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How reliable are extrapolations to infinite dilution of partial molar properties using Redlich–Kister fittings?

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ABSTRACT

An explicit method for uncertainty estimation associated with excess partial molar properties at infinite dilution calculated using standard uncertainties of Redlich–Kister parameters, fitted to data over the whole composition range, is presented for the first time. The application of this method to sets of accurate volumetric experimental data for aqueous water + ethanol binary mixtures, experimentally determined by different authors is made and the results are compared. A refinement of this method is also presented when, in very-diluted regions, Redlich–Kister lines deviate from experimental points more than their standard uncertainties. The procedure of uncertainty calculation is based on the Guide to the Expression of Uncertainty in Measurements (GUM).

1. Introduction

Reporting measurement uncertainty is fundamental in engineering and experimental sciences, principally when a measurement is intended to demonstrate an aspect of a scientific theory, or an innovative or improved method of measurement. The detection, description and analysis of errors are also goals to be achieved with the uncertainty evaluation. In addition, in some cases a preliminary uncertainty propagation analysis permits to identify the most significant contributions to the combined uncertainty of a property under measurement. From the anticipation of those contributions, we can gather important information on how the experiments might be developed or improved. The uncertainty associated with a result is also a measure of the degree to which that value is expected to agree with similar experimental determinations and is becoming a formal requirement for authors to report their measurements in some well-reputed journals. Hence, authors are coming under increasing pressure to report uncertainties as a means to demonstrate the quality of their results.

In the last decades limiting partial molar values of different thermodynamic properties such as volume, isobaric expansion, isentropic compression and isobaric heat capacity have been obtained and tabulated. The efforts of many authors in estimating those properties for homologous series of compounds and for compounds differing in polar head groups and branching [1–6] aim at a better understanding of solute–solvent interactions on the one hand, and at the application of group contribution methods on the other hand [7–11]. The latter purpose permits to predict values for further compounds using the convenient additive feature of these properties.

Two methods have been identified in the literature as preferentially used to reach the aforementioned goals. One of them, the classical method, applied to the very-diluted composition range is based on the extrapolation to infinite dilution of apparent molar values of the property of interest and the other makes use of model fitting coefficients, conveniently applied to the respective excess molar property, over the whole composition range, as is the case of the well-known Redlich–Kister (R–K) method in either of its two faces [12].

The calculation procedure to obtain uncertainties associated with limiting partial molar properties derived by the classical method is well established being mostly based on the standard uncertainty associated with the intercept which is statistically obtained from polynomial least-squares fitting of apparent molar properties as a function of molality [13–15]. Conversely some authors, including our group, have been using R–K expansions to obtain limiting partial molar values without presenting a clear explanation of the uncertainty claimed, either in implicit or in explicit form [16–19]. In this work we illustrate for the first time a reliable method of evaluating these standard uncertainties based on the standard uncertainties of the fitted R–K coefficients. This procedure brings out the possibility of data comparison and further adequate use on group contribution schemes. The formalism and methods applied were those outlined in the Guide to the Expression

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of Uncertainty in Measurements (GUM) [20] which is being adopted by worldwide organizations, representing a diversity of disciplines including chemical and chemical engineering sciences. Despite its prominence in all fields of measurements it is still largely ignored amongst researchers.

The main goal to be achieved in this article is then to ascertain uncertainties to limiting partial molar properties in order to allow comparison of values obtained by different authors. Otherwise these comparisons could not be done since the number of significant digits presented in most of the reports does not seem to be realistic.

2. Basics on uncertainty application according to GUM

The property of interest is modeled by a functional relationship between experimental measured quantities $x = \{x_i\}$ (input variables) and the measured result Y (output variable or measurand Y),

$$Y = f(x_i) \tag{1}$$

The combined standard uncertainty, $u(Y)$, can be obtained from the square root of its variance, $u^2(Y)$, expressed by Eq. (2),

$$u^2(Y) = \sum_{i=1}^{n}\sum_{j=1}^{n} \frac{\partial f}{\partial x_i}\frac{\partial f}{\partial x_j} u(x_i, x_j) = \sum_{i=1}^{n}\sum_{j=1}^{n} u(y_i, y_j) \tag{2}$$

where $(\partial f/\partial x_i)$ stands for $(\partial f/\partial x_i)_{x_k \neq x_i}$ and is designated sensivity coefficient; $u(x_i, x_j)$ is the covariance of $x_i\,x_j$ and $u(x_i, x_i) = u^2(x_i)$ or $u(x_j, x_j) = u^2(x_j)$ is the variance of x_i or x_j, respectively.

Thus for the input quantities the square of the standard uncertainty associated with the output estimate Y is given by Eq. (3)

$$u_i^2(y_i) = \left(\frac{\partial f}{\partial x_i}\right)^2 u^2(x_i) \tag{3}$$

and the covariance associated with the output estimate Y is represented by Eq. (4).

$$u_i(y_i)u_j(y_j) = \left(\frac{\partial f}{\partial x_i}\right)\left(\frac{\partial f}{\partial x_j}\right) u_i(x_i)u_j(x_j) \tag{4}$$

In our case we will apply Eq. (2) either to physical, empirical or to semi-empirical models including least-squares fittings.

3. Method of uncertainty assessment associated with limiting partial molar properties using the Redlich–Kister fitting method applied to excess molar properties

Although the present method is valid for any extensive property we will be concentrated on volume for the sake of simplicity. Partial molar volumes at infinite dilution are frequently obtained starting from excess molar volumes, V_m^E, which can be either directly evaluated using dilution dilatometers or indirectly from density values. In both cases Redlich–Kister (R–K) fitting equations such as Eq. (5), have been used to correlate V_m^E data, over the whole composition range. In Eq. (5)

$$V_m^E = x_1 x_2 \sum_{k=0}^{n} A_k (2x_2 - 1)^k \tag{5}$$

x_i stands for the mole fraction of both components. The number of A_k parameters can be statistically optimized using the F-test or other equivalent method.

Table 1

Least squares fitting coefficients of Eq. (5), their standard uncertainties in parenthesis and standard deviations of the fits, applied to data of: Marsh and Richards [22], a_i and a'_i (cm^3 mol^{-1}); Benson and Kiyohara [23], b_i (cm^3 mol^{-1}); and Arce et al. [24], c_i (cm^3 mol^{-1}), at T = 298.15 K.

a_0	−4.2431 (0.0042)	b_0	−4.2777 (0.0024)	c_0	−4.357 (0.052)
a_1	0.9623 (0.023)	b_1	0.9719 (0.016)	c_1	1.082 (0.10)
a_2	−1.0750 (0.061)	b_2	−1.1234 (0.048)	c_2	−1.055 (0.22)
a_3	0.6717 (0.19)	b_3	0.5574 (0.15)		
a_4	−2.6166 (0.19)	b_4	−2.4295 (0.17)		
a_5	1.0160 (0.46)	b_5	1.4274 (0.39)		
a_6	4.2201 (0.16)	b_6	4.0574 (0.16)		
a_7	−3.1334 (0.33)	b_7	−3.5276 (0.30)		
σ	0.0015		0.0015		0.023
a'_0	−21.076624 (0.13)				
a'_1	−17.537149 (0.13)				
σ	2.3×10^{-5}				

Since excess apparent molar volumes, $V_{\phi,i}^E$ can be calculated from Eq. (6), then substituting

$$V_{\phi,i}^E = \frac{V_m^E}{x_i} \tag{6}$$

V_m^E in this equation by the expression given in Eq. (5) and letting x_i tend to zero, limiting excess partial molar volumes, $V_i^{E,\infty}$, can be expressed in terms of the A_k coefficients. The resulting expressions already used by various authors [16,17,21] are given by Eqs. (7) and (8).

$$V_2^{E,\infty} = \sum_{i=\text{even}}^{k} A_i - \sum_{i=\text{odd}}^{k} A_i \tag{7}$$

$$V_1^{E,\infty} = \sum_{i=0}^{k} A_i \tag{8}$$

V_i^{∞} values can then be estimated using Eq. (9).

$$V_i^{\infty} = V_i^{E,\infty} + V_i^{*} \tag{9}$$

In order to obtain uncertainties associated with $V_i^{E,\infty}$ values obtained by means of Eqs. (7) and (8), standard uncertainties affecting A_i coefficients should be used in Eq. (2) applied to each particular case. It should be stressed that since these coefficients are not independent, all of the pair-wise covariances must be used.

To illustrate the method just described above we used sets of large number of accurate V_m^E values published by Marsh and Richards [22] and Benson and Kiyohara [23] for the system water (1) + ethanol (2). A third set of a smaller amount of data, published by Arce et al. [24] is also used to put in evidence that this method of limiting partial molar values evaluation must not be used when few experimental points are available near $x_i = 0$.

R–K parameters of Eq. (5), their standard deviation and standard deviations of the fits, derived from the data of Marsh and Richards [22], a_i, Benson and Kiyohara [23], b_i, and Arce et al. [24], c_i, are shown in Table 1.

Eqs. (7) and (8) were then used to calculate $V_i^{E,\infty}$ and the results are shown in Table 2, together with their standard uncertainties, for the three cases studied.

Table 2
Limiting partial excess molar volumes, $V_i^{\mathrm{E},\infty}$ (cm^3 mol^{-1}), and limiting partial molar volumes, V_i^{∞} (cm^3 mol^{-1}), calculated using Eqs. (7)–(9) for the system water (1) + ethanol (2) at T = 298.15 K.

Data from	$V_1^{\mathrm{E},\infty}$	$V_2^{\mathrm{E},\infty}$	V_1^{∞}	V_2^{∞}
Marsh and Richards [22] R–K 7th degree	−4.20 (0.26)	−3.23 (0.45)	13.87	55.45
Marsh and Richards [22] R–K 1st degree	–	−3.539 (3.3 × 10^{-3})	–	55.141
Benson and Kiyohara [23] R–K 7th degree	−4.34 (0.19)	−3.20 (0.32)	13.72	55.49
Arce et al. [24] R–K 2nd degree	−4.33 (0.17)	−6.49 (0.38)	13.74	52.19

Uncertainties have been calculated using Eq. (2) for the propagation of the uncertainties of the fitting parameters to the output variable. As already mentioned, since A_i coefficients are not independent, beyond the $k+1$ variances of the A_i coefficients, calculated using Eq. (3), all of the pair-wise covariances (in the number of $C_2^{k+1} = 28$ in the two first cases and $C_2^{k+1} = 3$ in the last case) have to be taken into account and calculated employing Eq. (4). V_i^{∞} values calculated by means of Eq. (9) are also shown in Table 2.

Analysis of Table 2 allows to conclude that while $V_i^{\mathrm{E},\infty}$ evaluated from the R–K coefficients using the data of Marsh and Richards [22] and Benson and Kiyohara [23] are the same within their mutual uncertainty, $V_2^{\mathrm{E},\infty}$ calculated using the data of Arce et al. [24], notwithstanding the small uncertainty quoted, presents a considerable lower value. This fact is due to the small number of points available in the water-rich region regardless the good agreement of experimental points with those of Refs. [22,23]. This evidence can be observed in Fig. 1, where we represent the experimental points of Refs. [22,24] and the respective R–K lines obtained in the water-rich region.

In fact, it can be seen that the real volumetric behaviour of the water + ethanol mixture in the displayed diluted region is ill described when few experimental data points (only two in the case of Ref. [24]) are supplied in this composition region. A similar problem has been recently highlighted by Richon and collaborators [25], while studying the binary hexamethyleneimine + water system.

A closer inspection of Fig. 1 leads us to further conclude that the R–K fitting line adjusted to data published by Marsh and Richards [22] does not fit very well the large amount of experimental points in this very-diluted region. This fact must be responsible for the apparent large uncertainty associated with $V_2^{\mathrm{E},\infty}$ shown in Table 2. In these cases it is useful to apply a R–K fitting equation of a lower degree to the experimental data points in this restricted region, thus overcoming the drawback pointed out by Richon and coworkers [25]. In fact these authors have criticized the use of R–K fitting over the entire composition range to accurately describe excess molar volumes in highly dilute aqueous amphiphile solutions. This procedure, previously adopted by our group [5,19], was then implemented using the composition range x_2 = 0–0.015. A R–K type equation of the 1st degree whose coefficients are also shown in Table 1, jointly with their standard deviation and the standard deviations of the fit, was applied to data of Ref. [22]. The resulting $V_2^{\mathrm{E},\infty}$ values and their associated uncertainties are presented in Table 2 together with the respective V_2^{∞} values. Much lower uncertainty associated with $V_2^{\mathrm{E},\infty}$ values ensuing from applying the 1st R–K degree fitting equation is noticeable. Comparing now $V_2^{\mathrm{E},\infty}$ values derived from Marsh and Richard data [22] using eight R–K parameters fitted to the entire composition range and only two, applied to the restricted composition range (x_2 up to 0.015), we can say that both values are the same within their mutual uncertainty.

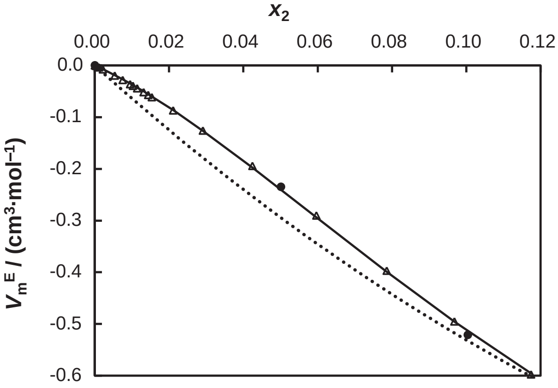

Fig. 1. Composition dependence of excess molar volume for the system water (1) + ethanol (2) at 298.15 K. △, experimental points of Ref. [22]; ●, experimental points of Ref. [24]; —, R–K line fitted to the experimental points of Ref. [22]; · · ·, R–K line fitted to the experimental points of Ref. [24].

4. Uncertainties associated with experimental excess molar volumes

In order to see how distant from the experimental values are R–K regressions of the 7th degree applied to data of Refs. [22,23], principally in the region of diluted solutions, we evaluated the error bars of the experimental points. Starting from $V_\mathrm{m}^\mathrm{E}/x_1x_2$ values of Ref. [22] the uncertainty of V_m^E values was calculated applying Eq. (2) to the propagation of the reported uncertainties (±0.2%) associated with $V_\mathrm{m}^\mathrm{E}/x_1x_2$ and with x (supported by the number of significant digits displayed over the whole composition range). The calculation procedure based on GUM is expressed by Eq. (10),

$$u^2\left[V_\mathrm{m}^\mathrm{E}\left(x, \frac{V_\mathrm{m}^\mathrm{E}}{x_1x_2}\right)\right] = \left[\frac{V_\mathrm{m}^\mathrm{E}}{x_1} + \frac{V_\mathrm{m}^\mathrm{E}}{x_2}\right]^2 u^2(x) + (x_1x_2)^2 u^2\left(\frac{V_\mathrm{m}^\mathrm{E}}{x_1x_2}\right) \quad (10)$$

The uncertainty budget for three experimental points, as examples, is shown in Table 3.

Fig. 2 shows a representation of the experimental points, the respective error bars and the R–K fitting curve at the two edges of the composition range. Thus, as anticipated, Fig. 2 shows that, while in the water-rich region the 7th degree R–K equation applied to the whole composition range does not represent the real behaviour of the mixture, it fits well the experimental points in the ethanol-rich region.

Starting now from data reported by Benson and Kiyohara [23] and since V_m^E values were calculated using Eq. (11),

$$V_\mathrm{m}^\mathrm{E} = V_\mathrm{m} - V_\mathrm{m}^\mathrm{id} = \frac{x_1M_1 + x_2M_2}{\rho} - \frac{x_1M_1}{\rho_1^*} - \frac{x_2M_2}{\rho_2^*} \quad (11)$$

where ρ is the density of the mixture, ρ_1^*, ρ_2^*, M_1 and M_2 are densities and molar masses of water and ethanol, respectively, the propagation of the reported standard uncertainties, associated with the input variables, into the output variable [Eq. (2)] is expressed by Eq. (12).

$$u^2[V_\mathrm{m}^\mathrm{E}(x,\rho)] = \left[\frac{(x_1M_1 + x_2M_2)}{\rho^2}\right]^2 u^2(\rho) + \left(\frac{x_1M_1}{\rho_1^{*2}}\right)^2 u^2(\rho_1^*)$$
$$+ \left(\frac{x_2M_2}{\rho_2^{*2}}\right)^2 u^2(\rho_2^*) + \left[\left(\frac{M_2 - M_1}{\rho}\right) + \frac{M_1}{\rho_1^*} - \frac{M_2}{\rho_2^*}\right]^2 u^2(x) \quad (12)$$

In Eq. (11) V_m and V_m^id are the real and ideal molar volumes of the mixtures at the same temperature and composition.

Table 3
Uncertainty budget for the output variable, V_m^E, as a function of the input variables x and V_m^E/x_1x_2 using the data of Marsh and Richards [22] or as a function of the input variables x, ρ, ρ_1^* and ρ_2^* using the data of Benson and Kiyhoara [23].

System water (1) + ethanol (2) at 298.15 K						
Input variables				Output variances	Total output variances	Output uncertainty
Quantity	Estimate	Standard uncertainty $u(x_i)$	Sensivity coefficient $(\partial f/\partial x_i)$	$u_i^2(y_i)$	$\sum_i u_i^2(y_i) \times 10^{12}$ (m^6 mol^{-2})	$u(Y) \times 10^6$ (cm^3 mol^{-1})
V_m^E/x_1x_2	-3.594×10^{-6}	7.2×10^{-9}	2.1×10^{-3}	2.4×10^{-22}	2.5×10^{-22}	1.6×10^{-5}
	-4.354×10^{-6}	8.7×10^{-9}	2.5×10^{-1}	4.6×10^{-18}	4.6×10^{-18}	2.1×10^{-3}
	-4.137×10^{-6}	8.3×10^{-9}	4.7×10^{-2}	1.5×10^{-19}	1.5×10^{-19}	3.9×10^{-4}
x	0.002144	1×10^{-6}	-3.6×10^{-6}	1.3×10^{-23}		
	0.44888	1×10^{-5}	-4.3×10^{-6}	1.9×10^{-21}		
	0.95066	1×10^{-5}	-4.1×10^{-6}	1.7×10^{-21}		
x	0.00478	2×10^{-5}	-1.2×10^{-5}	6.2×10^{-20}	2.0×10^{-19}	4.5×10^{-4}
	0.44899		-8.4×10^{-6}	2.8×10^{-20}	1.1×10^{-18}	1.1×10^{-3}
	0.94196		-5.2×10^{-6}	1.1×10^{-20}	4.0×10^{-18}	2.0×10^{-3}
ρ (kg m^{-3})	994.61	2×10^{-2}	1.8×10^{-8}	1.4×10^{-19}		
	870.00		4.0×10^{-8}	6.5×10^{-19}		
	792.31		7.1×10^{-8}	2.0×10^{-18}		
ρ_1^* (kg m^{-3})	997.043[a]	5×10^{-3}	1.8×10^{-8}	8.1×10^{-21}		
			1.0×10^{-8}	2.5×10^{-21}		
			1.1×10^{-9}	2.8×10^{-23}		
ρ_2^* (kg m^{-3})	784.962[b]	2×10^{-2}	3.6×10^{-10}	5.1×10^{-23}		
			3.4×10^{-8}	4.5×10^{-19}		
			7.0×10^{-8}	2.0×10^{-18}		

[a] Ref. [26].
[b] Ref. [23].

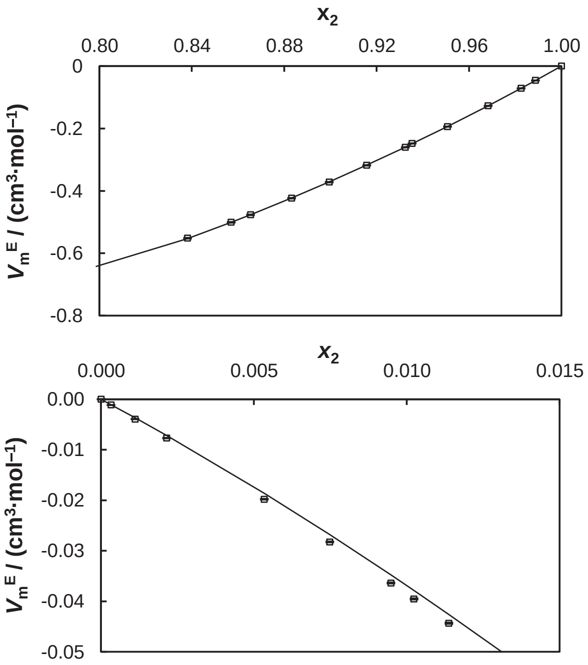

Fig. 2. Excess molar volumes for the system water (1) + ethanol (2) at 298.15 K. □, data of Ref. [22] with error bars inside. Full line stands for the R–K (7th degree) fitting curve.

Once again the uncertainty budget for three points, with compositions similar to those of the first example, was evaluated and is shown in Table 3. Graphical representations comparable to those of Fig. 2 have also been made. No display of this figure is shown since in this case equivalent features were found.

5. Summary of conclusions

A reliable method of evaluating uncertainties associated with limiting excess partial molar properties, calculated from standard deviations associated with the Redlich–Kister fitting parameters, over the entire composition range, were explicitly derived for the first time. Limiting values obtained from accurate experimental excess molar volumes for the water + ethanol mixture, together with the evaluation of the uncertainties associated with the experimental points led to the conclusion that, when in the solvent-rich regions R–K fitting lines are distant from the experimental points more than their standard uncertainties, a R–K fitting equation with a smaller number of parameters applied to the restricted diluted region only, should be used in order to obtain limiting partial molar values with a lower uncertainty. Nevertheless, it should be stressed that if the limiting values obtained by these two R–K based methods are the same within their mutual uncertainty, then it can be concluded that the number of experimental points are sufficient to reasonably describe the diluted region.

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