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Futility or usefulness of common implementations of the area and slope consistency tests for partial molar properties in binary mixtures

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ABSTRACT

The intercept method is usually employed for the calculation of partial molar properties in binary mixtures. Partial molar volumes are obtained from mixture mass density measurements. Partial molar enthalpies are obtained from heat of mixing measurements. If a fitting function is chosen to represent the mixture molar volume, it is shown here that the area test is fulfilled exactly, in a non-trivial way, only if the fitting function exactly matches the experimental values of the pure component molar volumes. Even a small discrepancy between these values and those given by the fitting function will be considerably enlarged when both sides of the area test equation are compared. If an n-th degree polynomial is chosen as the fitting function for the mixture molar volume, the exact fulfillment of the area test for the partial molar volumes will be achieved only if the polynomial is forced to pass exactly through the experimental values of the pure component molar volumes and, in consequence, the number of adjustable coefficients of the polynomial changes from $n+1$ to $n-1$. However, the easiest way to achieve the exact fulfillment of the area test for the partial molar volumes or the partial molar enthalpies is by making use of the popular Redlich–Kister expansion to represent the excess molar volume or the excess molar enthalpy of the mixture. It is also shown here that the slope consistency test will always be trivially fulfilled regardless of the form of the fitting function chosen to represent the mixture molar volume, so that a useful implementation of the slope test can only be made by using suitable interpolating functions, such as those of the cubic-spline kind, to represent the differences between the partial and the pure component molar volumes.

1. The area consistency test

The calculation of partial molar volumes (or enthalpies) in binary systems is covered in thermodynamics textbooks written for the chemical engineering curriculum [1–3]. The intercept method yields the following expressions for the partial molar volumes $\bar{V}_1$ and $\bar{V}_2$ of components 1 and 2 of a binary mixture:

$$\bar{V}_1 = \underline{V} + (1 - x_1)\left(\frac{d\underline{V}}{dx_1}\right) \tag{1a}$$

$$\bar{V}_2 = \underline{V} - x_1\left(\frac{d\underline{V}}{dx_1}\right), \tag{1b}$$

where $\underline{V}$ is the molar volume of the mixture and x_1 is the mole fraction of component 1. The partial molar volumes can also be calculated from the equivalent expressions

$$\bar{V}_1 - \underline{V}_1 = \Delta_{\text{mix}}\underline{V} + (1 - x_1)\frac{d}{dx_1}(\Delta_{\text{mix}}\underline{V}) \tag{2a}$$

$$\bar{V}_2 - \underline{V}_2 = \Delta_{\text{mix}}\underline{V} - x_1\frac{d}{dx_1}(\Delta_{\text{mix}}\underline{V}), \tag{2b}$$

where

$$\Delta_{\text{mix}}\underline{V} = \underline{V} - (x_1\underline{V}_1 + x_2\underline{V}_2) \tag{3}$$

with $\underline{V}_1$ and $\underline{V}_2$ as the molar volumes of the pure components. Eq. (3) defines the volume change on mixing $\Delta_{\text{mix}}\underline{V}$ (also known as excess molar volume of the mixture) as the difference between the mixture molar volume and the value of the molar volume corresponding to an ideal solution of the same composition as the mixture.

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a	polynomial coefficient
f	fitting function
g	fitting function
$\underline{G}^{ex}$	molar excess Gibbs energy
h	interpolating function
H	enthalpy
$\underline{H}^{ex}$	excess molar enthalpy
$\Delta_{mix}\underline{H}$	heat of mixing
N_i	number of moles of component *i*
P	pressure
P_i^{sat}	saturation pressure of component *i*
R	universal gas constant, 8.314 J/mol K
T	temperature
V	volume
$\underline{V}$	molar volume
$\underline{V}_i^{exp}$	experimental molar volume of component *i*
$\underline{V}^{ex}$	excess molar volume
$\bar{V}_i$	partial molar volume of component *i*
$\Delta_{mix}\underline{V}$	volume change on mixing
x_i	mole fraction of component *i*
δ	discrepancy
γ_i	activity coefficient of component *i*
$\underline{\theta}$	molar property
$\bar{\theta}_i$	partial molar property of component *i*

If volume V is changed to enthalpy H, equations similar to Eqs.(2a-2b) and (3) are obtained that allow the calculation of partial molar enthalpies from heat of mixing ($\Delta_{mix}\underline{H}$) measurements.

The starting point for the derivation of the area consistency test for the partial molar properties $\bar{\theta}_i$ of the components of a binary mixture is the following expression for the total differential of the corresponding mixture molar property $\underline{\theta}$:

$$d\underline{\theta} = \left(\frac{\partial\underline{\theta}}{\partial T}\right)_{P,N_i} dT + \left(\frac{\partial\underline{\theta}}{\partial P}\right)_{T,N_i} dP + \sum_i \bar{\theta}_i dx_i. \tag{4}$$

At constant temperature and pressure, and for a binary system, Eq. (4) becomes

$$d\underline{\theta} = (\bar{\theta}_1 - \bar{\theta}_2)dx_1. \tag{5}$$

Integration of Eq. (5) from $x_1 = 0$ to $x_1 = 1$ yields the area test equation:

$$\int_0^1 (\bar{\theta}_1 - \underline{\theta}_1)dx_1 = \int_0^1 (\bar{\theta}_2 - \underline{\theta}_2)dx_1. \tag{6}$$

Eq. (6) can be applied to partial molar volumes ($\theta = V$), calculated from mixture mass density measurements, or partial molar enthalpies ($\theta = H$), calculated from heat of mixing measurements. For partial molar volumes, Eq. (6) takes the form

$$\int_0^1 (\bar{V}_1 - \underline{V}_1)dx_1 = \int_0^1 (\bar{V}_2 - \underline{V}_2)dx_1, \tag{7}$$

where $\bar{V}_1$ and $\bar{V}_2$ are given by Eqs. (1a-1b), respectively. The integrals at both sides of Eq. (7) represent the total areas below the corresponding $\bar{V}_i - \underline{V}_i$ vs. x_1 curves. The implementation of this area test depends on the representation of the mixture molar volume $\underline{V}$ by some fitting function $f(x_1)$, from which the derivative $d\underline{V}/dx_1$ can be calculated, so that the partial molar volumes of components 1 and 2 are obtained from Eqs. (1a-1b), as follows:

$$\bar{V}_1 = f(x_1) + (1 - x_1)f'(x_1) \tag{8a}$$

$$\bar{V}_2 = f(x_1) - x_1 f'(x_1). \tag{8b}$$

Substitution of Eqs. (8a-8b) into the left-hand and right-hand sides of Eq. (7) yields

$$\int_0^1 (\bar{V}_1 - \underline{V}_1)dx_1 = \int_0^1 [f(x_1) + (1 - x_1)f'(x_1) - \underline{V}_1]dx_1 \tag{9a}$$

$$\int_0^1 (\bar{V}_2 - \underline{V}_2)dx_1 = \int_0^1 [f(x_1) - x_1 f'(x_1) - \underline{V}_2]dx_1. \tag{9b}$$

Given that the use of available software packages allows that a suitable function $f(x_1)$ can be chosen and fitted to the experimental data for the mixture molar volume $\underline{V}$, it seems that the implementation of the area consistency test for the partial molar volumes is feasible; moreover, it seems that such an implementation would be easy.

2. Futile implementations of the area test

2.1. General considerations

Since the mixture molar volume $\underline{V}$ is represented by the fitting function $f(x_1)$, it is appealing to replace the molar volumes of the pure components $\underline{V}_1$ and $\underline{V}_2$ by the values predicted from the fitting function. If the naïve assignments $\underline{V}_1 = f(1)$ and $\underline{V}_2 = f(0)$ are made, then Eqs. (9a-9b) become

$$\int_0^1 (\bar{V}_1 - \underline{V}_1)dx_1 = \int_0^1 [f(x_1) - x_1 f'(x_1)]dx_1 - f(0) \tag{10a}$$

$$\int_0^1 (\bar{V}_2 - \underline{V}_2)dx_1 = \int_0^1 [f(x_1) - x_1 f'(x_1)]dx_1 - f(0). \tag{10b}$$

The resulting equality of the right-hand sides of Eqs. (10a-10b) implies that both sides of the area test equation are the same, regardless of the quality of the fit of the experimental values for the mixture molar volume $\underline{V}$ or even the form of the fitting function $f(x_1)$.

For the sake of illustration, let us apply the area test equation to a set of mass density measurements for the system methanol (1) - n-pentane (2) reported by Orge et al [4]. The molar volume of the mixture can be obtained from the reported mole fractions and mass densities (see Table 1), and by means of the POLYMATH software package, the mixture molar volumes were fitted to the quadratic polynomial

$$\underline{V} = f(x_1) = a_0 + a_1 x_1 + a_2 x_1^2 \tag{11}$$

with coefficients $a_0 = 116.216$, $a_1 = -73.6867$, and $a_2 = -1.77435$ (from heretofore, this polynomial will be designated as P2-3).

From Eq. (11), the following expression is obtained for the derivative involved in Eqs. (1a-1b):

$$\frac{d\underline{V}}{dx_1} = f'(x_1) = a_1 + 2a_2 x_1 \tag{12}$$

Substitution of Eqs. (11) and (12) into Eqs. (1a-1b) leads to the following expressions for the partial molar volumes of the two components:

$$\bar{V}_1 = a_0 + a_1 + 2a_2 x_1 - a_2 x_1^2 \tag{13a}$$

$$\bar{V}_2 = a_0 - a_2 x_1^2. \tag{13b}$$

Values of $\bar{V}_1$ and $\bar{V}_2$ resulting from Eqs. (13a-13b) are reported in Table 1 (see results for quadratic polynomial P2-3).

If the naive assignments made to obtain Eqs. (10a-10b) are applied to the quadratic polynomial P2-3, the following expressions are obtained $\underline{V}_1 = f(1) = a_0 + a_1 + a_2$, $\underline{V}_2 = f(0) = a_0$. Substitution