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Excess differential thermodynamic properties

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Abstract

A strategy is described for the systematic generation of a complete set of partial derivatives of the four energy functions from a basis set of five measured properties: V_m, S_m, $C_{p,m}$, $(\delta V_m/\delta T)_p$ and either $(\delta V_m/\delta p)_T$ or $(\delta V_m/\delta p)_S$. The same set of equations applies to both pure substances and either real or ideal mixtures.

Examples are given of some excess differential properties of binary mixtures which exhibit unusual sensitivity to changes in composition

INTRODUCTION

References to differential thermodynamic properties of pure substances and mixtures occur frequently in physical chemistry textbooks and journal articles. Typically, the student of thermodynamics is made aware of the importance of a few of these properties, notably the heat capacities, expansivities and compressibilities, and of the theorems that provide the basis for the network of mathematical relationships that exist between them.

Several elaborate schemes for using these relationships to estimate properties which are not conveniently measureable, from combinations of quantities that are, have appeared in the literature [1,2]. Such schemes tend to be unnecessarily complicated and we are of the opinion that it is possible to cover the same ground in a less cryptic fashion.

We have been particularly interested in the nature of the composition dependence of the differential properties of binary liquid mixtures. We have devised a resonably straightforward computational strategy for evaluating a wide variety of such properties from a relatively small number of measurements. It is a simple matter to extend the scheme to include the estimation of the deviations of differential properties from the values for the corresponding ideal mixtures. In this context, properties that might normally be regarded as being of purely academic interest are found to assume a useful role.

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BASIC EQUATIONS

Our primary objective has been to devise a computational procedure to obtain estimates of differential quantities of the type $(\delta X/\delta Y)_Z$, where X may be any one of the four energy functions U, H, F or G, and Y and Z are any pair of the properties p, T, V and S. There is a total of 48 such properties. The temperature and pressure derivatives are extensive properties of the system while the volume and entropy derivatives are intensive. It is a simple matter to extend our procedure to embrace all 336 properties of the type $(\delta X/\delta Y)_Z$ when X, Y and Z can be any permutation of three of the eight quantities U, H, F, G, p, T, V and S.

It is appropriate to start with the familiar basic equations for a closed system

$$\mathrm{d}U = T\,\mathrm{d}S - p\,\mathrm{d}V \tag{1}$$

$$\mathrm{d}H = T\,\mathrm{d}S + V\,\mathrm{d}p \tag{2}$$

$$\mathrm{d}F = -S\,\mathrm{d}T - p\,\mathrm{d}V \tag{3}$$

$$\mathrm{d}G = -S\,\mathrm{d}T + V\,\mathrm{d}p \tag{4}$$

It should be noted that we have chosen the symbol F to represent the Helmholtz free energy function, rather than A which is more widely used in undergraduate texts.

We have found it convenient to separate the 48 properties into four groups, one for each of the possible variables, Y. From eqns. (1)–(4), one can easily construct Tables 1–4.

TABLE 1

Temperature derivatives

$(\delta U/\delta T)_p = T(\delta S/\delta T)_p - p(\delta V/\delta T)_p$	$(\delta F/\delta T)_p = -S - p(\delta V/\delta T)_p$
$(\delta U/\delta T)_V = T(\delta S/\delta T)_V$	$(\delta F/\delta T)_V = -S$
$(\delta U/\delta T)_S = -p(\delta V/\delta T)_S$	$(\delta F/\delta T)_S = -S - p(\delta V/\delta T)_S$
$(\delta H/\delta T)_p = T(\delta S/\delta T)_p$	$(\delta G/\delta T)_p = -S$
$(\delta H/\delta T)_V = T(\delta S/\delta T)_V + V(\delta p/\delta T)_V$	$(\delta G/\delta T)_V = -S + V(\delta p/\delta T)_V$
$(\delta H/\delta T)_S = V(\delta p/\delta T)_S$	$(\delta G/\delta T)_S = -S + V(\delta p/\delta T)_S$

TABLE 2

Pressure derivatives

$(\delta U/\delta p)_T = T(\delta S/\delta p)_T - p(\delta V/\delta p)_T$	$(\delta F/\delta p)_T = -p(\delta V/\delta p)_T$
$(\delta U/\delta p)_V = T(\delta S/\delta p)_V$	$(\delta F/\delta p)_V = -S(\delta T/\delta p)_V$
$(\delta U/\delta p)_S = -p(\delta V/\delta p)_S$	$(\delta F/\delta p)_S = -S(\delta T/\delta p)_S - p(\delta V/\delta p)_S$
$(\delta H/\delta p)_T = T(\delta S/\delta p)_T + V$	$(\delta G/\delta p)_T = V$
$(\delta H/\delta p)_V = T(\delta S/\delta p)_V + V$	$(\delta G/\delta p)_V = -S(\delta T/\delta p)_V + V$
$(\delta H/\delta p)_S = V$	$(\delta G/\delta p)_S = -S(\delta T/\delta p)_S + V$

TABLE 3

Volume derivatives

$(\delta U/\delta V)_T = T(\delta S/\delta V)_T - p$	$(\delta F/\delta V)_T = -p$
$(\delta U/\delta V)_p = T(\delta S/\delta V)_p - p$	$(\delta F/\delta V)_p = -S(\delta T/\delta V)_p - p$
$(\delta U/\delta V)_S = -p$	$(\delta F/\delta V)_S = -S(\delta T/\delta V)_S - p$
$(\delta H/\delta V)_T = T(\delta S/\delta V)_T + V(\delta p/\delta V)_T$	$(\delta G/\delta V)_T = V(\delta p/\delta V)_T$
$(\delta H/\delta V)_p = T(\delta S/\delta V)_p$	$(\delta G/\delta V)_p = -S(\delta T/\delta V)_p$
$(\delta H/\delta V)_S = V(\delta p/\delta V)_S$	$(\delta G/\delta V)_S = -S(\delta T/\delta V)_S + V(\delta p/\delta V)_S$

In addition to p, T, V, and S, there are 24 partial differential quantities that appear on the right-hand sides of the equations set out in Tables 1–4. Treating p and T as controlled entities and recognizing that $(\delta X/\delta Y)_Z = (\delta Y/\delta X)_Z^{-1}$, we find ourselves dealing with a set of 14 variables. That number can be further decreased by making use of the Maxwell relationships [3]

$$(\delta V/\delta T)_S = -(\delta S/\delta p)_V \tag{5}$$

$$(\delta p/\delta T)_S = (\delta S/\delta V)_p \tag{6}$$

$$(\delta S/\delta V)_T = (\delta p/\delta T)_V \tag{7}$$

$$-(\delta S/\delta p)_V = (\delta V/\delta T)_p \tag{8}$$

A further reduction from ten to eight variables is made possible by recognizing that

$$(\delta p/\delta T)_V = -(\delta V/\delta T)_p(\delta p/\delta V)_T \tag{9}$$

and

$$(\delta p/\delta T)_S = -(\delta S/\delta T)_p(\delta p/\delta S)_T \tag{10}$$

Two of those eight variables are the volume and entropy of the system. There is some freedom of choice in selecting the other six. We have chosen to concentrate on three pairs.

$$C_p = (\delta H/\delta T)_p = T(\delta S/\delta T)_p \tag{11}$$

TABLE 4

Entropy derivatives

$(\delta U/\delta S)_T = T - p(\delta V/\delta S)_T$	$(\delta F/\delta S)_T = -p(\delta V/\delta S)_T$
$(\delta U/\delta S)_p = T - p(\delta V/\delta S)_p$	$(\delta F/\delta S)_p = -S(\delta T/\delta S)_p - p(\delta V/\delta S)_p$
$(\delta U/\delta S)_V = T$	$(\delta F/\delta S)_V = -S(\delta T/\delta S)_V$
$(\delta H/\delta S)_T = T + V(\delta p/\delta S)_T$	$(\delta G/\delta S)_T = V(\delta p/\delta S)_T$
$(\delta H/\delta S)_p = T$	$(\delta G/\delta S)_p = -S(\delta T/\delta S)_p$
$(\delta H/\delta S)_V = T + V(\delta p/\delta S)_V$	$(\delta G/\delta S)_V = -S(\delta T/\delta S)_V + V(\delta p/\delta S)_V$

and

$$C_V = (\delta U/\delta T)_V = T(\delta S/\delta T)_V \tag{12}$$

where C_p and C_V are respectively the isobaric and isochoric (isometric) heat capacities of the system.

$$A_p = (\delta V/\delta T)_p \tag{13}$$

and

$$A_S = (\delta V/\delta T)_S = -(\delta S/\delta p)_V \tag{14}$$

$$K_T = -(\delta V/\delta p)_T \tag{15}$$

and

$$K_S = -(\delta V/\delta p)_S \tag{16}$$

A_p and A_S are extensive properties that are related to the isobaric and isentropic expansivities of the system. K_T and K_S are related to the isothermal and isentropic compressibilities. For condensed phase samples, C_p is more easily measured than C_V. Estimates of the molar quantity $A_{p,\mathrm{m}}$ can be derived from measurements of density at several different temperatures. Of the two quantities K_T and K_S, it is found that it is more convenient, for liquid samples, to determine K_S from ultrasonic speed measurements than to try to measure K_T directly.

Each of the three pairs of properties listed above are related by well-established equations

$$K_T = K_S + TA_p^2/C_p \tag{17}$$

$$C_V = C_p - TA_p^2/K_T \tag{18}$$

$$A_S = A_p - K_T C_p/TA_p \tag{19}$$

It is thus possible to express all of the 48 partial derivates of Tables 1–4 in terms of a basis set of five measurable molar quantities: V_m, S_m, $C_{p,\mathrm{m}}$, $A_{p,\mathrm{m}}$ and either $K_{S,\mathrm{m}}$ or $K_{T,\mathrm{m}}$. Bearing in mind that our objective has been to devise a computational scheme for generating estimates of those differential properties from experimental information, we have found it simpler to write expressions in terms of V, S, C_p and C_V, A_p and A_S and K_T and K_S, after having made use of eqns. (17)–(19). Such expressions are set out in Tables 5–8.

TABLE 5

Temperature derivatives

$(\delta U/\delta T)_p = C_p - pA_p$	$(\delta F/\delta T)_p = -S - pA_p$
$(\delta U/\delta T)_V = C_V$	$(\delta F/\delta T)_V = -S$
$(\delta U/\delta T)_S = -pA_S$	$(\delta F/\delta T)_S = -S - pA_S$
$(\delta H/\delta T)_p = C_p$	$(\delta G/\delta T)_p = -S$
$(\delta H/\delta T)_V = C_V + VA_p/K_T$	$(\delta G/\delta T)_V = -S + VA_p/K_T$
$(\delta H/\delta T)_S = VC_p/TA_p$	$(\delta G/\delta T)_S = -S + VC_p/TA_p$

TABLE 6

Pressure derivatives

$(\delta U/\delta p)_T = -TA_p + pK_T$	$(\delta F/\delta p)_T = pK_T$
$(\delta U/\delta p)_V = -TA_S$	$(\delta F/\delta p)_V = -SK_T/A_p$
$(\delta U/\delta p)_S = pK_S$	$(\delta F/\delta p)_S = -TSA_p/C_p + pK_S$
$(\delta H/\delta p)_T = -TA_p + V$	$(\delta G/\delta p)_T = V$
$(\delta H/\delta p)_V = -TA_S + V$	$(\delta G/\delta p)_V = -SK_T/A_p + V$
$(\delta H/\delta p)_S = V$	$(\delta G/\delta p)_S = -TSA_p/C_p + V$

TABLE 7

Volume derivatives

$(\delta U/\delta V)_T = TA_p/K_T - p$	$(\delta F/\delta V)_T = -p$
$(\delta U/\delta V)_p = C_p/A_p - p$	$(\delta F/\delta V)_p = -S/A_p - p$
$(\delta U/\delta V)_S = -p$	$(\delta F/\delta V)_S = -S/A_S - p$
$(\delta H/\delta V)_T = TA_p/K_T - V/K_T$	$(\delta G/\delta V)_T = -V/K_T$
$(\delta H/\delta V)_p = C_p/A_p$	$(\delta G/\delta V)_p = -S/A_p$
$(\delta H/\delta V)_S = -V/K_S$	$(\delta G/\delta V)_S = -S/A_S - V/K_S$

TABLE 8

Entropy derivatives

$(\delta U/\delta S)_T = T - pK_T/A_p$	$(\delta F/\delta S)_T = -pK_T/A_p$
$(\delta U/\delta S)_p = T - pTA_p/C_p$	$(\delta F/\delta S)_p = -TS/C_p - pTA_p/C_p$
$(\delta U/\delta S)_V = T$	$(\delta F/\delta S)_V = -TS/C_V$
$(\delta H/\delta S)_T = T - V/A_p$	$(\delta G/\delta S)_T = -V/A_p$
$(\delta H/\delta S)_p = T$	$(\delta G/\delta S)_p = -TS/C_p$
$(\delta H/\delta S)_V = T - V/A_S$	$(\delta G/\delta S)_V = -TS/C_V - V/A_S$

The expressions contained in Tables 5–8, taken in conjunction with eqns. (17)–(19), can be used to calculate all 48 differential properties from five measured quantities. These equations apply not only to pure substances but also to mixtures of a specific composition. In the case of mixtures, the same equations also serve to furnish estimates of the differential thermodynamic properties of "ideal" mixtures.

The equation that defines an ideal mixture, in the Raoult's law context of that term, of two liquid components is

$$G_{\mathrm{m}}^{\mathrm{id}} = X_{\mathrm{A}}\left(G_{\mathrm{A}}^{\ominus} + RT \ln X_{\mathrm{A}}\right) + X_{\mathrm{B}}\left(G_{\mathrm{B}}^{\ominus} + RT \ln X_{\mathrm{B}}\right) \tag{20}$$

where $G_{\mathrm{A}}^{\ominus}$ and $G_{\mathrm{B}}^{\ominus}$ are the chemical potentials of the pure components A and B, and X_{A} and X_{B} are the corresponding mole fractions. The mixing process is assumed to take place under isothermal and isobaric constraints.

From eqn. (20), one derives

$$S_{\mathrm{m}}^{\mathrm{id}} = X_{\mathrm{A}}\left(S_{\mathrm{A}}^{\ominus} - R \ln X_{\mathrm{A}}\right) + X_{\mathrm{B}}\left(S_{\mathrm{B}}^{\ominus} - R \ln X_{\mathrm{B}}\right) \tag{21}$$

and

$$V_{\mathrm{m}}^{\mathrm{id}} = X_{\mathrm{A}} V_{\mathrm{A}}^{\ominus} + X_{\mathrm{B}}^{\ominus} V_{\mathrm{B}}^{\ominus} \tag{22}$$

Further

$$C_{p,\mathrm{m}}^{\mathrm{id}} = X_{\mathrm{A}} C_{p,\mathrm{A}}^{\ominus} + X_{\mathrm{B}} C_{p,\mathrm{B}}^{\ominus} \tag{23}$$

$$A_{p,\mathrm{m}}^{\mathrm{id}} = X_{\mathrm{A}} A_{p,\mathrm{A}}^{\ominus} + X_{\mathrm{B}} A_{p,\mathrm{B}}^{\ominus} \tag{24}$$

$$K_{T,m}^{\mathrm{id}} = X_{\mathrm{A}} K_{T,\mathrm{A}}^{\ominus} + X_{\mathrm{B}} K_{T,\mathrm{B}}^{\ominus} \tag{25}$$

$C_{V,\mathrm{m}}^{\mathrm{id}}$, $A_{S,\mathrm{m}}^{\mathrm{id}}$ and $K_{S,\mathrm{m}}^{\mathrm{id}}$ are not mole-fraction-weighted adducts of the corresponding properties of the pure components but can be derived using eqns. (17)–(19). Ideal differential properties, $(\delta X/\delta Y)_Z^{\mathrm{id}}$, can then be determined using the equations set out in Tables 5–8.

For the extensive properties, one defines the excess molar quantities by

$$Q^{\mathrm{E}} = Q_{\mathrm{m}} - Q_{\mathrm{m}}^{\mathrm{id}} \tag{26}$$

For intensive properties, the departures (or deviations) from ideality should be referred to as such rather than as excess quantities.

In the study of binary mixtures, there is a considerable interest in the nature of the composition dependence of their thermodynamic properties. It has been observed that precipitous changes in the mole fraction derivatives, $\mathrm{d}Q^{\mathrm{E}}/\mathrm{d}X_{\mathrm{A}}$, result from and are indicators of significant variations in their patterns of molecular aggregation.

We have found that several of the excess differential properties of binary aqueous systems exhibit very interesting patterns of composition dependence. We have chosen to show some of those properties for the three systems $\mathrm{MeOH} + \mathrm{H_2O}$, $\mathrm{EtOH} + \mathrm{H_2O}$ and $1 - \mathrm{PrOH} + \mathrm{H_2O}$. We have limited ourselves to those properties that can be determined from experimental values of V_{m}, $C_{p,\mathrm{m}}$, $A_{p,\mathrm{m}}$ and $K_{S,\mathrm{m}}$, in view of the paucity of suitable entropy data.

The molar volumes, isobaric heat capacities, and $A_{p,\mathrm{m}}$ values are taken from the work of Benson and coworkers [4,5]. The $K_{S,\mathrm{m}}$ values for MeOH + water were taken from ref. 6, while those for the other two systems were taken from ref. 7.

Table 9 lists the experimental values for the pure substances at 25 ° C and 1 atm. pressure. Table 10 gives the values derived for $C_{V,\mathrm{m}}$, $A_{S,\mathrm{m}}$ and $K_{T,\mathrm{m}}$.

We note that there are relatively small differences between the respective $C_{p,\mathrm{m}}$ and $C_{V,\mathrm{m}}$ values of the four substances. The same is true of the differences between the $K_{S,m}$ and $K_{T,m}$ values. However, there are very substantial differences between the $A_{p,\mathrm{m}}$ and $A_{S,\mathrm{m}}$ values.

TABLE 9

Experimental values for selected properties of water, methanol, ethanol and 1-propanol

	H_2O	MeOH	EtOH	1-PrOH
V_m (cm^3 mol^{-1})	18.069	40.75	58.68	75.18
S_m (J K^{-1} mol^{-1})	69.91	126.8	160.7	192.9
$C_{p,m}$ (J K^{-1} mol^{-1})	75.29	81.21	112.6	144.1
$A_{p,m}$ (mm^3 K^{-1} mol^{-1})	4.65	48.94	63.73	75.41
$K_{S,m}$ (mm^3 MPa^{-1} mol^{-1})	8.09	43.02	57.40	64.76

TABLE 10

Derived values of $C_{V,m}$, $A_{S,m}$ and $K_{T,m}$ for water, methanol, ethanol and 1-propanol

	H_2O	MeOH	EtOH	1-PrOH
$C_{V,m}$ (J K^{-1} mol^{-1})	74.50	67.43	94.87	121.94
$A_{S,m}$ (mm^3 K^{-1} mol^{-1})	−439.6	−239.4	−340.3	−415.1
$K_{T,m}$ (mm^3 MPa^{-1} mol^{-1})	8.17	51.81	68.15	76.53

TABLE 11

Estimates of selected differential thermodynamic properties

	H_2O	MeOH	EtOH	1-PrOH
$(\delta H/\delta T)_{V,m}$ (J K^{-1} mol^{-1})	84.77	105.9	149.8	196.0
$(\delta H/\delta T)_{S,m}$	981.9	226.8	347.9	481.8
$(\delta H/\delta p)_{T,m}$ (cm^3 mol^{-1})	16.68	26.16	39.68	52.70
$(\delta U/\delta V)_T$ (MPa)	169.5	281.6	278.8	293.8
$(\delta U/\delta V)_p$	−16202	−1659	−1767	−1911
$(\delta H/\delta V)_T$	−2041	−505	−582	−689
$(\delta U/\delta S_T$ (+298.15 K)	−0.1759	−0.1059	−0.1069	−0.1015
$(\delta U/\delta S)_p$ (+298.15 K)	−0.0018	−0.0180	−0.0169	−0.0156
$(\delta H/\delta S)_T$ (K)	−3590	−535	−623	−699
$(\delta H/\delta S)_V$ (K)	339	468	470	479

In Table 11, we have set out a number of values that we have estimated for other differential properties.

As we stated at the outset, our original interest in obtaining estimates of the differential thermodynamic properties stemmed from a desire to find those which, for binary systems, exhibit particularly interesting, and hopefully informative, patterns of composition dependence.

Among the extensive properties, those which appear to be the most interesting are the excess isentropic properties, $(\delta U/\delta T)_S$ and $(\delta H/\delta T)_S$. Plots of those properties for the three alkanol + water system are shown in Figs. 1 and 2 respectively. Similar plots have been published for some alkoxyethanol + water systems [8] and also for the ethylene glycol + water

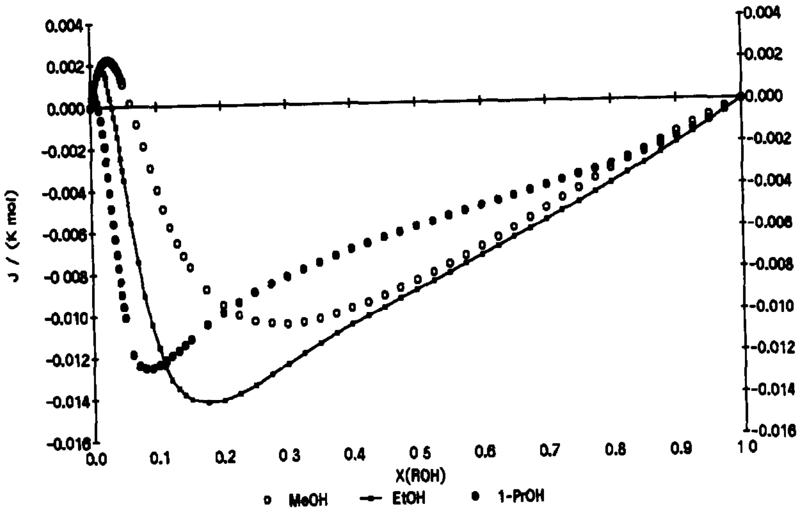

Fig. 1 Excess molar $(\delta U/\delta T)_S$ for some alkanol + water systems at 25 °C (J K^{-1} mol^{-1}).

system [9]. One notes that the curves for the three alkanol + water systems in each of the two figures have several features in common; there are some obvious trends associated with increasing alkyl chain length. It is our contention that in an aqueous environment all amphiphilic species tend to possess, to varying extents, patterns of molecular aggregation that are labile analogs of those identified in detergent + water systems. We have attempted to justify our approach in an earlier publication [10]. It is argued that the changes in the patterns of hydrophobic aggregation that result from changes

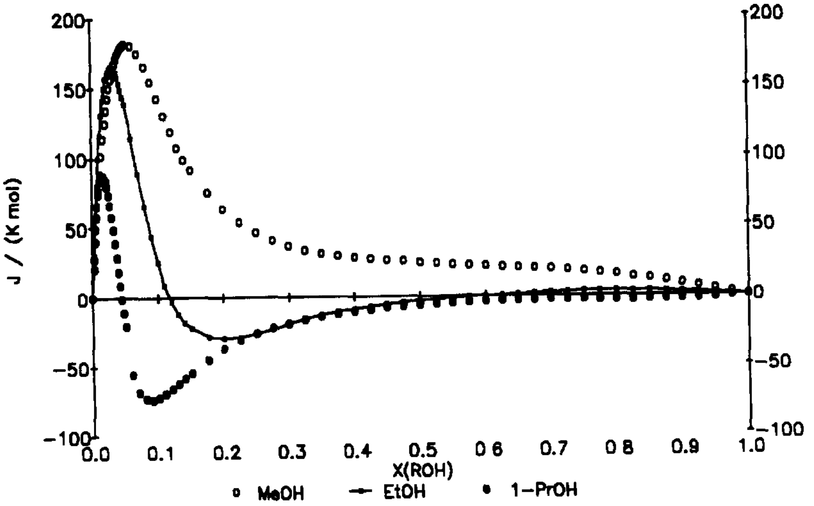

Fig. 2 Excess molar $(\delta H/\delta T)_S$ for some alkanol + water systems at 25 °C (J K^{-1} mol^{-1}).

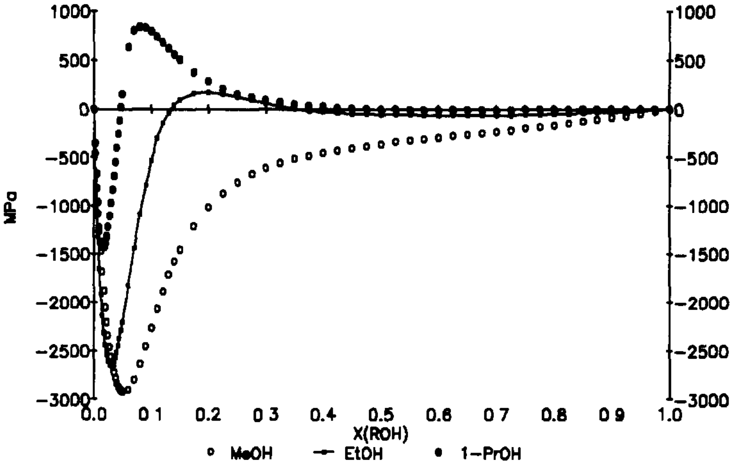

Fig 3. Deviations of $(\delta U/\delta V)_p$ from ideality for some alkanol + water systems at 25 °C

in composition are reflected by the manner in which the macroscopic properties vary.

One way of examining the composition dependence of the macroscopic properties is to generate curves which can be subjected to visual scrutiny. The raw data curves frequently appear to have no obviously dramatic features. There exist, however, several data-reduction procedures which have the merit of enhancing the visual impact of interesting types of composition sensitivity. These include calculations of apparent molar, or excess molar, properties, the reduced excess molar properties, $Q^E/(X_A(1-X_A))$, partial molar properties and the derivatives, dQ^E/dX_A. The differential thermodynamic properties appear to make a useful addition to that list.

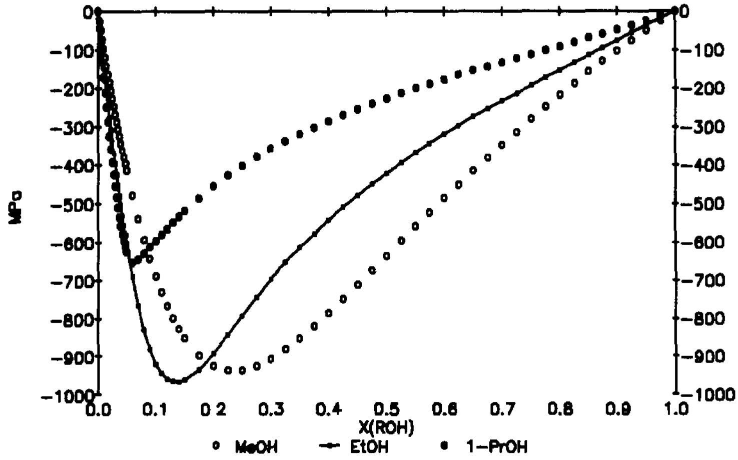

Fig 4 Deviations of $(\delta H/\delta V)_S$ from ideality for some alkanol + water systems at 25 °C.

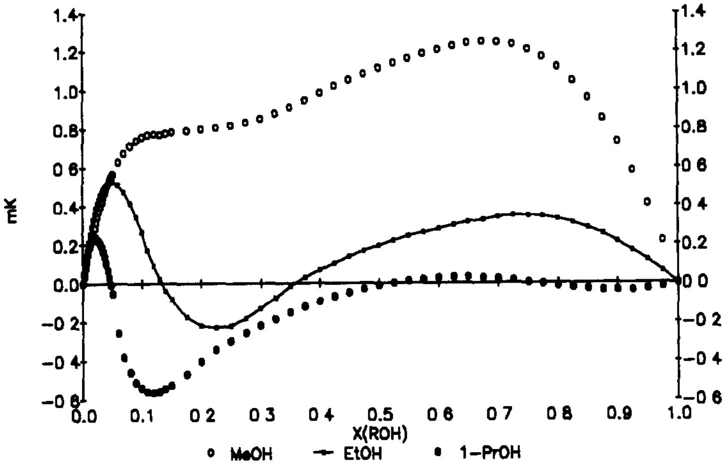

Fig 5 Deviations of $(\delta U/\delta S)_p$ from ideality for some alkanol + water systems at 25 °C.

The alternative is to devise analytic models which serve the dual purpose of fitting the data and, from the values of their optimized parameters, furnish indications of the nature of the system under investigation.

For the intensive properties, the differences between the estimates derived from an experimental data base and those calculated for an ideal system are referred to as deviations from ideality, as opposed to excess quantities.

Among the more interesting of the sets of these "deviation" curves, for the alkanol + water systems, are $(\delta U/\delta V)_p^{\mathrm{D}}$ (Fig. 3), $(\delta H/\delta V)_S^{\mathrm{D}}$ (Fig. 4) and $(\delta U/\delta S)_p^{\mathrm{D}}$ (Fig. 5).

SUMMARY

In this article, we have described a systematic strategy for estimating a wide variety of differential thermodynamic properties of pure or mixed systems from a relatively limited experimental data base. It should be pointed out that while this strategy involves relationships that are clearly set out in many textbooks, we know of no treatment that has addressed the issue of identifying the experimental basis for total thermodynamic characterization.

The principal utility of our strategy is, in our view, the provision of a means of obtaining sensitive empirical indicators of the existence of significant shifts in the composition dependence of the molecular-scale aggregative characteristics of binary mixtures.

We note, in passing, that it is an interesting exercise to generate the equations of Tables 5–8 for an ideal gas sample. In that case, the number of experimental entities that appear on the right-hand sides is reduced to just S_{m} and $C_{p,\mathrm{m}}$. Integration of those equations provides us with expressions for changes in the thermodynamic properties under the conditions of constant T, p, V and S. The same type of treatment could be applied to other equations of state.

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REFERENCES AND NOTES

1 E.A. Coomes, in R.C Weast (Ed), Handbook of Chemistry and Physics, 51st edn., Chemical Rubber Company, 1970 p. D-80

2 G.A. Estevez, K. Yang and B.B. Dasgupta, J Chem Educ., 60 (1989) 890.

3 The theorems of differential calculus that provide us with eqn. (5)–(10) and (17)–(19) are presented, usually without proof, in most undergraduate physical chemistry texts

4 G.C Benson and O Kiyohara, J Solution Chem , 9 (1980) 791

5 G.C Benson, P.J. D'Arcy and O. Kiyohara, J. Solution Chem., 9 (1980) 931

6 G. Douhéret, A. Khadir and A. Pal, Thermochim Acta, 142 (1989) 219

7 O. Kiyohara and G C. Benson, J Solution Chem., 10 (1981) 281

8 G. Douhéret, A. Pal and M.I Davis, J. Chem Soc Faraday Trans. I., 85 (1989) 2723

9 G. Douhéret, A Pal, H Hoiland, O. Anowi and M.I Davis, J Chem. Thermodyn., 23 (1991) 569

10 M.I Davis and G. Douhéret, Thermochim. Acta, 188 (1991) 229