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THERMODYNAMICS OF SOLUTIONS: SELECTED ASPECTS *

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ABSTRACT

This article reviews recent advances in the thermodynamics of (dilute) non-electrolyte solutions. The focus is on high-precision experimental techniques. Some of the problems encountered in data reduction and data correlation are discussed.

“Der einzige sichere Führer auf dem Weg der weiteren Entwicklung bleibt stets die Messung...”
Max Planck (1926), *Physikalische Gesetzlichkeit.*

INTRODUCTION

The large number of articles containing experimental data on thermodynamic properties of pure fluids and fluid mixtures, as well as new experimental techniques and the concurrent significant advances in theory, demonstrate the unabated, rapid growth of this field [1–21]. Given the variety of topics and the unavoidable limits imposed by a conference presentation, this review cannot be exhaustive. In fact, it is very limited in scope, being focussed essentially on only two topics, both of which reflect to a large extent the author's current research interests: dilute solutions of non-electrolytes and liquid mixtures containing a strongly polar component. The author apologises for the omission of many other equally important and active areas.

THE THERMODYNAMICS OF SOLUTIONS, ESPECIALLY DILUTE SOLUTIONS

Current interest in solution thermodynamics is closely linked to: (a) advances in the theory of liquids in general; (b) advances in the design of

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measuring equipment; and (c) important practical applications in surprisingly diverse areas. In theory, solution properties may be accounted for in terms of solvent–solvent, solvent–solute and solute–solute interactions. Experimentally, this separation corresponds to the study of the pure components, and to the determination of any given quantity from the high-dilution region to the composition of interest. At high dilution, solute–solute effects are essentially absent. Thus, the infinite dilution limit allows the testing of theories tailored for the description of solvation effects, whereas finite concentration properties supply information relevant to the discussion of solute–solute interaction due to pairs, triplets, and so forth. When aqueous solutions of non-electrolytes are involved, the terms hydrophobic hydration and hydrophobic interaction are in general use [22,23]. As far as practical applications are concerned, data on dilute solutions are frequently needed in biomedical technology, environmental pollution control, geochemistry and chemical process design. The last of these fields includes such important areas as coal gasification, enhanced oil recovery, natural-gas and synthetic-gas purification (gas sweetening), custody transfer of chemicals, such as slightly impure carbon dioxide or ethylene (which takes place at conditions near the respective critical points), sludge oxidation, waste water treatment and so forth. The properties of dilute solutions, with emphasis on interdisciplinary aspects, will undoubtedly continue to attract pure and applied research for many years to come.

What then are the quantities of interest to be determined by experiment, i.e. by vapour–liquid equilibrium (VLE) measurements, calorimetry and densimetry/dilatometry? A vapour–liquid equilibrium is characterised by the equality of the component fugacities in both phases. For a binary solution, to which we shall now confine our attention,

$$f_i^{\mathrm{V}}(T, P, y_i) = f_i^{\mathrm{L}}(T, P, x_i) \qquad i = 1, 2 \tag{1}$$

Two *entirely equivalent* formal procedures are commonly used to establish the link with experiment: the (ϕ, ϕ) method and the (ϕ, γ) method. The decision as to which approach should be preferred for solving actual problems, though by and large a matter of taste, is subject to important practical constraints [2,9,11,13,15,16]. High-pressure vapour–liquid equilibria are conveniently treated in terms of the (ϕ, ϕ) approach, because the use of a single equation of state (EOS) valid for *both* phases has some computational advantage. At low to moderate pressures, thermodynamic analysis (data reduction and VLE calculations) is preferably based upon the (ϕ, γ) formalism. Here, an EOS is required for the low-density vapour phase only, whereas for the liquid phase, a suitable activity coefficient model is introduced.

When adopting the (ϕ, γ) method, in particular when dealing with a supercritical solute 2, determination of the Henry fugacity $H_{2,1}(T, P_{\mathrm{s},1})$ is of central importance. This quantity is rigorously accessible from isothermal

VLE measurements according to

$$H_{2,1}(T,\ P_{s,1}) = \lim_{x_2\to 0}\left(f_2^{L}/x_2\right) = \lim_{\substack{x_2\to 0\\ y_2\to 0}}\left(\phi_2^{V} y_2 P/x_2\right) \qquad (2)$$

or equivalently by

$$H_{2,1}(T,\ P_{s,1}) = \left(\mathrm{d}f_2^{L}/\mathrm{d}x_2\right)_{x_2=0} = \phi_2^{V\infty}(T,\ P_{s,1})P_{s,1}\left(\mathrm{d}y_2/\mathrm{d}x_2\right)_{x_2=0} \qquad (3)$$

At the same temperature and at the vapour pressure $P_{s,1}$ of the solvent 1, the corresponding liquid-phase constant-pressure activity coefficients (unsymmetric convention), $\gamma_2' \equiv f_2^{L}/x_2 H_{2,1}$, are then obtained via

$$\ln \gamma_2'(T,\ P_{s,1},\ x_2) = \ln\left(\frac{\phi_2^{V}(T,\ P,\ y_2)y_2 P}{x_2 H_{2,1}(T,\ P_{s,1})}\right) - \int_{P_{s,1}}^{P} \frac{V_2^{L}(T,\ P,\ x_2)}{RT}\,\mathrm{d}P \qquad (4)$$

This sequential approach is most frequently used in data reduction. It simply reflects the focussing of interest on the solute in a composition range very close to the pure solvent. Relations to quantities based on the symmetric convention, that is on the Lewis–Randall rule, are readily established [9,11,16,19,20]. For example, at constant temperature and pressure, the activity coefficient $\gamma_2 \equiv f_2^{L}/x_2 f_2^{L\star}$ is related to γ_2' through

$$\gamma_2 = \gamma_2' \gamma_2^{\infty} \qquad (5)$$

$$\gamma_2^{\infty} = H_{2,1}/f_2^{L\star} \qquad (6)$$

and the corresponding excess molar Gibbs energies obey

$$(G^{E} - G^{E\prime})/RT = x_2 \ln \gamma_2^{\infty} \qquad (7)$$

The ideal-solution models based on Henry's Law and on the Lewis–Randall rule are illustrated in Fig. 1.

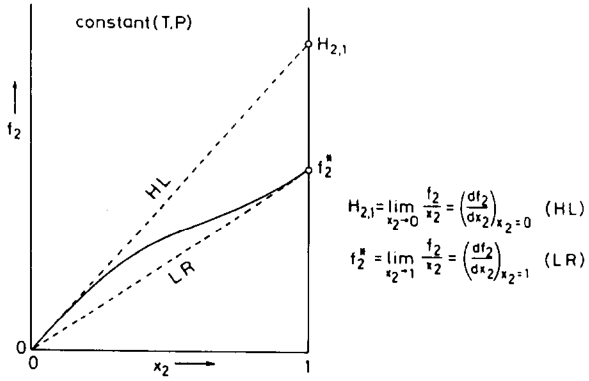

Fig. 1. Composition dependence of component fugacity f_2 in a binary solution at constant T and P. $f_2^{\star}$ is the fugacity of pure component 2 and $H_{2,1}$ is the Henry fugacity. The dashed lines represent the Lewis–Randall rule (LR) and Henry's Law (HL), respectively.

For a supercritical solute, there is no experimental value for the pure-substance liquid-state fugacity, $f_2^{L\star}$. One may, however, obtain the fugacity in a pure hypothetical liquid (h.l.) state through essentially arbitrary processes, each giving a different set of symmetrically normalised activity coefficients that satisfy, of course, the defining relation

$$\gamma_2 f_2^{L(h.l.)\star} \equiv f_2^L/x_2 \tag{8}$$

While perhaps not particularly attractive from the fundamental point of view of molecular theory, the latter approach has had some fair success in practical applications.

The connection with the EOS formalism is illustrated by the following eminently useful relations [9,11,16,19,20]. From the general definition of the fugacity coefficient of component i in, say, a liquid solution

$$\phi_2^L(T, P, x_2) \equiv f_2^L(T, P, x_2)/x_2 P \tag{9}$$

and the defining relation, eqn. (2), the rigorous expression

$$\phi_2^{L\infty} \equiv \lim_{x_2 \to 0} \phi_2^L(T, P, x_2) = H_{2,1}(T, P)/P \tag{10}$$

is obtained. In addition

$$\gamma_2 = \phi_2^L/\phi_2^{L\star} \tag{11}$$

$$\gamma_2' = \phi_2^L/\phi_2^{L\infty} \tag{12}$$

and

$$\gamma_2^\infty = \gamma_2/\gamma_2' = \phi_2^{L\infty}/\phi_2^{L\star} \tag{13}$$

Vapour–liquid equilibria at elevated pressures are often discussed in terms of K values defined by

$$K_i \equiv y_i/x_i \tag{14}$$

which may thus be expressed as

$$K_i = \phi_i^L/\phi_i^V = \gamma_i f_i^{L\star}/\phi_i^v P \tag{15}$$

$$= \gamma_i' H_{i,j}/\phi_i^V P \tag{16}$$

Fugacity coefficients may be calculated from any suitable EOS. If a pressure-explicit EOS is used, at constant temperature and composition

$$\ln \phi_i = \int_0^\rho \left[\left(\frac{\partial(nZ)}{\partial n_i} \right)_{T,\rho/n,n_j} - 1 \right] \rho^{-1}\, d\rho - \ln Z \tag{17}$$

where $\rho \equiv V^{-1}$ is the molar density of the mixture.

Both the temperature and pressure dependences of the quantities introduced above are readily calculated [2,9–11,16,19,20]. For example, for the

Henry fugacity

$$(\partial \ln H_{2,1}/\partial T)_P = -\Delta H_2^{\infty}/RT^2 \tag{18}$$

$$(\partial \ln H_{2,1}/\partial P)_T = V_2^{L\infty}/RT \tag{19}$$

and

$$(\partial \, \Delta \, H_2^{\infty}/\partial T)_P = \Delta C_{p,2}^{\infty} \tag{20}$$

Equations (18) and (20) form the basis for comparison of calorimetrically determined enthalpy and heat capacity changes on solution with results obtained from van't Hoff analysis of high-precision VLE data of dilute solutions. A few selected recent experimental contributions to this field will be presented, in the briefest of terms, in the next section.

The effect of pressure on the Henry fugacity is rigorously given by eqn. (19). However, simplistic application, in the form of the Krichevsky–Kasarnovsky equation, for the extraction of infinite-dilution partial molar volumes, $V_2^{L\infty}$, from high-pressure gas-solubility data may yield unreliable results [2,11,13,24,25]. In such systems, the Poynting correction and the 'composition effect' embodied in the activity coefficient frequently cancel each other to a significant extent [26,27]. The preferred experimental method for determining $V_2^{L\infty}$ (and V_2^{L}) is either dilatometry [28,29] or densimetry [30–32] at very small mole fractions.

EXPERIMENTAL: DILUTE SOLUTIONS

During the last decade, advances in the design of measuring equipment, primarily dedicated to dilute solutions, have been quite impressive. Several specialised reviews devoted to VLE, PvT measurements and calorimetry have been published (see the Introduction). In this section, only a few representative apparatuses and some corresponding problems encountered in data reduction and presentation will be discussed.

Synthetic as well as analytical methods have been reported for VLE measurements. With adequate design and proper handling, both techniques are capable of yielding precise data. The synthetic method is illustrated by the automated instruments constructed by Tucker et al. [33,34] and Tominaga et al. [35]. An analytical method for VLE measurements on highly dilute solutions of gases in liquids has been developed by Rettich, Battino and Wilhelm (RBW) [36–38]. It is based on the earlier work of Benson et al. [39,40]. Vapour-phase and liquid-phase equilibrium compositions are determined via classical PvT measurements, and Henry fugacities $H_{2,1}(T, P_{s,1})$ are obtained according to the rigorous prescription in eqn. (2). The essential parts of the apparatus are shown in the flow diagram in Fig. 2. The imprecision of the RBW technique is usually about ±0.05%. The method is thus superior to any other used for gas solubilities.

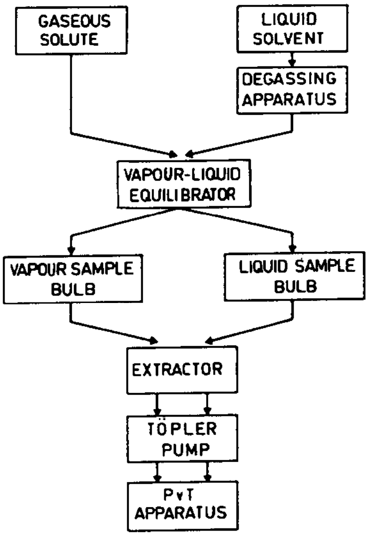

Fig. 2. Block diagram of the experimental arrangement used in the RBW high-precision gas-solubility apparatus [36–38].

The practical implementation of the thermodynamically rigorous relations in eqns. (2), (3) and (4) hinges on the availability of some auxiliary information. Specifically, a vapour-phase EOS is needed for the evaluation of the fugacity coefficients (frequently, the virial equation of state is convenient), and $V_2^L(T, P, x_2)$ at high dilution is needed to account for the influence of pressure on the liquid-phase fugacity. If no experimental results are available, one has to rely upon semi-empirical estimation methods, such as the Tsonopoulos correlation for the second virial coefficients [41], and scaled-particle theory [42] or the Handa–Benson method [43] for the partial molar volume of solute at infinite dilution.

Once experimental Henry fugacities for a given solute–solvent system are collected over a certain temperature range, the question arises as to their most satisfactory mathematical representation as a function of temperature (Fig. 3). In the absence of theoretically well-founded models of general validity, essentially empirical relations are used [36–40,44–47], subject, however, to some important thermodynamic constraints. Whatever representation is selected, any wide temperature-range correlation for $H_{2,1}(T, P_{s,1})$ extending up to the critical region must incorporate the correct limiting behaviour as $T \rightarrow T_{c,1}$ and $P_{s,1} \rightarrow P_{c,1}$. First

$$\lim_{T \rightarrow T_{c,1}} H_{2,1}(T, P_{s,1}) = P_{c,1}\phi_2^{V\infty}(T_{c,1}, P_{c,1}) \tag{21}$$

which follows immediately [16] from eqn. (10). Somewhat less direct derivations may be found in refs. 9, 11, 48 and 49. For the limiting slope, Schotte

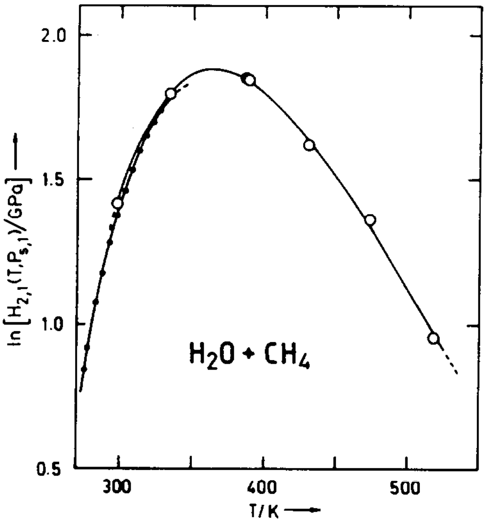

Fig. 3. Plot of $\ln[H_{2,1}(T,\ P_{s,1})/\text{GPa}]$ against temperature T for methane dissolved in water: ●, Rettich et al. [36] (percentage deviation is about ±0.05%); ○, Crovetto et al. [44] (percentage deviation is between 1 and 2%).

[50] has shown that provided the solute is the more volatile component, as in the case of methane dissolved in water

$$\lim_{T\to T_{c,1}} \left[\mathrm{d}\ln H_{2,1}(T,\ P_{s,1})/\mathrm{d}T\right] = -\infty \tag{22}$$

Such behaviour has been predicted by Wheeler [51] and by non-classical critical point scaling [15,52]. The partial molar heat capacity at infinite dilution diverges, as expected, towards positive infinity [53,54]. That is to say

$$\lim_{\substack{T\to T_{c,1}\\ P\to P_{c,1}}} \Delta C_{p,2}^{\infty} = +\infty \tag{23}$$

as the critical point of the solvent is approached from lower temperatures (Fig. 4). When $T_{c,1}$ is approached from higher temperatures, $C_{p,2}^{\infty}$ tends towards negative infinity. This remarkable behaviour is demonstrated in the recent careful calorimetric study by Biggerstaff and Wood [54] of aqueous solutions of argon, xenon and ethene at temperatures up to 720 K and pressures up to 33 MPa.

To date, the most popular empirical correlation schemes are those elaborated by Clarke and Glew [45] and by Benson et al. [39,40]. Their respective merits have been discussed repeatedly. Evidently, simple linearisation methods, such as the one suggested by Jonah [55], are of only very limited utility.

When a comparison between, say, enthalpy changes on the basis of eqn. (18) (van 't Hoff approach) and direct calorimetric measurements is desired, the fitting equation representing the temperature dependence of the Henry

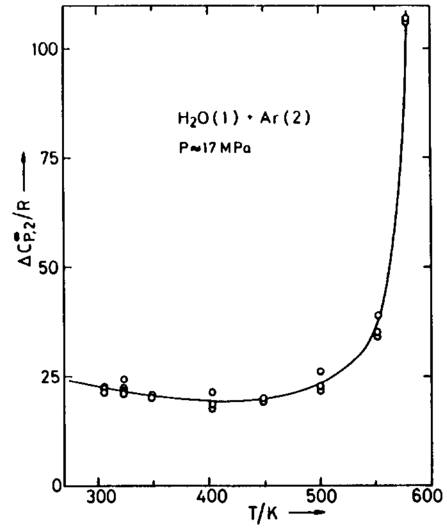

Fig. 4. Temperature dependence of the heat capacity change $\Delta C^{\infty}_{p,2}/R$ for argon dissolved in water at about 17 MPa total pressure [53].

fugacity has to be judiciously selected. The $H_{2,1}(T, P_{s,1})$ values at different temperatures refer, of course, to different pressures, $P_{s,1}(T)$, whence the partial molar enthalpy change on solution is rigorously given by

$$\Delta H_2^{\infty}(T, P_{s,1})/RT = \frac{\mathrm{d}\ln[H_{2,1}(T, P_{s,1})/\mathrm{Pa}]}{T\,\mathrm{d}(1/T)} + \frac{V_2^{\mathrm{L}\infty}}{R}\frac{\mathrm{d}P_{s,1}}{\mathrm{d}T} \tag{24}$$

Equation (24) has been introduced by us [11,36–38] to obtain accurate ΔH_2^{∞} values from high-precision gas solubility measurements. Analogous relations are readily derived [11] for $\Delta C^{\infty}_{p,2}$. For several gases dissolved in water, ΔH_2^{∞} and $\Delta C^{\infty}_{p,2}$ values obtained from VLE experiments using the RBW apparatus have recently been shown to agree excellently with calorimetrically determined values [16,53,56–59].

This section is concluded with a few comments concerning the analytical representation of composition and temperature dependence of unsymmetrically normalised activity coefficients obtained through application of eqn. (4). For each temperature and reference pressure $P_{s,1}(T)$, the composition dependence of γ_2' can be described by any convenient correlating equation compatible with the number and precision of the experimental data. In general, modelling closely follows the established procedures for the symmetrically normalised activity coefficients. For instance, from the simplest non-trivial expression for the excess molar Gibbs energy, the one-parameter equation

$$\ln \gamma_2'(T, P_{s,1}, x_2) = A(T, P_{s,1})(x_1^2 - 1) \tag{25}$$

is obtained. Whenever a multi-parameter correlation is indicated, Wohl-type equations have a special appeal. The temperature dependence of the fit parameters, say $A(T, P_{s,1})$, is usually accounted for by correlations resembling those used for the Henry fugacity. Excess partial molar enthalpies and heat capacities may then be obtained by appropriate differentiation [19].

EXPERIMENTAL: MIXTURES CONTAINING A STRONGLY POLAR COMPONENT

Mixtures of practical interest for the chemist or chemical engineer are usually complex mixtures, that is to say the intermolecular potential energy functions characterising the various components differ strongly, thereby giving rise to pronounced thermodynamic non-ideality. These differences may be advantageously discussed in terms of differences in molecular size, shape anisotropy, dispersion forces, polarity, polarizability, flexibility, etc. [10] (Fig. 5). In many mixtures dipolar and quadrupolar interactions contribute significantly to orientational effects. These effects are intimately linked to molecular structure, and thus show a very diverse picture. Complex cooperative phenomena are frequently involved.

In order to study the orientational effects due to polar–polar interaction, considerable time and effort have been devoted to the systematic experimental determination of excess enthalpies, excess volumes, excess heat capacities at constant pressure, and the higher-order mixing quantities of binary liquid mixtures containing a strongly polar substance and an essentially non-polar hydrocarbon. Reports documenting the advances achieved have been presented at several AFCAT meetings [60].

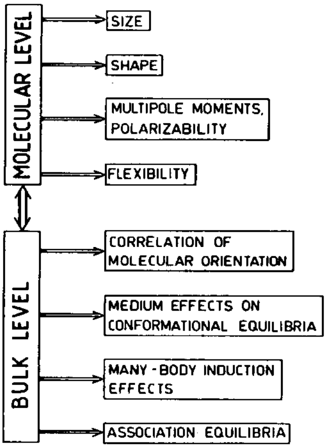

Fig. 5. Some important aspects of the description of fluids on the molecular and bulk level.

For the purpose of characterising the effective polarity of a molecule, one may define a reduced dipole moment according to [1]

$$\tilde{\mu}^2 \equiv \vec{\mu}^2/(4\pi\epsilon_0\sigma^3\epsilon) \tag{26}$$

or equivalently, by virtue of the corresponding states principle, by either of the following expressions

$$\tilde{\mu}^2 \equiv \vec{\mu}^2 N_A/(4\pi\epsilon_0 V_c k_B T_c) \tag{27}$$

$$\tilde{\mu}^2 \equiv \vec{\mu}^2 P_c/(4\pi\epsilon_0 k_B^2 T_c^2) \tag{28}$$

As long as the temperature is sufficiently high, that is to say as long as

$$\vec{\mu}^2 N_A/(4\pi\epsilon_0 V k_B T) \ll 1 \tag{29}$$

the orientation effects are essentially swamped by thermal randomisation. When the temperature is lowered, preferred orientations of considerable stability are observed. One way of treating these effects is through application of Guggenheim's quasi-chemical theory [61], as recently suggested by Saint-Victor and Patterson [62]. In this approach, the excess molar enthalpy is separated into random (r) and non-random (nr) contributions

$$\begin{aligned} H^E/N_A &= H_r^E/N_A + H_{nr}^E/N_A \\ &= x_1x_2(w - T\,\mathrm{d}w/\mathrm{d}T) - (x_1x_2)^2(w - T\,\mathrm{d}w/\mathrm{d}T)(\mathrm{e}^{2w/zk_BT} - 1) \\ &\quad + \cdots \end{aligned} \tag{30}$$

where $w = a + b/T$ is the interchange free energy parameter. Thus, for the excess molar heat capacity at constant pressure, the rough approximations

$$\begin{aligned} C_p^E/R &= C_{p,r}^E/R + C_{p,\,nr}^E/R \\ &= -x_1x_2\frac{T}{k_B}\frac{\mathrm{d}^2w}{\mathrm{d}T^2} + (x_1x_2)^2\left[\left(w - T\frac{\mathrm{d}w}{\mathrm{d}T}\right)^2\frac{2}{zk_B^2T^2}\mathrm{e}^{2w/zk_BT}\right. \\ &\quad \left. + \frac{T}{k_B}\frac{\mathrm{d}^2w}{\mathrm{d}T^2}(\mathrm{e}^{2w/zk_BT} - 1)\right] + \cdots \end{aligned} \tag{31a}$$

$$\approx -2x_1x_2b/k_BT^2 + 2z^{-1}(H^E/RT)^2 \tag{31b}$$

are obtained. The random term in C_p^E is negative, as expected for mixtures where dipole–dipole order is being broken in the mixing process. On the other hand, the non-random contribution is positive and has zero slope against mole fraction at the ends of the composition range, see eqn. (31a). Both terms increase in magnitude with decreasing temperature. They can account qualitatively for the appearance of W-shaped C_p^E curves. Such 'unusual' composition dependence, first reported by Grolier et al. in 1982 at the 37th Annual Calorimetry Conference [63], is now recognized as being of wide occurrence in mixtures of the type: a strongly polar substance + an

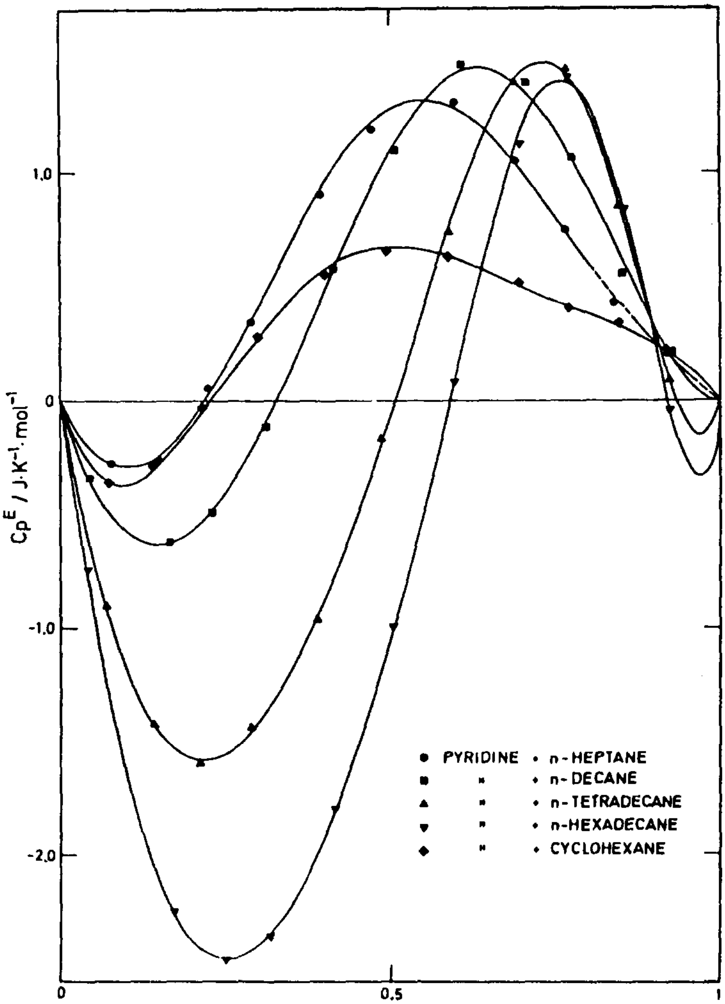

Fig. 6. Excess molar heat capacities C_p^{E} of $\{x_1\mathrm{C_5H_5N} + x_2n\text{-}\mathrm{C}_l\mathrm{H}_{2l+2}\}$ at 298.15 K and atmospheric pressure [60c].

alkane. Representative examples are given in Fig. 6; additional mixtures showing W-shaped curves for C_p^{E} against x have been investigated in refs. 60a–c and 62–68. Many of these systems are rather close to phase separation at an upper critical solution temperature (UCST).

When a UCST is approached from the homogeneous region at constant pressure and at constant critical composition, the heat capacity diverges weakly according to [1]

$$C_{p,x_c} = C_{p,x_c}^{\text{non-critical}} + A_c t^{-\alpha}, \qquad t \equiv (T - T_c)/T_c \tag{32}$$

with a critical exponent $\alpha = 0.11$. Evidently, the quasi-chemical approximation severely underestimates the non-random contribution to C_p^{E} and becomes, in fact, qualitatively incorrect for $T \to T_c$.

Any detailed discussion of W-shaped, or nearly W-shaped, heat capacities, C_p^E, must first focus on obtaining the normal, non-critical contribution to the heat capacity in the spirit of eqn. (32). Although not difficult in principle, this separation nonetheless necessitates the acquisition of a substantial number of experimental calorimetric results over a temperature range close to the UCST and over the entire composition range, $0 \leq x \leq 1$. The recent work of Kalali et al. [68] on bis(2-dichloroethyl)ether + 2,2,4-trimethylpentane is a step in this direction. Because the isobaric expansivity diverges with the same critical exponent as $T \rightarrow T_c$ at $x = x_c$, similar comments also apply to this quantity.

CONCLUDING REMARKS

In this review recent progress concerning dilute liquid non-electrolyte solutions as well as results pertaining to liquid mixtures containing a strongly polar component have been briefly surveyed. More detailed accounts, including experimental and statistical-mechanical aspects, may be found in several of the articles quoted above and in refs. 69 and 70. Suffice it to say that advances in instrumentation for calorimetry, *PvT* measurements and VLE measurements have made possible the determination of thermophysical properties and phase equilibria of fluid systems with unparalleled precision, accuracy and speed over large ranges of temperature and pressure. The concomitant discovery of hitherto unknown and sometimes quite spectacular effects has been exciting, and has decisively influenced the theoretical advances.

LIST OF SYMBOLS

A	parameter in the one-parameter Redlich–Kister equation
A_c	critical amplitude
C_p	molar heat capacity of a mixture at constant pressure
C_p^E	excess molar heat capacity
$C_{p,i}^{\ominus}$	molar heat capacity of pure i in the perfect-gas state
$C_{p,i}^{L\infty}$	partial molar heat capacity of i at infinite dilution in the liquid phase
$\Delta C_{p,i}^{\infty}$	$\equiv C_{p,i}^{L\infty} - C_{p,i}^{\ominus}$, heat capacity change upon solution of i
f	fugacity
f_i	component fugacity of i in a solution
G^E	excess molar Gibbs energy
H^E	excess molar enthalpy
$H_{2,1}$	Henry fugacity (solute 2 dissolved in solvent 1)
$H_i^{\ominus}$	molar enthalpy of pure i in the perfect-gas state

$H_i^{\mathrm{L}\infty}$	partial molar enthalpy of i at infinite dilution in the liquid phase
ΔH_i^{∞}	$\equiv H_i^{\mathrm{L}\infty} - H_i^{\ominus}$, enthalpy change upon solution of i
k_B	Boltzmann's constant
K_i	$\equiv y_i/x_i$, the K value of i
n	$= \Sigma n_i$, total amount of substance
n_i	amount of substance i
N_A	Avogadro's constant
P	pressure
$P_{\mathrm{s},i}$	vapor pressure of pure i
R	gas constant
T	thermodynamic temperature
v	volume
V	molar volume of a mixture
V_i	partial molar volume of i
w	Guggenheim's free energy interchange parameter
x_i	liquid-phase mole fraction
y_i	vapour-phase mole fraction
z	lattice coordination number
Z	$\equiv PV/RT$, compressibility factor

Greek letters

α	critical exponent
γ_i	liquid-phase activity coefficient
$\vec{\mu}$	permanent electric dipole moment
$\tilde{\mu}$	reduced dipole moment
ϵ	depth of minimum of pair potential energy function
ϵ_0	permittivity of vacuum
ρ	$\equiv V^{-1}$, molar density
σ	collision diameter at which the pair-wise potential energy is zero
ϕ_i	fugacity coefficient of i in a solution
$\phi_i^{\mathrm{L}\infty}$	fugacity coefficient of i at infinite dilution in the liquid phase

Subscripts

i, j	general indexes; usually, $i = 1$ denotes the solvent and $i = 2$ denotes the solute
c	critical quantity
s	saturation condition

Superscripts

E	excess
L	liquid phase

V	vapour phase
$\star$	pure substance
$\ominus$	perfect-gas state
∞	infinite dilution
$'$	unsymmetric convention

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