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ANALYTICAL METHOD OF CALCULATING THERMODYNAMIC PROPERTIES IN TERNARY SYSTEMS

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ABSTRACT

In this paper, an analytical method is proposed for calculating thermodynamic properties in a ternary system from known partial molar excess property of one component or from known excess molar property of the system. Analytical procedures are suggested for ten kinds of experimental data to ensure the thermodynamically consistency and calculation accuracy. The method is much faster than graphical methods and not subject to human error. The method is particularly useful to the ternary systems for which the experimental points are scattered randomly or the properties of some boundaries are unknown.

I. INTRODUCTION

In our previous papers [1,2], graphic methods of calculating ternary thermodynamic properties were proposed. Calculations and verifications can be done only along the special paths such as constant mole fraction lines, constant mole ratio lines and isoactivity lines. If the experimental points are scattered randomly or only available over a restricted region, or if the properties of the boundaries of ternary systems shown in Fig. 1 are unknown, the graphic calculations and verifications would be very difficult. So it seems to be necessary to develop a complete analytical method to overcome these graphic difficulties. Such a method is described

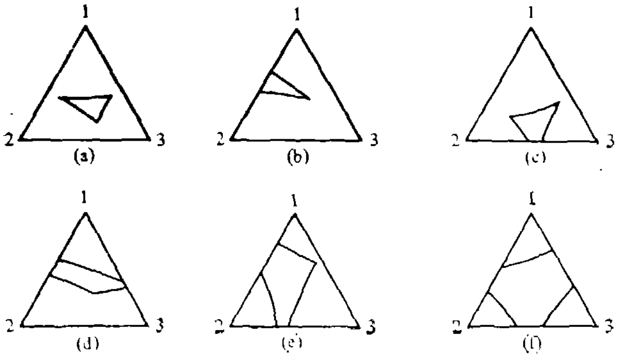

Fig. 1. Schematic diagram of phase boundaries for a ternary system.

here. By using this method, the thermodynamic properties of those ternary systems can be calculated, quickly and more accurately, from known partial molar excess property of one component or from its corresponding integral property.

II. Analytical Formulae

1. *Ternary Analytical Formulae*

Let x_1, x_2, x_3 and ϕ_1, ϕ_2, ϕ_3 be respectively the mole fractions and partial molar excess properties of component 1,2 and 3 in a ternary system 1-2-3; and let ϕ be the corresponding integral property. This paper utilizes the following composition variables:

$$y = 1 - x_1, \tag{1}$$

$$t = \frac{x_3}{x_2 + x_3}. \tag{2}$$

Therefore, for the ternary system, the excess molar property is

$$\phi = (1 - y)\phi_1 + (1 - t)y\phi_2 + ty\phi_3, \tag{3}$$

the Gibbs-Duhem equation is

$$(1 - y)d\phi_1 + (1 - t)yd\phi_2 + tyd\phi_3 = 0, \tag{4}$$

while ϕ_1, ϕ_2, ϕ_3 and ϕ can be expressed as power series in y and t as follows:

$$\phi_1 = \sum_{j=0}^{j'} \sum_{k=0}^{k'} b_{jk} y^j t^k, \tag{5}$$

$$\phi_2 = \sum_{j=0}^{j'} \sum_{k=0}^{k'} c_{jk} y^j t^k, \tag{6}$$

$$\phi_3 = \sum_{j=0}^{j'} \sum_{k=0}^{k'} d_{jk} y^j t^k, \tag{7}$$

$$\phi = \sum_{j=0}^{j'} \sum_{k=0}^{k'} e_{jk} y^j t^k, \tag{8}$$

where all the coefficients are limited and the upper limits j' and k' can be selected in accordance with the number of terms found necessary to get a smooth fit with a less standard error of estimate.

As shown in the Appendix, substituting Eqs. (5)—(8) into Eqs. (3) and (4) gives

$$c_{jk} = b_{jk} - \left(\frac{j + 1 - k}{j}\right) b_{(j+1)k}, \tag{9}$$

$$d_{jk} = b_{jk} - \left(\frac{j + 1 - k}{j}\right) b_{(j+1)k} - \left(\frac{k + 1}{j}\right) b_{(j+1)(k+1)}, \tag{10}$$

$$e_{jk} = -\frac{1}{j - 1} b_{jk}. \tag{11}$$

Since $(\phi_1)_{y=0}=(\phi)_{y=0}=0$ for the pure component 1, all the coefficients b_{0k} and e_{0k} respectively in Eqs. (5) and (8) must be zero. Since the fractions in Eqs. (9) and (10) when $j=0$ or in Eq. (11) when $j=1$ becomes $\frac{0}{0}$, all the coefficients b_{1k} must also be zero. As shown in Eqs. (43) and (44), the coefficients $c_{0k}(k\geqslant 1)$, $d_{0k}(k\geqslant 1)$ and $e_{1k}(k\geqslant 2)$ in Eqs. (6)—(8) also have zero value. Therefore, Eqs. (5)—(8) can be rewritten as

$$\phi_1=\sum_{j=2}^{j'}\sum_{k=0}^{k'} b_{jk}y^jt^k, \tag{12}$$

$$\phi_2=c_{00}+\sum_{j=1}^{j'}\sum_{k=0}^{k'} c_{jk}y^jt^k, \tag{13}$$

$$\phi_3=d_{00}+\sum_{j=1}^{j'}\sum_{k=0}^{k'} d_{jk}y^jt^k, \tag{14}$$

$$\phi=e_{10}y+e_{11}yt+\sum_{j=2}^{j'}\sum_{k=0}^{k'} e_{jk}y^jt^k, \tag{15}$$

where the relationships between b_{jk} $(j\geqslant 2)$, $c_{jk}(j\geqslant 1)$, $d_{jk}(j\geqslant 1)$ and $e_{jk}(j\geqslant 2)$ are determined by Eqs. (9)—(11), the relationships between c_{00}, d_{00}, e_{10}, e_{11} and other coefficients are determined by the equations shown in the following sections.

2. *Binary Analytical Formulae*

According to Eqs. (1) and (2), we have $t=0$ for 1-2 binary system, $t=1$ for 1-3 binary system and $y=1$ for 2-3 binary system.

For 1-2 binary system, Eqs. (12), (13) and (15) become

$$(\phi_1)_{t=0}=\sum_{j=2}^{j'} b_{j0}y^j, \tag{16}$$

$$(\phi_2)_{t=0}=\sum_{j=0}^{j'} c_{j0}y^j, \tag{17}$$

$$(\phi)_{t=0}=\sum_{j=1}^{j'} e_{j0}y^j. \tag{18}$$

For 1-3 binary system, Eqs. (12),(14) and (15) become

$$(\phi_1)_{t=1}=\sum_{j=2}^{j'} b_j^*y^j, \tag{19}$$

$$(\phi_3)_{t=1}=\sum_{j=0}^{j'} d_j^*y^j, \tag{20}$$

$$(\phi)_{t=1} = \sum_{j=1}^{j'} e_j^* y^j. \tag{21}$$

For 2-3 binary system, Eqs. (13)—(15) become

$$(\phi_2)_{y=1} = \sum_{k=2}^{k'} c_k^{**} t^k, \tag{22}$$

$$(\phi_3)_{y=1} = \sum_{k=0}^{k'} d_k^{**} t^k, \tag{23}$$

$$(\phi)_{y=1} = \sum_{k=1}^{k'} e_k^{**} t^k. \tag{24}$$

Clearly, the coefficients in Eqs. (19)—(24) can be written as the sum of those in Eqs. (12)—(15) as follows:

$$b_j^* = \sum_{k=0}^{k'} b_{jk}, \tag{25}$$

$$d_j^* = \sum_{k=0}^{k'} d_{jk}, \tag{26}$$

$$e_j^* = \sum_{k=0}^{k'} e_{jk}, \tag{27}$$

$$c_k^{**} = \sum_{j=0}^{j'} c_{jk}, \tag{28}$$

$$d_k^{**} = \sum_{j=0}^{j'} d_{jk}, \tag{29}$$

$$e_k^{**} = \sum_{j=1}^{j'} e_{jk}. \tag{30}$$

Since $c_0^{**} = c_1^{**} = e_0^{**} = 0$, Eqs. (28) and (30) yield

$$\sum_{j=0}^{j'} c_{j0} = \sum_{j=0}^{j'} c_{j1} = \sum_{j=1}^{j'} e_{j0} = 0. \tag{31}$$

Similar to Eqs. (9)—(11), the relationships between the coefficients in Eqs. (19)—(24) can be written as

$$d_j^* = b_j^* - \left(\frac{j+1}{j}\right) b_{(j+1)}^*, \tag{32}$$

$$e_j^* = -\frac{1}{j-1} b_j^*. \tag{33}$$

$$d_k^{**} = c_k^{**} - \left(\frac{k+1}{k}\right) c_{(k+1)}^{**}, \tag{34}$$

$$e_k^{**} = -\frac{1}{k-1} c_k^{**}. \tag{35}$$

3. *Analytical Formulae for Pure Components*

According to Eqs. (1) and (2), we have $y=0$ for the pure component 1, $y=1$ and $t=0$ for the pure component 2, $y=t=1$ for the pure component 3.

As derived by Darken[4], the property of the pure component 1 can be expressed as

$$(\phi_2)_{y=0,t=t} = (\phi_2)_{y=0,t=0}, \tag{36}$$

$$(\phi_3)_{y=0,t=t} = (\phi_3)_{y=0,t=1}, \tag{37}$$

$$\begin{aligned}\left(\frac{\phi}{y}\right)_{y=0,t=t} &= (1-t)\left(\frac{\phi}{y}\right)_{y=0,t=0} + t\left(\frac{\phi}{y}\right)_{y=0,t=1} \\ &= (1-t)(\phi_2)_{y=0,t=0} + t(\phi_3)_{y=0,t=1},\end{aligned} \tag{38}$$

so that

$$\delta \equiv \left(\frac{\phi}{y}\right)_{y=0,t=t} - \left[(1-t)\left(\frac{\phi}{y}\right)_{y=0,t=0} + t\left(\frac{\phi}{y}\right)_{y=0,t=1}\right] = 0. \tag{39}$$

From Eqs. (6)—(8) and (36)—(38), we have

$$\sum_{k=0}^{k'} c_{0k} t^k = c_{00}, \tag{40}$$

$$\sum_{k=0}^{k'} d_{0k} t^k = \sum_{k=0}^{k'} d_{0k}, \tag{41}$$

$$\sum_{k=0}^{k'} e_{1k} t^k = (1-t) e_{10} + t \sum_{k=0}^{k'} e_{1k} = (1-t) c_{00} + t \sum_{k=0}^{k'} d_{0k}, \tag{42}$$

which yield

$$c_{0k} = d_{0k} = 0 \quad (k \geqslant 1), \tag{43}$$

$$e_{1k} = 0 (k \geqslant 2), \tag{44}$$

$$e_{10} = c_{00}, \tag{45}$$

$$e_{11} = d_{00} - c_{00}. \tag{46}$$

Substituting Eq. (43) into Eq. (26) gives

$$d_0^* = d_{00}. \tag{47}$$

Substituting Eq. (44) into Eq. (27) gives

$$e_1^* = e_{10} + e_{11}. \tag{48}$$

For the pure component 2

$$(\phi_2)_{y=1,t=0} = (\phi)_{y=1,t=0} = 0.$$

Eqs. (17) and (18) then give

$$c_{00} = -\sum_{j=1}^{j'} c_{j0}, \tag{49}$$

$$c_{10} = -\sum_{j=2}^{j'} c_{j0}. \tag{50}$$

For the pure component 3

$$(\phi_3)_{y=1,t=1} = (\phi)_{y=1,t=1} = 0.$$

Then Eq. (14) yields

$$d_{00} = -\sum_{j=1}^{j'} \sum_{k=0}^{k'} d_{jk}. \tag{51}$$

Eqs. (20), (21), (23) and (24) yield

$$d_0^* = -\sum_{j=1}^{j'} d_j^*, \tag{52}$$

$$e_1^* = -\sum_{j=2}^{j'} e_j^*, \tag{53}$$

$$d_0^{**} = -\sum_{k=1}^{k'} d_k^{**}, \tag{54}$$

$$e_1^{**} = -\sum_{k=2}^{k'} e_k^{**}. \tag{55}$$

4. *Ternary Analytical Formulae With Binary Coefficients*

Let us define new functions

$$A_1 \equiv \phi_1 - \sum_{j=2}^{j'} b_{j0} y^j, \tag{56}$$

$$B_1 \equiv \phi_1 + y^2 \sum_{k=2}^{k'} e_k^{**} t^k, \tag{57}$$

$$C_1 \equiv \phi_1 - \left[(1-t)\sum_{j=2}^{j'} b_{j0} y^j + t \sum_{j=2}^{j'} b_j^* y^j\right], \tag{58}$$

$$D_1 \equiv \phi_1 - \sum_{j=2}^{j'} b_{j0} y^j + y^2 \sum_{k=2}^{k'} e_k^{**} t^k, \tag{59}$$

$$E_1 \equiv \phi_1 - \left[(1-t)\sum_{j=2}^{j'} b_{j0} y^j + t \sum_{j=2}^{j'} b_j^* y^j - y^2 \sum_{k=1}^{k'} e_k^{**} t^k\right], \tag{60}$$

$$A \equiv \phi - \sum_{j=1}^{j'} e_{j0} y^j, \tag{61}$$

$$C \equiv \phi - \left[(1-t)\sum_{j=1}^{j'} e_{j0} y^j + t \sum_{j=1}^{j'} e_j^* y^j\right], \tag{62}$$

$$E \equiv \phi - \left[(1-t)\sum_{j=1}^{j'} e_{j0}y^j + t\sum_{j=1}^{j'} e_j^* y^j + y^2 \sum_{k=1}^{k'} e_k^{**} t^k\right]. \tag{63}$$

From Eqs. (12) and (56),

$$A_1 = \sum_{j=2}^{j'} \sum_{k=1}^{k'} b_{jk} y^j t^k. \tag{64}$$

According to Eqs. (11), (30) and (44),

$$e_k^{**} = -\left(b_{2k} + \sum_{j=3}^{j'} \frac{1}{j-1} b_{jk}\right), \quad (k \geqslant 2). \tag{65}$$

From Eqs. (12), (57) and (65),

$$B_1 = \sum_{j=2}^{j'} b_{j0} y^j + \sum_{j=2}^{j'} b_{j1} y^j t + \sum_{j=3}^{j'} \sum_{k=2}^{k'} b_{jk} t^k \left(y^j - \frac{1}{j-1} y^2\right). \tag{66}$$

From Eqs. (12), (25) and (58)

$$C_1 = \sum_{j=2}^{j'} \sum_{k=2}^{k'} b_{jk} y^j (t^k - t). \tag{67}$$

From Eqs. (57), (59) and (66),

$$D_1 = \sum_{j=2}^{j'} b_{j1} y^j t + \sum_{j=3}^{j'} \sum_{k=2}^{k'} b_{jk} t^k \left(y^j - \frac{1}{j-1} y^2\right). \tag{68}$$

According to Eqs. (30), (44) and (55),

$$\sum_{k=1}^{k'} e_k^{**} t^k = \sum_{k=2}^{k'} e_k^{**} (t^k - t) = \sum_{j=2}^{j'} \sum_{k=2}^{k'} e_{jk} (t^k - t). \tag{69}$$

From Eqs. (11), (12), (58), (60), (67) and (69),

$$E_1 = \sum_{j=3}^{j'} \sum_{k=2}^{k'} b_{jk} \left(y^j - \frac{1}{j-1} y^2\right)(t^k - t). \tag{70}$$

From Eqs. (15) and (61),

$$A = e_{11} y t + \sum_{j=2}^{j'} \sum_{k=1}^{k'} e_{jk} y^j t^k. \tag{71}$$

From Eqs. (15), (27), (44) and (62),

$$C = \sum_{j=2}^{j'} \sum_{k=2}^{k'} e_{jk} y^j (t^k - t). \tag{72}$$

From Eqs. (15), (62), (63), (69) and (72),

$$E = \sum_{j=3}^{i'} \sum_{k=2}^{k'} e_{jk} (y^j - y^2)(t^k - t). \tag{73}$$

III. Analytical Procedures

The standard errors of binary-selected data in the literature are generally not only different from each other, but much smaller than those of ternary experimental data as well. In order to keep the original accuracy of the binary data, to ensure the thermodynamical consistency between binary and ternary data and to improve reasonably the calculation accuracy of ternary data, it seems to be necessary to fit binary-selected data by a least-squares technique at first, and then to take the obtained binary coefficients as the boundaries in the fitting process of ternary data. Thus, we introduce the analytical procedures for ten kinds of experimental data as follows, in which the procedures (1)—(6) can be used for the calculation of partial molar excess properties of other two components in a ternary system and the corresponding integral property of the system from known partial molar excess property of one component, while the procedures (7)—(10) are suitable for the calculation of partial molar excess properties of all three components from known corresponding integral property of the system.

(1) If only ternary experimental data, ϕ_1, are available (Fig. 1 (a)), the ternary data can be fitted by Eq. (12), giving all the b_{jk} coefficients; the coefficients $c_{jk}(j \geqslant 1)$, $d_{jk}(j \geqslant 1)$ and $e_{jk}(j \geqslant 2)$ can then be calculated by Eqs. (9)—(11); the coefficients c_{00}, d_{00}, e_{10} and e_{11} can be calculated by Eqs. (49), (51), (45) and (46), respectively; the values of ϕ_2, ϕ_3 and ϕ can be calculated by Eqs. (13)—(15).

(2) If ternary experimental data ϕ_1 and 1-2 binary-selected data $(\phi_1)_{t=0}$ are available (Fig. 1 (b)), the binary data can be fitted by Eq. (16) giving all the b_{j0} coefficients, the obtained b_{j0} coefficients and the ternary data ϕ_1 give the coefficients $b_{jk}(j \geqslant 2,\ k \geqslant 1)$ in terms of Eqs. (56) and (64). Then, the calculation of all the c_{jk}, d_{jk} and e_{jk} coefficients and the ϕ_2, ϕ_3 and ϕ values can still be done by the method described in the first procedure.

(3) If ternary experimental data ϕ_1 and 2-3 binary-selected data $(\phi_2)_{y=1}$ are available (Fig. 1 (c)), the binary data can be fitted by Eq. (22) giving all the c_k^{**} coefficients, then the coefficients $e_k^{**}(k \geqslant 2)$ can be calculated by Eq. (35). The obtained coefficients $e_k^{**}(k \geqslant 2)$ and the ternary data ϕ_1 give the coefficients $b_{j0}(j \geqslant 2), b_{j1}(j \geqslant 2)$ and $b_{jk}(j \geqslant 3, k \geqslant 2)$ in terms of Eqs. (57) and (66). The remaining coefficients $b_{2k}(k \geqslant 2)$ can be calculated by Eq. (65). Then, the c_{jk}, d_{jk}, e_{jk} coefficients and the ϕ_2, ϕ_3 and ϕ values can still be calculated by the method described in the first procedure.

(4) If ternary experimental data ϕ_1 and both 1-2 and 1-3 binary-selected data $(\phi_1)_{t=0}$ and $(\phi_1)_{t=1}$ are available (Fig. 1(d)), the binary data can be fitted by Eqs. (16) and (19) giving all the b_{j0} and b_j^* coefficients. The obtained binary coefficients and the ternary data give the coefficients b_{jk} $(j \geqslant 2, k \geqslant 2)$ in terms of Eqs. (58) and (67). The remaining coefficients $b_{j1}(j \geqslant 2)$ can be calculated by Eq. (25). Then, the c_{jk}, d_{jk}, e_{jk} coefficients and the ϕ_2, ϕ_3, ϕ values can be calculated by the method described in the first procedure.

(5) If ternary experimental data ϕ_1 and both 1-2 and 2-3 binary-selected data $(\phi_1)_{t=0}$ and $(\phi_2)_{y=1}$ are available (Fig. 1(e)), the binary data can be fitted by Eqs. (16) and (22) giving all the b_{j0} and c_k^{**} coefficients, then the coefficients

$e_k^{**}(k \geqslant 2)$ can be calculated by Eq. (35). The obtained binary coefficients b_{j0}, $e_k^{**}(k \geqslant 2)$ and the ternary data ϕ_1 give the coefficients $b_{j1}(j \geqslant 2)$ and $b_{jk}(j \geqslant 3, k \geqslant 2)$ in terms of Eqs. (59) and (68). The remaining coefficients $b_{2k}(k \geqslant 2)$ can be calculated by Eq. (65). Then the c_{jk}, d_{jk}, e_{jk} coefficients and ϕ_2, ϕ_3, ϕ values can be calculated by the method described in the first procedure.

(6) If ternary experimental data ϕ_1 and all the 1-2, 1-3 and 2-3 binary-selected data, $(\phi_1)_{t=0}, (\phi_1)_{t=1}$ and $(\phi_2)_{y=1}$ are available (Fig. 1 (f)), the binary data can be fitted by Eqs. (16), (19) and (22) giving all the b_{j0}, b_j^* and c_k^{**} coefficients; then all the e_k^{**} coefficients can be calculated by Eqs. (35) and (55). The obtained binary coefficients b_{j0}, b_j^* and e_k^{**} and the ternary data ϕ_1 give the coefficients $b_{jk}(j \geqslant 3, k \geqslant 2)$ in terms of Eqs. (60) and (70). The remaining coefficients $b_{2k}(k \geqslant 2)$ and $b_{j1}(j \geqslant 2)$ can be calculated by Eqs. (65) and (25) respectively. Then all the c_{jk}, d_{jk}, e_{jk} coefficients and ϕ_2, ϕ_3, ϕ values can be calculated by the method described in the first procedure.

(7) If only ternary experimental data ϕ are available (Fig. 1(a)), the ternary data can be fitted by Eq. (15) giving all the e_{jk} coefficients, the coefficients b_{jk} $(j \geqslant 2), c_{jk}(j \geqslant 1)$ and $d_{jk}(j \geqslant 1)$ can be calculated by Eqs. (9)—(11); the remaining coefficients c_{00} and d_{00} can be calculated by Eqs. (45) and (46). Then the values of ϕ_1, ϕ_2 and ϕ_3 can be calculated by Eqs (12)—(14).

(8) If ternary experimental data ϕ and 1-2 binary-selected data $(\phi)_{t=0}$ are available (Fig. 1(b)), the binary data can be fitted by Eq. (18) giving all the e_{j0} coefficients, the obtained e_{j0} coefficients and the ternary data give the coefficients e_{11} and $e_{jk}(j \geqslant 2, k \geqslant 1)$ in terms of Eqs. (61) and (71). Then all the b_{jk}, c_{jk}, d_{jk} coefficients and ϕ_1, ϕ_2, ϕ_3 values can be calculated by the method described in the seventh procedure.

(9) If ternary experimental data ϕ and both 1-2 and 1-3 binary-selected data $(\phi)_{t=0}$ and $(\phi)_{t=1}$ are available (Fig. 1(d)), the binary data can be fitted by Eqs. (18) and (21) giving all the e_{j0} and e_j^* coefficients. The obtained binary coefficients and ternary data give the coefficients $e_{jk}(j \geqslant 2, k \geqslant 2)$ in terms of Eqs. (62) and (72). Then the remaining coefficients $e_{j1}(j \geqslant 1)$ can be calculated by Eqs. (27) and (48). All the b_{jk}, c_{jk}, d_{jk} coefficients and ϕ_1, ϕ_2, ϕ_3 values can be calculated by the method described in the seventh procedure.

(10) If ternary experimental data ϕ and all the 1-2, 1-3 and 2-3 binary-selected data $(\phi)_{t=0}, (\phi)_{t=1}$ and $(\phi)_{y=1}$ are available (Fig. 1 (f)), the binary data can be fitted by Eqs. (18), (21) and (24) giving all the e_{j0}, e_j^* and e_k^{**} coefficients. The obtained binary coefficients and ternary data give the coefficients $e_{jk}(j \geqslant 3, k \geqslant 2)$ in terms of Eqs. (63) and (73). The remaining coefficients $e_{2k}(k \geqslant 2)$ can be calculated by Eqs. (11) and (65), while $e_{j1}(j \geqslant 1)$ by Eqs. (27) and (48). Then all the b_{jk}, c_{jk}, d_{jk} coefficients and ϕ_1, ϕ_2, ϕ_3 values can still be calculated by the method described in the seventh procedure.

By using simple component transformations, the analytical calculation of ternary systems with other unknown boundaries can also be done by the above-mentioned procedures. For example, if only ternary experimental data ϕ_t and 1-3 binary-selected data $(\phi_1)_{t=1}$ are available, we can put $1' = 1, 2' = 3, 3' = 2$, and then calculate the properties in the ternary system 1'-2'-3' by using the second procedure.

IV. Example of Application

We have calculated graphically the thermodynamic properties of the Cd-Bi-Pb system in Refs. [1, 2]. The results are in good agreement with those of Elliott[5] and Moser[6]. To verify the new method, we can calculate analytically the excess chemical potentials μ_2^E and μ_3^E from known μ_1^E values (putting 1 = Cd, 2 = Bi, 3 = Pb) in the system at 760K and then compare the analytical results with the graphical ones in Refs. [1, 6].

Smooth fits were obtained for the Cd-Bi-Pb system by using the sixth procedure with three sets of upper limits $j' = k' = 5$, $(j+k)_{\max} = 7$; $k' = 4$, $j' = (j+k)_{\max} = 6$ and $j' = k' = 6$, $(j+k)_{\max} = 8$. The standard error of estimate with the latter one seems slightly better than those with the former two. So we only report the calculations with the latter one here.

Table 1 shows four sets of binary coefficients b_{j0}, b_j^*, c_k^{**} and e_k^{**}. The former three were obtained by the least-squares fit to binary data, while the latter

Table 1

Some Coefficients in Analytical Formulae for Cd-Bi, Cd-Pb, Bi-Pb Binary Systems (760 K, J/mol)

	b_{j0}	b_j^*		c_k^{**}	e_k^{**}
$j=1$	0.00	0.00	$k=1$	0.00	−5004.21
$j=2$	15997.00	17587.74	$k=2$	−4937.47	4937.47
$j=3$	−97208.48	−34334.73	$k=3$	−619.08	309.54
$j=4$	178781.19	55171.33	$k=4$	1787.38	−595.79
$j=5$	−134798.21	−47330.76	$k=5$	−2113.61	528.40
$j=6$	37137.17	16667.88	$k=6$	877.06	−175.41

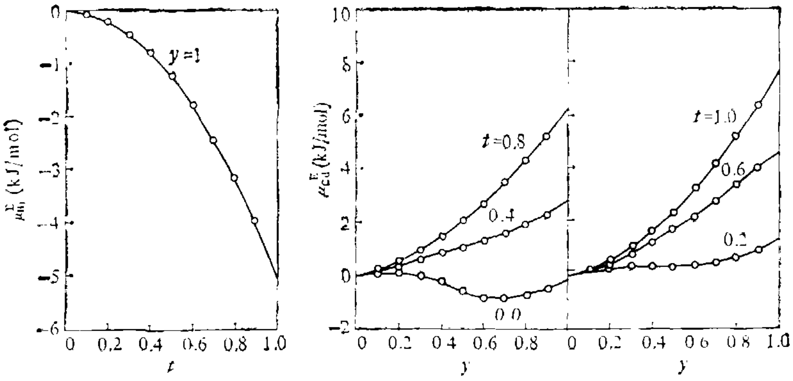

Fig. 2. Least-squares fit to binary and ternary data of the excess chemical potentials in the Cd-Bi-Pb system at 760K.
$y = 1 - x_{Cd}$, $t = x_{Pb}/(x_{Bi} + x_{Pb})$.

one was calculated by Eqs. (35) and (55).

Table 2 shows the ternary coefficients b_{jk}, c_{jk}, d_{jk} and e_{jk}. As shown in Fig 2, a smooth fit without "hills and valleys" has been obtained. The standard error of estimate was 11.11 J/mol for Cd-Bi binary system, 3.74 J/mol for Cd-Pb binary system, 1.29 J/mol for Bi-Pb binary system and 25.93 J/mol for Cd-Bi-Pb ternary system. In Fig. 3, the calculated values of μ_2^E and μ_3^E by the analytical method are compared with those in Refs. [1, 6]. The analytical results satisfy Eqs. (36) and (37), and agree more closely with the previous graphical ones[1,6].

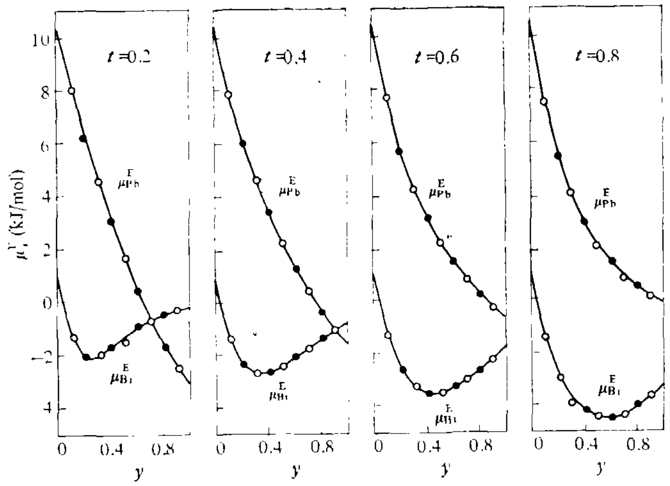

Fig. 3. Excess chemical potentials of Bi and Pb in the Cd-Bi-Pb system at 760K. ○, Moser and Zadbyr[6]; ●, Wang and Zhou[1]; —— this work.

V. Discussion

Wohl[7] and Nikol'skii[8] proposed analytical formulae of thermodynamic properties for the 1-2-3 ternary system. But Pelton and Flengas[9] pointed out that Wohl's and Nikol'skii's relations were not easy to fit by a least-squares technique and did not contain the boundary conditions relating to calculation accuracy. Pelton-Flengas' method takes the 2-3 binary system as boundary condition that was first suggested by Darken[4] for his graphic treatment and utilizes y and t defined by Eqs. (1) and (2) as the composition variables that was first introduced by Wagner[3] in his graphic treatment. Pelton-Flengas' analytical procedure is very easy, so it has widely been used for the analytical treatment of experimental data[10-16]. Recently, however, we[1,17] corrected some obvious mistakes inherent in Pelton-Flengas' relations for some ternary systems and pointed out the importance of boundaries to calculation accuracy of ternary thermodynamic properties.

The shortcomings of using Pelton-Flengas' method is as follows: (i) It is thermodynamically inconsistent for the lack of boundary conditions. For example, according to Darken[4], $(\phi_2)_{y=0,t=t}$ and $(\phi_3)_{y=0,t=t}$ for the pure component 1 should be independent of t and the δ function defined by Eq. (39) must be zero. As shown in Figs. 4 and 5, however, Pelton-Flengas' method always yield the results

Table 2

The Coefficients in Analytical Formulae for Cd-Bi-Pb Ternary System (760 K, J/mol)

		$k=0$	$k=1$	$k=2$	$k=3$	$k=4$	$k=5$	$k=6$
$j=2$	b_{jk}	15997.00	−6405.63	1056.00	11292.96	8077.40	−12605.40	175.41
$j=3$	b_{jk}	−97208.48	231376.75	−181100.72	−53886.22	42329.95	24153.99	
$j=4$	b_{jk}	178781.19	−566635.37	578287.65	−49322.39	−85939.75		
$j=5$	b_{jk}	−134798.21	483891.83	−523550.00	127125.62			
$j=6$	b_{jk}	37137.17	−133878.48	113409.19				
$j=0$	c_{jk}	714.38						
$j=1$	c_{jk}	−31993.99	6405.63	0.00	11292.96	16154.80	−37816.20	701.65
$j=2$	c_{jk}	161809.71	−237782.38	91606.36	11292.96	29242.38	11548.59	175.41
$j=3$	c_{jk}	−335583.41	798012.12	−566625.84	−37445.42	42329.95	24153.99	
$j=4$	c_{jk}	347278.95	−1050527.20	970950.15	−112885.20	−85939.75		
$j=5$	c_{jk}	−179362.82	617770.31	−614277.35	127125.62			
$j=6$	c_{jk}	37137.17	−133878.48	113409.19				
$j=0$	d_{jk}	10311.73						
$j=1$	d_{jk}	−25588.36	4293.64	−33878.89	−21016.64	79181.80	−38868.67	701.65
$j=2$	d_{jk}	46121.34	−56681.66	172435.69	−73366.94	−31142.61	11548.59	175.41
$j=3$	d_{jk}	−146704.94	412487.01	−517303.44	77140.92	42329.95	24153.99	
$j=4$	d_{jk}	226306.00	−788752.20	875605.93	−112885.20	−85939.75		
$j=5$	d_{jk}	−152587.12	572406.63	−614277.35	127125.62			
$j=6$	d_{jk}	37137.17	−133878.48	113409.19				
$j=1$	e_{jk}	714.38	9597.35					
$j=2$	e_{jk}	−15997.00	6405.63	−1056.00	−11292.96	−8077.40	12605.40	−175.41
$j=3$	e_{jk}	48604.24	−115688.37	90550.36	26943.11	−21164.98	−12077.00	
$j=4$	e_{jk}	−59593.73	188878.46	−192762.56	16440.80	28646.59		
$j=5$	e_{jk}	33699.55	−120972.96	130887.50	−31781.41			
$j=6$	e_{jk}	−7427.43	26775.70	−22681.84				

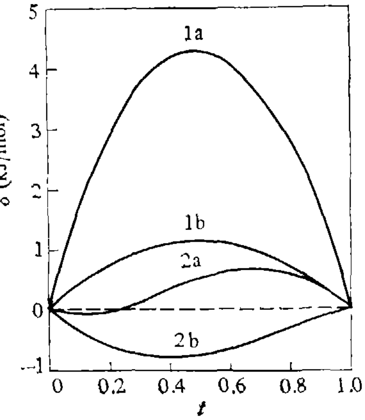

Fig. 4. The δ values calculated from the Pelton-Flengas' relations for some ternary systems.

1, AgCl-NaCl-RbCl system at 1073K[10]; 2, Bi-Pb-Sn system at 773 K[11]; a, $\phi = H^E$ (excess molar enthalpy); b, $\phi = G^E$ (excess molar free energy).

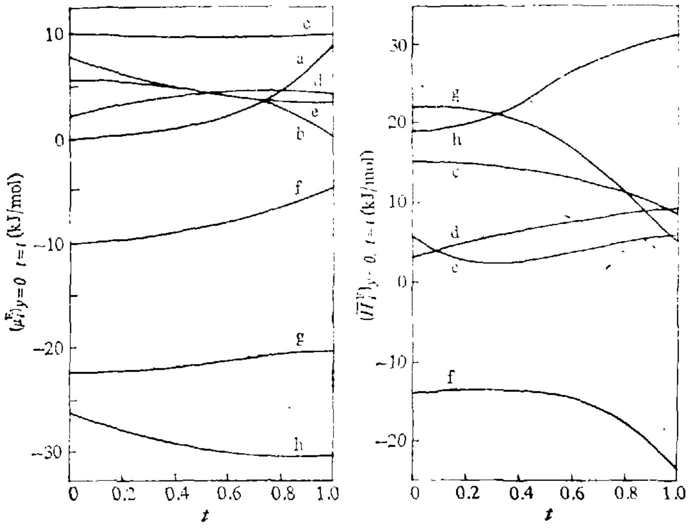

Fig. 5. The $(\mu_i^E)_{y=0,t=t}$ and $(\bar{H}_i^E)_{y=0,t=t}$ values calculated from the Pelton-Flengas' relations for some ternary systems.
a, i = Bi in Cd-Bi-Sn system at 773 K[9]; b, i = Sn in Cd-Bi-Sn system at 773 K[9]; c, i = Pb in Cd-Pb-Sn system at 760 K[12]; d, i = Sn in Cd-Pb-Sn system at 760 K[12]; e, i=NaCl in AgCl-NaCl-RbCl system at 1073 K[10]; f, i=RbCl in AgCl-NaCl-RbCl system at 1073 K[10]; g, i = Cd in Mg-Cd-In system at 850 K[15]; h, i = In in Mg-Cd-In system at 850 K[15].

that $\delta, (\phi_2)_{y=0,t=t}$ and $(\phi_3)_{y=0,t=t}$ are the functions of t. (ii) It often does not fit 1-2 and 1-3 binary-selected data well, since the standard error of ternary experimental data is generally much larger than that of binary-selected data[18], but Pelton-Flengas' method fits the ternary data and 1-2, 1-3 binary-selected data at the same time by a least-squares technique. For example, Moser[14] found that the Pelton-Flengas' relation for excess chemical potential of Mg in Mg-In-Sn system differed from the experimental data of Mg-In binary system (Fig. 6). (iii) It cannot be utilized to the ternary systems (e. g., the O-U-Pu solid solution[19]) for which the properties of 2-3 binary system or of its corresponding boundary shown in Fig. 1 (a), (b), (c) are unknown.

The analytical method presented in this paper overcomes all the disadvantages of the above-mentioned methods. The data of pure components, binary and ternary systems satisfy each other thermodynamically. The fitting results are always in excellent agreement with the binary-selected data. Moreover, it can be utilized to the ternary systems with any kinds of unknown boundaries. Each calculation sample only needs some dozens of second, using a PDP-11/70 electron computer and the Fortain 77 computer programs designed for the purpose. The results not only agree more closely with the reliable graphic calculations in the literature, but can further be used in phase diagram calculations.

Appendix

Differentiating Eq. (3) and then comparing the result with Eq. (4), we

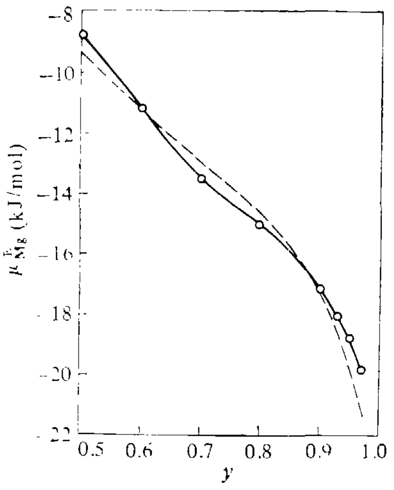

Fig. 6. Least-squares fit to experimental values of the excess chemical potenial of Mg in Mg-In binary system at 923 K, O, experimental data[14]; ——, this method; ----, Pelton-Flengas' method[14].

obtain

$$d\phi = (\phi_2 - \phi_1)dy + t(\phi_3 - \phi_2)dy + y(\phi_3 - \phi_2)dt,$$

which yields

$$\left(\frac{\partial\phi}{\partial y}\right)_t = (\phi_2 - \phi_1) + t(\phi_3 - \phi_2) = \frac{\phi - \phi_1}{y},$$

$$\left(\frac{\partial\phi}{\partial t}\right)_y = y(\phi_3 - \phi_2) = \frac{y}{t}\left(\frac{\partial\phi}{\partial y}\right)_t - \frac{y}{t}(\phi_2 - \phi_1);$$

or

$$\phi = \phi_1 + y\left(\frac{\partial\phi}{\partial y}\right)_t, \tag{A-1}$$

$$\phi_2 = \phi_1 + \left(\frac{\partial\phi}{\partial y}\right)_t - \frac{t}{y}\left(\frac{\partial\phi}{\partial t}\right)_y, \tag{A-2}$$

$$\phi_3 = \phi_2 + \frac{1}{y}\left(\frac{\partial\phi}{\partial t}\right)_y. \tag{A-3}$$

Substituting Eqs. (5)—(8) into Eq. (A-1) gives

$$\sum_{j=0}^{j'}\sum_{k=0}^{k'} e_{jk}y^j t^k = \sum_{j=0}^{j'}\sum_{k=0}^{k'} b_{jk}y^j t^k + \sum_{j=0}^{j'}\sum_{k=0}^{k'} e_{jk}(j)y^j t^k,$$

$$\sum_{j=0}^{j'}\sum_{k=0}^{k'} e_{jk}(1 - j)y^j t^k = \sum_{j=0}^{j'}\sum_{k=0}^{k'} b_{jk}y^j t^k. \tag{A-4}$$

From Eq. (A-4) we can obtain Eq. (11).

Substituting Eqs. (5)—(8) into Eq. (A-2) gives

$$\sum_{j=0}^{j'}\sum_{k=0}^{k'} c_{jk}y^j t^k = \sum_{j=0}^{j'}\sum_{k=0}^{k'} b_{jk}y^j t^k + \sum_{j=0}^{j'}\sum_{k=0}^{k'} e_{jk}(j)y^{j-1}t^k - \sum_{j=0}^{j'}\sum_{k=0}^{k'} e_{jk}(k)y^{j-1}t^k,$$

$$\sum_{j=0}^{j'}\sum_{k=0}^{k'} c_{jk}y^j t^k = \sum_{j=0}^{j'}\sum_{k=0}^{k'} b_{jk}y^j t^k + \sum_{j=-1}^{j'-1}\sum_{k=0}^{k'} e_{(j+1)k}(j+1-k)y^j t^k. \qquad \text{(A-5)}$$

From Eqs. (11) and (A-5) we can obtain Eq. (9).

Substituting Eqs. (5)—(8) into Eq. (A-3) gives

$$\sum_{j=0}^{j'}\sum_{k=0}^{k'} d_{jk}y^j t^k = \sum_{j=0}^{j'}\sum_{k=0}^{k'} c_{jk}y^j t^k + \sum_{j=0}^{j'}\sum_{k=0}^{k'} e_{jk}(k)y^{j-1}t^{k-1},$$

$$\sum_{j=0}^{j'}\sum_{k=0}^{k'} d_{jk}y^j t^k = \sum_{j=0}^{j'}\sum_{k=0}^{k'} c_{jk}y^j t^k + \sum_{j=-1}^{j'-1}\sum_{k=-1}^{k'-1} e_{(j+1)(k+1)}(k+1)y^j t^k. \qquad \text{(A-6)}$$

From Eqs. (9), (11) and (A-6) we can obtain Eq. (10).

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