MgCl_2}$ in the RbCl-$MgCl_2$ system[8] at 717°C are plotted in Figs. 6(*a*) and 6(*b*) respectively (A = RbCl; B = $MgCl_2$). The smoothed heavy curve in Fig. 6(*b*) was drawn by eye, and 100 equidistant dummy data points were read off this curve every 1 mole pct. It was found that about 50 coefficients were required in the Legendre expansion (Eq. [27]) in order to fit the curve to within one width of the line drawn in Fig. 6(*b*). While 50 coefficients may seem to be quite a large number, these coefficients need only be recorded to a maximum of 4 significant digits. For purposes of comparison, in Fig. 6(*b*) are also shown the curves generated by 19 coefficient fits using the Legendre expansion and also using a simple power series (Eq. [2]). The Legendre expansion already gives a quite acceptable fit except near $X_{MgCl_2} = 0.0$. The power series, however, has started to break down, particularly near $X_{MgCl_2} = 1.0$ due to the large errors involved in manipulating the extremely large numbers, even though all calculations were performed with 16 significant digit (DOUBLE PRECISION) accuracy, and the power series were "nested" within the computer subroutine in order to bring all round-off errors to an absolute possible minimum (see Appendix 1). Increasing the number of coefficients in the simple power series expansion now only serves to increase the error, and so the smooth curve in Fig. 6(*b*) cannot be satisfactorily represented by a simple power series.

Legendre Series Representation in Less-Complicated Systems

In the preceding section, we have shown the advantages of a Legendre expansion over the simple power series in obtaining analytical representations of thermodynamic properties in systems where many coefficients are required to give a satisfactory representation. However, even for simple systems, in which only a few coefficients (5 or less) can satisfactorily describ the properties, the Legendre expansion is still preferable to the simple power series, as will now be demonstrated.

In Fig. 7 are plotted the α functions of the relative molar integral enthalpies ($\alpha_{\text{int}} = \Delta h/X_A X_B$) for the binary liquid alloy systems of Sn with the Group IIb metals.[6] The first four coefficients of the Legendre expansions for each system are listed in Table IV, and the generated curves using 4 coefficients are drawn in Fig. 7.

We see from Table IV that, for each system, the absolute value of the coefficients decreases markedly as we go down the series from q_0 to q_3. Hence, we can deduce that adding the fourth coefficient, q_3, has had only a very slight effect upon the overall fit. This may be compared to the case of a simple power series representation where the final coefficient is generally one of the largest.

Table IV. Coefficients of the Legendre Expansions of $\alpha_{\text{int}} = \Delta h/X_A X_B$ (kcal) for Liquid Binary Systems of Sn with Group IIb Metals

Hg-Sn	Cd-Sn	Zn-Sn
$q_0 = 0.845$	$q_0 = 1.800$	$q_0 = 3.313$
$q_1 = -0.453$	$q_1 = -0.365$	$q_1 = -1.372$
$q_2 = 0.069$	$q_2 = 0.108$	$q_2 = 0.456$
$q_3 = -0.019$	$q_3 = -0.060$	$q_3 = -0.261$

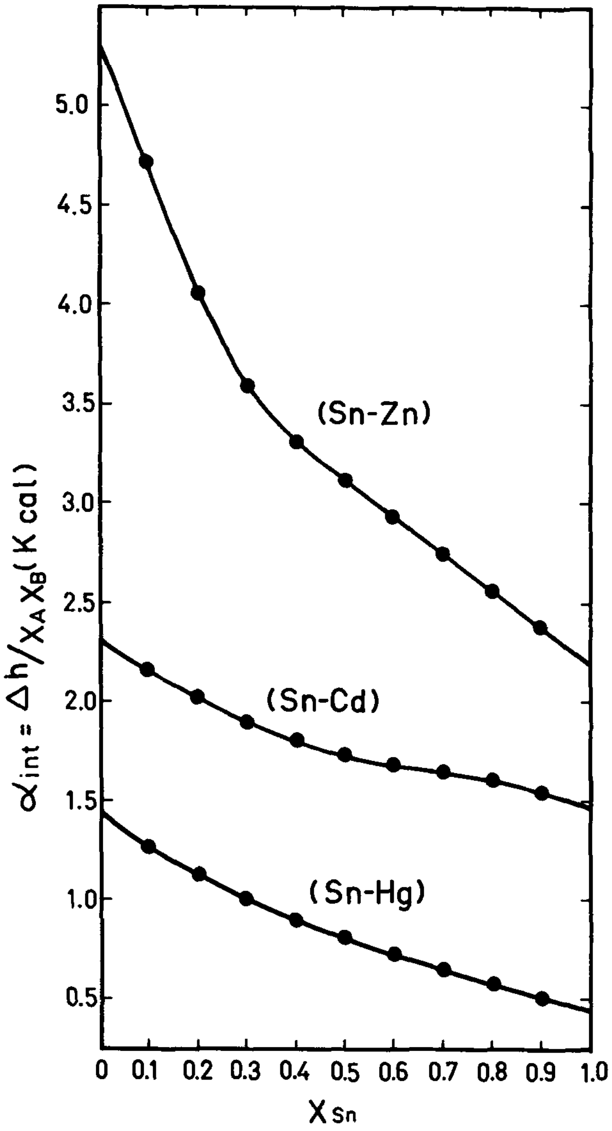

Fig. 7—α function of the relative integral molar enthalpy[6] in liquid systems of Sn with group IIb metals.

The orthogonality of the Legendre series ensures that adding additional coefficients does not affect the numerical values of the preceding coefficients. Consequently, mathematical and/or physical significance can be attributed to the coefficients. For example, the first coefficient, q_0, is the "average" value of the α function over the interval $0 \le X_B \le 1$. That is, from Eqs. [23], [24], and [37]:

$$q_0 = \int_0^1 \alpha_{\text{int}} \cdot dx \qquad [53]$$

and Eq. [53] is true no matter how many coefficients we use in the series. The next coefficient, q_1, is a measure of the "average slope" of the curve, as can be appreciated by examining the plot of $P_1(x)$ in Fig. 1. From Eqs. [23], [24], and [37]:

$$q_1 = 3 \int_0^1 f(x) \cdot P_1(x)\, dx \qquad [54]$$

The coefficient q_2 gives the "average parabolic character" of the curve, etc. Thus, the coefficients q_0 and q_1 are a more meaningful measure of the "regular" and "sub-regular" character of the thermodynamic property than are the first two coefficients of a simple power series expansion. This leads to the possibility of interpreting the first few coefficients of the Legendre expansion in terms of atomistic models. For example, q_0 could be related to the change in "average bond energy" upon mixing the pure components, and q_1 could be related to the second-nearest-neighbor effects, etc.

In comparing the three Sn-M systems in Table IV, we see that there is a general trend in the values of each coefficient q_n as M proceeds down Group IIb. (For the 4 coefficients in Table IV, only q_1 fails to exhibit an obvious trend.) From this we can imply that Legendre expansions provide a means of estimating thermodynamic properties of unmeasured systems by interpolation or extrapolation, as well as providing an easy means of comparison of thermodynamic properties of different systems.

FOURIER SERIES

1. Sine Series. It has been proposed[9] that excess integral properties be represented by an orthogonal Fourier sine series:

$$\omega^E = \sum_{n=1}^{n'} q_n \sin(n\pi X_B) \qquad [55]$$

which is orthogonal over the interval $0 \le X_B \le 1$. The main objection to this representation is that thermodynamic properties of solutions, for physical reasons, are not well represented by trigonometric functions. For example, the α function is not finite in the dilute regions. That is: $\alpha_{\text{int}} = \omega^E/X_A X_B = \infty$ when $X_A = 0.0$ and when $X_B = 0.0$ if Eq. [55] is used for ω^E. Differentiation of Eq. [55] yields the expansion for ω_A^E:

$$\omega_A^E = \sum_{n=1}^{n'} q_n \cdot (\sin(n\pi X_B) - n\pi X_B \cdot \cos(n\pi X_B)) \qquad [56]$$

Again, $\alpha_A = \omega_A^E/X_B^2 = \infty$ when $X_B = 0.0$, and there is the additional undesirable restriction that $d\omega_A^E/dX_B \approx 0$ at $X_B = 1.0$. Furthermore, the generated Eq. [56] is no longer an orthogonal series.

2. Cosine Series. If we fit the α function of the partial molar excess property to the Fourier cosine series:

$$\alpha_A = \omega_A^E/X_B^2 = a_0 + \sum_{n=1}^{n'} a_n \cdot \cos(n\pi X_B) \qquad [57]$$

there is still the undesirable restriction that $d\alpha_A/dX_B \approx 0$ when $X_B = 0.0$ and $X_B = 1.0$. Of course, if a large number of coefficients are used to fit the curves, then the dilute regions over which $d\alpha_A/dX_B \rightarrow 0$ can be reduced to a negligible composition range. For the smoothed curves of Figs. 4 and 6, fits were obtained using Eq. [57] which were generally as good as were the fits using the Legendre expansion for the same numbers of coefficients. However, for simple systems such as those in Fig. 7, many more terms have to be used to obtain a satisfactory representation using Eq. [57] than are necessary when a Legendre expansion (or a simple power series) are used.

By integration (Gibbs-Duhem integration) of Eq. [57], the following expansions for α_B and α_{int} are generated:

$$\alpha_B = \omega_B^E/X_A^2 = a_0 + \frac{1}{X_A^2} \cdot \Bigg[C - a_0 - \sum_{n=1}^{n'} a_n \left(\frac{\sin(n\pi X_B)}{n\pi} + X_A X_B \cos(n\pi X_B)\right)\Bigg] \qquad [58]$$

$$\alpha_{\text{int}} = \omega^E/X_A X_B = \frac{1}{X_A} \cdot \Bigg[C - a_0 X_B - \sum_{n=1}^{n'} \frac{a_n}{n\pi} \sin(n\pi X_B)\Bigg] \qquad [59]$$

where C is a constant of integration which has the same value in both Eqs. [58] and [59]. Again we see that the calculated functions are no longer orthogonal series, and we also note that $\alpha_B = \infty$ when $X_B = 0.0$. Analogous problems will arise if we fit the integral α function to an equation of the form of Eq. [57] and generate the corresponding partial properties.

CHEBYSHEV POLYNOMIALS

Chebyshev polynomials appear attractive for the representation of thermodynamic properties in binary systems, since they are well-known in the field of numerical analysis for the "Chebyshev economization principle." Furthermore, they are quite similar to the Legendre polynomials. The first three Chebyshev polynomials, transposed to the interval $0 \le x \le 1$ are:

$$\begin{aligned} T_0(x) &= 1 \\ T_1(x) &= 2x - 1 \\ T_2(x) &= 8x^2 - 8x + 1 \end{aligned} \qquad [60]$$

The general recursion relationship is:

$$T_n(x) = 2(2x - 1)\, T_{n-1}(x) - T_{n-2}(x) \qquad [61]$$

The α functions may be expanded as Chebyshev series:

$$\alpha_{\text{int}} = \sum_{n=0}^{n'} q_n T_n(X_B) \qquad [62]$$

$$\alpha_A = \sum_{n=0}^{n'} a_n T_n(X_B) \qquad [63]$$

$$\alpha_B = \sum_{n=0}^{n'} b_n T_n(X_B) \qquad [64]$$

The coefficient relationships are as follows:

$$a_n = (n+1) q_n + \sum_{k=1}^{(n+k)=n'} (-1)^k (2n + 2\delta k) q_{n+k} \qquad [65]$$

$$\delta = \tfrac{1}{2} \text{ if } n = 0$$
$$\delta = 1 \text{ if } n > 0$$

$$b_n = (n+1) q_n + \sum_{k=1}^{(n+k)=n'} (2n + 2\delta k) q_{n+k} \qquad [66]$$

The Chebyshev polynomials are not truly orthogonal, but since each function $T_n(x)$ has one more extremum in the interval $0 \le x \le 1$ than does $T_{n-1}(x)$, the coefficients of a Chebyshev expansion tend to decrease as n increases, and do not become unmanageably large as in the case of a simple power series. Since Chebyshev and Legendre expansions are both polynomial expansions, exactly the same curve, with exactly the same r.m.s. deviation is generated if the data points are fitted by a least squares analysis to either series for the same number of coefficients. The Chebyshev polynomials may be made orthogonal over the interval $0 \le x \le 1$ by multiplying each term by the weighting factor $(4x - 4x^2)^{-1/4}$, but this markedly increases the mathematical complexity and would not yield any advantages over the Legendre expansion.

OTHER ORTHOGONAL POLYNOMIALS

Williams[9] has proposed a method of grouping polynomial terms into "Z functions," $Z_n(x)$, in a concept similar to the Legendre or Chebyshev polynomials. The excess properties ω^E, ω_A^E, or ω_B^E, rather than the α functions, are fitted to an expansion in terms of the Z functions. The advantage of this representation is that it is fully consistent with Darken's quadratic formalism[3,9] in the dilute regions. The disadvantages are that the series is only approximately orthogonal, and that no recursion relationship has been found which will generate members of the series $Z_n(x)$ for $n > 6$.

Laguerre and Hermite polynomials are unsuitable for fitting thermodynamic properties of binary systems since they are orthogonal over the intervals $0 \le x \le \infty$ and $-\infty \le x \le \infty$ respectively. There are many other orthogonal polynomials which we have not considered, but generally, all tend to be more complex than those which have been discussed above, and consequently they are unsuitable for simple representation of thermodynamic solution properties.

SUMMARY AND CONCLUSIONS

In Tables V and VI are summarized the pertinent equations for simple power series and for Legendre expansions for the α functions.

Table V. Summary of Simple Power Series Relationships

$$\alpha_{\text{int}} = \omega^E/X_A X_B = \sum_{n=0}^{n'} q_n X_B^n$$

$$\alpha_A = \omega_A^E/X_B^2 = \sum_{n=0}^{n'} a_n X_B^n$$

$$\alpha_B = \omega_B^E/X_A^2 = \sum_{n=0}^{n'} b_n X_B^n$$

Coefficient Relationships:

$$b_n = (n+1)q_n$$

$$a_n = (n+1)(q_n - q_{n+1})$$

$$a_n = b_n - \frac{n+1}{n+2}\cdot b_{n+1}$$

By convention, any coefficient a_n, b_n, q_n is zero if $n > n'$.

If a partial property α_A *is known, and* α_B *and* α_{int} *are to be calculated* then:

$$\alpha_B = \sum_{n=0}^{n'} b_n X_B^n + C/X_A^2$$

$$\alpha_{\text{int}} = \sum_{n=0}^{n'} q_n X_B^n + C/X_A$$

The constant of integration C is zero if the entire composition range to $X_A = 0.0$ is covered so that the end point condition $\omega_B^E = \omega_{\text{int}} = 0.0$ when $X_A = 0.0$ can be used. (The calculation of α_A and α_B when the integral property α_{int} is known does not involve a constant of integration.)

Stability function:

$$\psi = 1 + \frac{X_A X_B}{RT}\cdot\frac{d^2 g^E}{dX_B^2} = 1 + \frac{X_A X_B}{RT}\sum_{n=0}^{n'} \theta_n X_B^n$$

$$\theta_n = (n+1)(n+2)(q_{n+1} - q_n)$$

Table VI. Summary of Legendre Expansion Relationships

$$\alpha_{\text{int}} = \omega^E/X_A X_B = \sum_{n=0}^{n'} q_n P_n(X_B)$$

$$\alpha_A = \omega_A^E/X_B^2 = \sum_{n=0}^{n'} a_n P_n(X_B)$$

$$\alpha_B = \omega_B^E/X_A^2 = \sum_{n=0}^{n'} b_n P_n(X_B)$$

where

$$P_0(x) = 1$$

and

$$P_n(x) = \frac{(2n-1)(2x-1)}{n}\cdot P_{n-1}(x) - \frac{(n-1)}{n}\cdot P_{n-2}(x)$$

and

$$\int_0^1 [P_n(x)]^2\,dx = 1/(2n+1)$$

Coefficient Relationships:

$$a_n = (n+1)q_n + (2n+1)\sum_{k=1}^{(n+k)=n'} (-1)^k q_{n+k}$$

$$b_n = (n+1)q_n + (2n+1)\sum_{k=1}^{(n+k)=n'} q_{n+k}$$

$$q_n = a_n/(n+1) + (2n+1)\sum_{k=1}^{(n+k)=n'} \frac{1}{(n+k)(n+k+1)}\,a_{n+k}$$

$$q_n = b_n/(n+1) + (2n+1)\sum_{k=1}^{(n+k)=n'} \frac{(-1)^k}{(n+k)(n+k+1)}\,b_{n+k}$$

$$b_n = a_n + (2n+1)\sum_{k=1}^{(n+k)=n'} \frac{k(2n+k+1)}{(n+k)(n+k+1)}\,a_{n+k}$$

By convention, any coefficient a_n, b_n, q_n is zero if $n > n'$.

If a partial property α_A *is known and* α_B *and* α_{int} *are to be calculated* then:

$$\alpha_B = \sum_{n=0}^{n'} b_n P_n(X_B) + C/X_A^2$$

$$\alpha_{\text{int}} = \sum_{n=0}^{n'} q_n P_n(X_B) + C/X_A$$

The constant of integration C is zero if the entire composition range to $X_A = 0.0$ is covered so that the end point condition $\omega_B^E = \omega_{\text{int}} = 0.0$ when $X_A = 0.0$ can be used. (The calculation of α_A and α_B when the integral property α_{int} is known does not involve a constant of integration.)

Stability function:

$$\psi = 1 + \frac{X_A X_B}{RT}\frac{d^2 g^E}{dX_B^2} = 1 + \frac{X_A X_B}{RT}\sum_{n=0}^{n'} \theta_n P_n(X_B)$$

$$\theta_n = -(n+1)(n+2)q_n - 2(2n+1)\sum_{k=1}^{(n+k)=n'} q_{n+2k}$$

Symmetry relations:

$P_n(X_A) = P_n(X_B)$ when n is even

$P_n(X_A) = -P_n(X_B)$ when n is odd

Thus, for example, if we write:

$$\alpha_{\text{int}} = \sum_{n=0}^{n'} q_n P_n(X_B) = \sum_{n=0}^{n'} q_n^* P_n(X_A)$$

then:

$q_n^* = q_n$ if n is even

$q_n^* = -q_n$ if n is odd

and similarly for the expansions for α_A, α_B, and ψ.

We conclude that orthogonal series provide a more rational analytical representation of thermodynamic properties of binary systems which are homogeneous over a wide composition range for the following reasons:

(1) Systems of any complexity can be fitted to any desired degree of precision simply by including more terms in the expansion. The coefficients are all of the same order or smaller than the first few coefficients, and all calculations and storage can be performed with only a very few significant digits (SINGLE PRECISION).

(2) The coefficients are completely uncorrelated, provided that the thermodynamic properties are represented over the entire composition range of the binary system, and so the coefficients provide a basis for comparison between systems and a more meaningful physical interpretation.

We further conclude that the orthogonal Legendre expansion of the α functions is preferable to the other orthogonal or approximately orthogonal series considered because:

(1) The Legendre expansions are algebraic functions of the mole fractions. Since quasi-chemical theory predicts that excess thermodynamic functions are generally algebraic functions (rather than trigonometric or other transcendental functions), the Legendre expansion is, in general, more capable of efficiently representing the thermodynamic property than, say, a Fourier series.

(2) The Legendre expansion gives finite and other-

wise well-behaved α functions in the dilute regions.

(3) The first and second coefficients are the "regular" and "sub-regular" solution terms, respectively, and the values of these coefficients are independent of the total number of coefficients used in the expansion.

(4) The expansions for the α_A, α_B, and α_{int} functions are all orthogonal expansions, and so the series expansion of, say, α_B, calculated by the coefficient relationship equations (derived from the Gibbs-Duhem equation) from known values of the coefficients for the Legendre expansion of α_A, will itself also be an orthogonal Legendre expansion. The coefficients of the three series for α_A, α_B, and α_{int} are all interrelated by simple equations.

It is proposed that thermodynamic properties in binary systems be stored in computers by first drawing the best curve "by eye" to the experimental α function points (thus ensuring proper thermodynamic behavior in the dilute regions) and then fitting this *smoothed* curve to the appropriate Legendre expansion (Eqs. [26] to [28].

One could, of course, fit a Legendre expansion by a least squares analysis to the original data points, but the coefficients so obtained would only approximate the true orthogonal coefficients, and there is no *a priori* statistical rationale for doing this anyway. Only one set of coefficients (either the a_n, the b_n, or the q_n) need be stored, and in general they need only be stored to a maximum of about four significant digits. All the thermodynamic functions (ω_A, ω_B, ω, stability function, etc) can then readily be generated by a standard computer subroutine.

Furthermore, by storing one set of coefficients for the relative molar enthalpy Δh, and one set for the molar excess entropy s^E, and by assuming these functions to be independent of temperature, we can generate all thermodynamic solution properties for a phase at any temperature as well as at any composition.

APPENDIX 1

SIMPLE POWER SERIES

Coefficient Relationships

Substituting Eqs. [1] and [3] into the following thermodynamic relationship,

$$\omega_B^E = \omega^E + (1 - X_B)\cdot\frac{d\omega^E}{dX_B} \qquad [A1]$$

and noting that $X_A = 1 - X_B$, we obtain, after expansion, the equation:

$$\sum_{n=0}^{n'} (b_n - (n+1)q_n)(X_B^n - 2X_B^{n+1} + X_B^{n+2}) = 0 \qquad [A2]$$

Since this equation must be true for all values of X_B, it follows that:

$$b_n = (n+1)q_n \qquad [A3]$$

Substituting Eqs. [2] and [3] into the Gibbs-Duhem equation:

$$X_A\cdot\frac{d\omega_A^E}{dX_B} + X_B\cdot\frac{d\omega_B^E}{dX_B} = 0 \qquad [A4]$$

we obtain, after expansion, the equation

$$\sum_{n=0}^{n'} (n+2)(a_n - b_n)X_B^n + \sum_{n=1}^{n'} nb_nX_B^{n-1} = 0 \qquad [A5]$$

We now replace the dummy variable n in the second summation by $(n+1)$:

$$\sum_{n=0}^{n'} (n+2)(a_n - b_n) + \sum_{n=0}^{n'} (n+1)b_{n+1}X_B^n = 0 \qquad [A6]$$

Equating coefficients of X_B^n for all n, we obtain the relationship

$$a_n = b_n - \frac{n+1}{n+2}\cdot b_{n+1} \qquad [A7]$$

which can be combined with Eq. [A3] to give the relationship

$$a_n = (n+1)(q_n - q_{n+1}) \qquad [A8]$$

Stability Function

Expand the stability function, ψ, as a simple power series in X_B:

$$\psi = 1 + \frac{X_AX_B}{RT}\cdot(d^2g^E/dX_B^2) = 1 + \frac{X_AX_B}{RT}\sum_{n=0}^{n'}\theta_nX_B^n \qquad [A9]$$

Substituting the expansion

$$g^E = X_AX_B\sum_{n=0}^{n'} q_nX_B^n \qquad [A10]$$

into Eq. [A9], differentiating, and re-arranging, we obtain the equation:

$$\sum_{n=0}^{n'}\theta_nX_B^n = \sum_{n=0}^{n'}(n+1)(n+2)(q_{n+1} - q_n)X_B^n \qquad [A11]$$

Equating coefficients of X_B^n, we obtain the relationship:

$$\theta_n = (n+1)(n+2)(q_{n+1} - q_n) \qquad [A12]$$

Nesting Power Series

Given the coefficients A_n of a simple power series expansion of some function $f(X)$:

$$f(X) = \sum_{n=0}^{n'} A_nX^n \qquad [A13]$$

where n' is relatively large ($n' > 5$), it may be shown that the truncation error involved in calculating $f(X)$ for a given value of X is minimized by "nesting" the series (Horner's Rule):

$$f(X) = (A_0 + X(A_1 + X(A_2 + X(A_3 + X(\,\ldots\ldots\ldots + X(A_{n-1} + X(A_n)))))\ldots.) \qquad [A14]$$

APPENDIX 2

LEGENDRE EXPANSION

Coefficient Relationships

Substitute Eqs. [26] and [27] into the following thermodynamic relationship:

$$\omega_A^E = \omega^E - X_B \cdot \frac{d\omega^E}{dX_B} \qquad [A15]$$

to give the expression:

$$X_B^2 \sum_{n=0}^{n'} a_n P_n(X_B) = X_B^2 \sum_{n=0}^{n'} q_n P_n(X_B) - X_A X_B^2 \cdot \sum_{n=0}^{n'} q_n \cdot \frac{dP_n(X_B)}{dX_B} \qquad [A16]$$

$P_n(X_B)$ can be represented by the following general expression:

$$P_n(X_B) = \sum_{k=0}^{N(n)} F(n,k)(2X_B - 1)^{n-2k} \qquad [A17]$$

$$N(n) = n/2 \text{ if } n \text{ is even}$$

$$N(n) = \frac{n-1}{2} \text{ if } n \text{ is odd}$$

where:

$$F(n,k) = \frac{(-1)^k (2n-2k)!}{2^n k!\,(n-k)!\,(n-2k)!} \qquad [A18]$$

(Note: When actually calculating the Legendre functions $P_n(X_B)$, it is preferable to use the recursion relationship Eq. [35] rather than Eq. [A17] and [A18], since calculating by Eq. [A17] and [A18] would involve taking the difference between large powers of X_B, thus resulting in the same round-off errors which occur when simple power series are used.)

Let

$$(2X_B - 1) = z \qquad [A19]$$

Substitute Eqs. [A17] to [A19] into Eq. [A16]:

$$\sum_{n=0}^{n'} \sum_{k=0}^{N(n)} (q_n - a_n + (n-2k) q_n) F(n,k) z^{n-2k} - \sum_{n=1}^{n'} \sum_{k=0}^{N(n)} q_n (n-2k) F(n,k) z^{n-2k-1} = 0 \qquad [A20]$$

We now replace the dummy variable n in the second summation by $(n+1)$, noting also that

$$F(n+1, k) = \frac{(2n+1-2k)}{(n+1-2k)} \cdot F(n,k) \qquad [A21]$$

We thus obtain the expression:

$$\sum_{n=0}^{n'} \sum_{k=0}^{N(n)} (q_n - a_n + (n-2k) q_n - (2n+1-2k) q_{n+1}) \cdot F(n,k) z^{n-2k} = 0 \qquad [A22]$$

Let

$$n - 2k = m, \qquad [A23]$$

and substitute into Eq. [A22]:

$$\sum_{m=0}^{n'} \sum_{k=0}^{N(n'-m)} (-a_{m+2k} + (1+m) q_{m+2k} - (1+2m+2k) q_{m+2k+1}) \cdot \frac{(-1)^k (2m+2k)!}{2^{m+2k} k!\,(m+k)!\,m!} \cdot z^m = 0 \qquad [A24]$$

Eq. [A24] must be true for all z. Thus:

$$\sum_{k=0}^{N(n'-n)} (-a_{n+2k} + (1+n) q_{n+2k} - (1+2n+2k) q_{n+2k+1}) \cdot \frac{(-1)^k (2n+2k)!}{2^{2k} k!\,(n+k)!} = 0 \qquad [A25]$$

where the dummy variable "m" has been renamed "n".

If we expand Eq. [A25] for $n' = 5$, we obtain the set of Eqs. [43], which, by inspection, gives us the general relationship Eq. [38]. This relationship can be verified to be equivalent to Eq. [A25] by direct calculation for any value of n'.

To now calculate the relationship between the coefficients b_n and q_n of the expansions [26] and [28], we proceed just as above using the thermodynamic relationship in Eq. [A1] as our starting point. The result of these calculations is the relationship in Eq. [39].

By expanding Eqs. [38] and [39] for any value of n' and rearranging terms, we can arrive at Eqs. [40] to [42] by inspection. By direct substitution, the set of Eqs. [38] to [42] can be shown to be self-consistent.

Stability Function

Let:

$$\psi = 1 + \frac{X_A X_B}{RT} \cdot (d^2 g^E / dX_B^2) = 1 + \frac{X_A X_B}{RT} \sum_{n=0}^{n'} \theta_n P_n(X_B) \qquad [A26]$$

where

$$g^E = X_A X_B \sum_{n=0}^{n'} q_n P_n(X_B) \qquad [A27]$$

Substitute Eq. [A27] into Eq. [A26], making use also of Eq. [A19]:

$$\sum_{n=0}^{n'} \theta_n P_n(z) = (1 - z^2) \sum_{n=0}^{n'} q_n \frac{d^2 P_n(z)}{dz^2} - 4z \cdot \sum_{n=0}^{n'} q_n \frac{dP_n(z)}{dz} - 2 \sum_{n=0}^{n'} q_n P_n(z) \qquad [A28]$$

Substitute Eqs. [A17] and [A18] into Eq. [A28]:

$$\sum_{n=0}^{n'} \theta_n P_n(z) = \sum_{n=0}^{n'} \sum_{k=0}^{N(n)} q_n F(n,k) z^{n-2k-2} - \sum_{n=0}^{n'} \sum_{k=0}^{N(n)} \cdot q_n [(n-2k)(n-2k-1) + 4(n-2k) + 2] \cdot F(n,k) z^{n-2k} \qquad [A29]$$

Replacing the dummy variable n by $(n+2)$ in the first summation on the right-hand-side of Eq. [A29], we obtain, after some rearrangement:

$$\sum_{n=0}^{n'} \sum_{k=0}^{N(n)} [\theta_n - (2n-2k+1)(2n-2k+3) q_{n+2} + ((n-2k)(n-2k+3) + 2) q_n] \cdot F(n,k) z^{n-2k} = 0 \qquad [A30]$$

We now replace $(n-2k)$ by m, and equate coefficients of z^m to give:

$$\sum_{k=0}^{N(n'-m)} [\theta_{m+2k} - (2m+2k+1)(2m+2k+3) q_{m+2k+2} + (m+1)(m+2) q_{m+2k}] \frac{(-1)^k (2m+2k)!}{2^{2k} k!\,(m+k)!} = 0 \qquad [A31]$$

which is true for all m. By expanding Eq. [A31] for arbitrary values of n', we can arrive at Eq. [52] by inspection. Direct substitution for any n' then shows the equivalency of Eqs. [A31] and [52].

TABLE OF SYMBOLS

a_n	n-th coefficient of series expansion of α_A
b_n	n-th coefficient of series expansion of α_B
c_n	n-th coefficient of a general orthogonal series expansion
C	constant of integration
$f(x)$	general function of x
$F(n, k)$	function defined in Eq. [A18]
g^E	integral molar excess free energy
g_i^E	partial molar excess free energy of component i
Δh	relative integral molar enthalpy
Δh_i	partial relative molar enthalpy of component i
n'	upper summation limit of summation index n
$N(n)$	an upper summation limit defined in Eq. [A17]
$P_n(x)$	n-th Legendre polynomial
q_n	n-th coefficient of series expansion of α_{int}
R	Gas constant (1.987 cal mole^{-1} deg^{-1})
s^E	integral molar excess entropy
s_i^E	partial molar excess entropy of component i
T	temperatuve (Kelvin)
$T_n(x)$	n-th Chebyshev polynomial
$W(n)$	normalization factor of the n-th term of an orthogonal set
x	general independent variable
X_i	mole fraction of component i
α_i	alpha function of the partial molar excess property of component i. $\alpha_i = \omega_i^E/(1 - X_i)^2$
α_{int}	alpha function of the integral molar excess property. $\alpha_{\text{int}} = \omega^E/X_A X_B$
θ_n	n-th coefficient of series expansion of the stability function
ξ_n	n-th coefficient of an expansion obtained by a least squares analysis
$\bar{\rho}$	root mean square deviation of a least squares regression analysis
$\phi_n(x)$	n-th function of an orthogonal set of functions
ψ	stability function
ω	any relative integral molar property
ω_i	any relative partial molar property of component i
ω^E	any integral molar excess property
ω_i^E	any partial molar excess property of component i

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