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Thermochimica Acta 300 (1997) 159–168

thermochimica
acta

Caloric properties of dilute nonelectrolyte solutions: A success story

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Received 18 November 1996; accepted 20 November 1996

Abstract

Selected aspects of the thermodynamics of very dilute solutions of gases in liquids, in particular aqueous solutions, are reviewed and connected with recent high-precision experimental techniques [vapor–liquid equilibrium measurements (VLE), calorimetry and densimetry]. Some of the problems encountered in data reduction and data correlation over large temperature ranges, including the critical region, are discussed. The focus is on caloric properties, such as partial molar enthalpy changes on solution, ΔH_2^∞, and partial molar heat capacity changes on solution, $\Delta C_{P,2}^\infty$: *direct* calorimetric methods are compared with *indirect* methods based on VLE studies as a function of temperature (*van't Hoff approach*). © 1997 Elsevier Science B.V.

Keywords: Dilute solutions; Gas solubilities; Henry fugacities; Partial molar enthalpy changes on solution; Partial molar heat capacity changes on solution; Partial molar volumes at infinite dilution

1. Introduction

It is a genuine pleasure to join so many distinguished friends and colleagues in preparing *Volume 300* of *Thermochimica Acta.* This number is truly impressive, even more so when one considers that only 25 years have elapsed since the inception of this journal. It is clear proof of the vitality and unabated growth of calorimetry and thermal analysis, which represent the two most important scientific/technical disciplines covered by the journal. On such a festive occasion, there exist several ways to prepare an article on one or more of the scientific topics one is currently interested in. For instance, one possibility would be to present a formal review of the state-of-the-art, while another would be to provide a detailed presentation of my own contributions to the field. Neither approach appeals to me particularly, mainly for the following reasons: space limitations preclude an exhaustive survey of a broader area, and so do time limitations because of other commitments I have to honor, because of teaching loads, and last but not least because of administrative chores at my home university. Instead I have chosen something like a middle path by selecting a rather narrow topic to which I have contributed, that is to say I will give a (subjective) account of the corresponding activities during, say, the last 15 years. This narrow field concerns vapor–liquid equilibria (VLE) and caloric properties of *dilute* nonelectrolyte solutions, with the focus being on solutions of gases in liquid water. Even here, citations will *not* be comprehensive but simply reflect my preferences and idiosyncrasies. For the omission of some important papers and the neglection of several related research areas I would like to offer my apologies in advance.

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0040-6031/97/$17.00
PII S0040-6031(96)03131-0

Why, now, my long-term interest in VLE, where one component is near or already above its respective critical temperature? The study of the solubility of gases in liquids has, in addition to its profound theoretical interest, many important practical applications [1–6]. In fact, research activities can be traced to requirements originating in surprisingly diverse areas of the pure and applied sciences. For instance, chemical process design often needs reliable data for VLE of multicomponent systems containing one or more gases (noncondensables). Other areas, where gas solubilities are frequently needed, are geochemistry, environmental science and biomedical technology. Since life cannot exist without water, studies of aqueous solutions of simple nonpolar substances, in particular of the rare gases and of hydrocarbons, have held a prominent position in biophysics. Perhaps most important, studies on such model systems provide information on *hydrophobic effects* [7] which are thought to be of pivotal importance for the formation and stability of higher order structures of biological substances, such as proteins and nucleic acids, and the stability of cell membranes. Membranes are perhaps the most ubiquitous cellular structures in living systems. They provide the cell with a permeability barrier and are involved in a large number of cellular functions [8,9]. Conventionally, membranes are envisaged to consist of a lipid bilayer matrix in which membrane-bound proteins are incorporated, and one assumes that the constituent lipids (and proteins) are mobile by virtue of the fluid nature of the lipid bilayer. Lipid bilayers consist of two distinct regions reflecting the structure of lipid amphiphiles:

- The hydrophobic interior is fairly homogeneous and consists of *hydrocarbon chains*.
- The hydrophilic head-group region may contain charged groups or a wide range of nonionic *polar groups*, which are in contact with the aqueous surroundings.

Thus, the continued interest in the solubility of gases in *n*-alkanes as well as *n*-alkan-1-ols is not surprising [10–17]. In passing, I note the use of experimental *n*-octan-1-ol/water partition coefficients for correlating anesthetic potency of general anaesthetics.

In this communication, the most relevant findings of our work on *dilute aqueous solutions of gases* will be summarized briefly. Particular emphasis will be placed upon a comparison of enthalpy changes and heat capacity changes on solution obtained via *van't Hoff analysis* of high-precision solubility measurements with *directly* obtained *calorimetric* results. I emphasize that until quite recently, precision measurements of the solubility over sufficiently large ranges of temperature constituted the *only* source of information on partial molar enthalpy changes on solution (enthalpies of solution, for short) and, a fortiori, on partial molar heat capacity changes on solution of sparingly soluble gases in liquids. In fact, direct calorimetric measurements, with rather low precision, were first attempted in 1959 on rare gases dissolved in water [18]. In 1973, Jadot [19] measured the enthalpies of solution of some hydrocarbon gases in several *n*-alkanes, benzene and tetrachloromethane at 298.15 K, also with low precision, using a Tian–Calvet calorimeter. His apparatus appears unsuitable for measuring the enthalpy of solution of low-solubility gases in water. Several years later Cone et al. [20] described a batch calorimetric method for determining the enthalpy of solution of hydrocarbons in nonpolar liquids. Because of the uncertain nature of the various corrections, their results are unreliable, as demonstrated by the subsequent work of Battino and Marsh [21]. These latter authors used a modified isothermal displacement calorimeter [22] to measure the enthalpy of solution of several gases in cyclohexane, benzene and tetrachloromethane at 298.15 K and 318.15 K, with an imprecision ranging from about ±200 J mol^{-1} to ±500 J mol^{-1}. Continued efforts at the Thermochemistry Laboratory in Lund, Sweden, and in the Chemistry Department of the University of Colorado in Boulder, Colorado, USA, respectively, have resulted in the development of two types of very precise flow microcalorimeters designed for the determination of enthalpies of solution of slightly soluble gases in water [23,24]. Both the batch method (1982) and the steady-state method (1984) give comparable results, about one order of magnitude more precise than those of Battino and Marsh. The first direct calorimetric determination of the heat capacity of an aqueous solution of a slightly soluble gas has been published at the end of 1985 by Biggerstaff et al. [25]. Its measuring principle is that of the conventional Picker flow microcalorimeter [26–29].

2. Thermodynamic and experimental background

It is far beyond the scope of this work to discuss available experimental methods tailored for application to dilute solutions. Those potentially interested in precision apparatus are referred to surveys, for instance, by Clever and Battino [30], Wilhelm [3,31], Hallén and Wadsö [32], Grolier [33] and Wadsö [34]. Let it suffice to point out, that flow calorimetric measurements are fairly direct measurements, and despite sophisticated designs they require relatively little additional information and data manipulation to obtain the desired enthalpy and heat capacity changes on solution from the primary experimental results. The most important auxiliary quantities are the densities of the pure solvents and of the solutions. They are most conveniently determined with a vibrating-tube densimeter [29,35–40], an instrument which has allowed the acquisition of precision density data to become virtually routine. On the other hand, to obtain thermodynamically well-defined and reliable quantities from VLE measurements, data reduction has to be considerably more complex and requires substantially more auxiliary data. By way of example, I will present the most salient points of data reduction associated with the use of our high-precision *analytic* gas solubility apparatus [41–44]. By and large, the method adopted for use with our medium-precision *synthetic*, fully automated Ben-Naim/Baer-type instrument is similar (for details, see Refs. [6,13,14,45–47]). In this context, high-precision implies an average random error (imprecision) of about ±0.05% or less in conjunction with a maximum systematic error (inaccuracy) of about ±0.05% or less; the imprecision associated with the Ben-Naim/Baer type apparatus is roughly ±0.5%, and the corresponding inaccuracy is estimated to be smaller than ±0.2%.

Our high-precision analytical method for VLE measurements on dilute solutions of gases in liquids is based on an earlier work of Benson and Krause [48,49]. The technique used to degas the solvent (water in all cases) has been described [50]: the maximum residual of dissolved air after degassing is estimated to be 0.001% or less of the saturation value at room temperature and atmospheric pressure. The equilibrator used to assure saturation of water by gas is essentially that described by Benson and Krause. It is housed in a large water thermostat. To attain reproducible results, we use equilibration times of up to 60 h, although the usual range is from 16 to 48 h. The temperature drift of the thermostat during equilibration never exceeds ±0.003 K. Temperatures T are determined with Leeds and Northrup knife-blade platinum resistance thermometers, which are checked weekly in triple-point-of-water cells, and twice each year in an NBS-certified benzoic acid cell.

After attaining equilibrium, say after 24 h, vapor-phase (V) and liquid-phase (L) samples of precisely known volumes ν^V and ν^L, respectively, are isolated. First, the gas contained in ν^V is dried and then Töpler-pumped into the manometric system to determine the amount of pure gas by classical $P\nu T$ measurements. Then the gas dissolved in the liquid-phase sample bulb ν^L is extracted, dried and transferred to the manometric system, where the amount of pure gas is determined. The calibrated volumes are known to about ±0.001%, while the pressure P is measured with a Ruska quartz Bourdon tube manometer with an imprecision of less than ±0.01%. The manometer is checked periodically against a gas-lubricated piston pressure gauge with traceability of calibration to the National Bureau of Standard (now NIST). The essential parts of the apparatus are shown in the flow diagram in Fig. 1. The precision and accuracy which

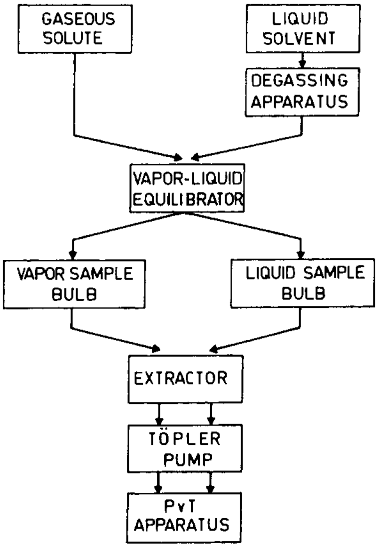

Fig. 1. Block diagram of the experimental arrangement used in the Rettich–Battino–Wilhelm (RBW) high-precision gas-solubility apparatus [41–44].

may be achieved with this type of equipment surpasses that of any previous design, including the one of Cook and Hanson [51].

From the measured quantities, the *Henry fugacity* $H_{2,1}(T,P_{s,1})$ (also known as Henry's Law constant) of solute 2 (gas) dissolved in liquid solvent 1, at experimental temperature T and vapor pressure $P_{s,1}$ of the pure solvent,

$$H_{2,1}(T, P_{s,1}) = \lim_{x_2 \to 0_{P \to P_{s,1}}} \left[y_2 P \hat{\phi}_2^{V}(T, P, y_2)/x_2 \right], \tag{1}$$

is obtained through straightforward though tedious extrapolation to $x_2 \to 0, P \to P_{s,1}$. Here, x_2 is the liquid-phase mole fraction of dissolved gas, y_2 the mole fraction of gas in the coexisting vapor phase, and $\hat{\phi}_2^{V}(T, P, y_2)$ the corresponding vapor-phase component fugacity coefficient at experimental temperature T and total pressure P. While the mole fractions are experimentally determined quantities, $\hat{\phi}_2^{V}$ has to be obtained independently. Strictly speaking, for the determination of x_2, besides the molar volume $V_{s,1}^{L*}$ of pure liquid at saturation, the partial molar volume V_2^{L} of the gas in the liquid solution must be known, which in the high-dilution region is, for all practical purposes, essentially equal to the partial molar volume at infinite dilution, $V_2^{L\infty}$. For the determination of y_2, equation-of-state information on the vapor phase is needed. For measurements at such low pressures as in our work ($P < 120$kPa), the virial equation in pressure at the second-virial-coefficient level is adequate and most convenient for the description of real-gas behavior. Hence

$$\hat{\phi}_2^{V}(T, P, y_2) = \exp[(RT)^{-1} P(B_{22} + y_1^2 \Delta_{12})], \tag{2}$$

where B_{22} is the second virial coefficient of pure gas, $\Delta_{12} = 2B_{12} - (B_{11} + B_{22})$, B_{11} is the second virial coefficient of pure solvent vapor, B_{12} the second virial cross-coefficient, and R the gas constant. For computational details of the rapidly converging iteration procedure used to calculate the total pressure, the vapor-phase mole fraction and the vapor-phase component fugacity coefficient, see Rettich et al. [41].

In brief, the auxiliary quantities needed for a thermodynamically rigorous data reduction of gas solubility measurements in liquids at low pressures with our high-precision apparatus are the vapor pressure of the solvent, the second virial coefficients of the pure components, the second virial cross-coefficient, the molar volume of the pure liquid solvent, and the partial molar volume of the gas at infinite dilution in the liquid phase. Usually, reliable sources exist for vapor pressures and densities, and hence molar volumes, of the pure solvents under consideration. For instance, the vapor pressure of water was calculated from the Chebyshev polynomial given by Ambrose and Lawrenson [52], and for the liquid water density we used the values given by Kell [53]. The second virial coefficient of pure water vapor was taken from O'Connell [54], while those of the gases were taken from the compilation of Dymond and Smith [55]. When no experimental data on second virial cross-coefficients were available, B_{12} was estimated using a generalized corresponding states correlation due to Tsonopoulos [56], in conjunction with suitably selected semiempirical methods for estimating the binary interaction parameter characteristic for each binary. For all solutions of gases in water investigated so far, experimentally determined partial molar volumes at infinite dilution reported in the literature have been used. For the solutions of gases in *n*-alkanes and *n*-alkane-l-ols [13,14], the partial molar volumes at infinite dilution were calculated via a semiempirical correlation developed by Handa et al. [57].

Once experimental Henry fugacities for a given solute/solvent system have been collected over a certain temperature range, the question arises as to their most satisfactory mathematical representation as a function of temperature. In the absence of theoretically well-founded models of general validity, one has to rely on essentially empirical fitting equations, subject, however, to some important thermodynamic constraints. Depending on the choice of variables, i.e. T or $1/T$, for expanding the enthalpy of solution (see later) either the Clarke–Glew (CG) equation [58]

$$\ln[H_{2,1}(T, P_{s,1})/\text{Pa}] = A_0 + A_1(T/\text{K})^{-1} + A_2 \ln(T/\text{K}) + \sum_{i=3}^{n} A_i (T/\text{K})^{i-2}, \tag{3}$$

or the Benson–Krause (BK) equation [48,49]

$$\ln[H_{2,1}(T, P_{s,1})/\text{Pa}] = \sum_{i=0}^{m} a_i (T/\text{K})^{-i} \tag{4}$$

are obtained. On the basis of the ability to fit very accurate $H_{2,1}(T,P_{s,1})$ data over large temperature ranges, and of simplicity, the BK power series in $1/T$ appears to be superior. Whichever representation is selected, any correlation for $H_{2,1}(T,P_{s,1})$ extending up to the critical region *must* incorporate the thermodynamically correct limiting behavior for $T \rightarrow T_{c,1}$ and $P_{s,1} \rightarrow P_{c,1}$:

$$\lim_{T\rightarrow T_{c,1}} H_{2,1}(T,\, P_{s,1}) = P_{c,1}\hat{\phi}_2^{V\infty}(T_{c,1},\, P_{c,1}), \quad (5)$$

where $T_{c,1}$ and $P_{c,1}$ are the critical temperature and pressure of the solvent, and $\hat{\phi}_2^{V\infty}$ is the component fugacity coefficient of the solute at infinite dilution in the vapor phase. As I have shown some time ago [4,5,31,59], this exact limiting value follows directly from the generally valid relation

$$H_{2,1}(T,\, P) = P\hat{\phi}_2^{L\infty}(T,\, P) \quad (6)$$

and the equilibrium condition prevailing at the critical point. A somewhat different proof was presented in Refs. [2,3,60] exploiting the exact relation between the Henry fugacity and the Ostwald coefficient L_2^{∞} at infinite dilution. As far as the limiting slope is concerned, for *volatile* solutes

$$\lim_{T\rightarrow T_{c,1}} \{\mathrm{dln}[H_{2,1}(T,\, P_{s,1})/\mathrm{Pa}]/\mathrm{d}T\} = -\infty \quad (7)$$

when the critical point of the solvent is approached along the coexistence curve [61]. Nonclassically, the temperature derivative of $\ln[H_{2,1}(T,\, P_{s,1})/\mathrm{Pa}]$ diverges as $|T - T_{c,1}|^{\beta-1}$, where the critical exponent $\beta = 0.326$.

3. Selected results and discussion

As already pointed out, until recently precision measurements of Henry fugacities over sufficiently large temperature ranges, i.e. van't Hoff analysis of the solubility data, constituted the only reliable source of information on partial molar enthalpy changes on solution ΔH_2^{∞} and the partial molar heat capacity changes on solution $\Delta C_{P,2}^{\infty}$. Specifically [2-5,31,41,60]

$$\frac{\Delta H_2^{\infty}(T,\, P_{s,1})}{RT} \equiv \frac{H_2^{L\infty} - H_2^{*pg}}{RT} = -T\frac{\mathrm{dln}[H_{2,1}(T,\, P_{s,1})/\mathrm{Pa}]}{\mathrm{d}T} + \frac{V_2^{L\infty}}{R}\frac{\mathrm{d}P_{s,1}}{\mathrm{d}T}, \quad (8)$$

and by an analogous argument

$$\frac{\Delta C_{P,2}^{\infty}(T,\, P_{s,1})}{R} \equiv \frac{C_{P,2}^{L\infty} - C_{P,2}^{*pg}}{R} = \frac{\mathrm{d}\Delta H_2^{\infty}(T,\, P_{s,1})}{R\mathrm{d}T} - \frac{1}{R}\left[V_2^{L\infty} - T\left(\frac{\partial V_2^{L\infty}}{\partial T}\right)_P\right]\frac{\mathrm{d}P_{s,1}}{\mathrm{d}T} \quad (9)$$

$$= -2T\frac{\mathrm{dln}[H_{2,1}(T,\, P_{s,1})/\mathrm{Pa}]}{\mathrm{d}T} - T^2\frac{\mathrm{d}^2\ln[H_{2,1}(T,\, P_{s,1})/\mathrm{Pa}]}{\mathrm{d}T^2} + 2\frac{T}{R}\frac{\mathrm{d}V_2^{L\infty}}{\mathrm{d}T}\frac{\mathrm{d}P_{s,1}}{\mathrm{d}T} - \frac{T}{R}\left(\frac{\partial V_2^{L\infty}}{\partial P}\right)_T\left(\frac{\mathrm{d}P_{s,1}}{\mathrm{d}T}\right)^2 + \frac{TV_2^{L\infty}}{R}\frac{\mathrm{d}^2P_{s,1}}{\mathrm{d}T^2}. \quad (10)$$

Here, $H_2^{L\infty}$ is the partial molar enthalpy of the solute at infinite dilution in the liquid solvent, $C_{P,2}^{L\infty}$ the partial molar heat capacity at constant pressure of the solute at infinite dilution in the liquid solvent [both at the vapor pressure $P_{s,1}(T)$ of the solvent], and H_2^{*pg} and $C_{P,2}^{*pg}$ are the molar enthalpy and the molar heat capacity at constant pressure, respectively, of the pure solute in the perfect-gas state. The ordinary differential quotients in Eq. (8) [9] Eq. (10) indicate differentiation while maintaining *orthobaric* conditions: the first term on the rhs of Eqs. (8) and (9), respectively, as well as the first and the second term on the rhs of Eq. (10) may all be obtained from any one of the selected fitting equations, say Eq. (4). This leads to

$$\frac{\Delta H_2^{\infty}(T,\, P_{s,1})}{RT} = \sum_{i=1} iA_i(T/\mathrm{K})^{-i} + \frac{V_2^{L\infty}}{R}\frac{\mathrm{d}P_{s,1}}{\mathrm{d}T} \quad (11)$$

and

$$\frac{\Delta C_{P,2}^{\infty}(T,\, P_{s,1})}{R} = \sum_{i=2} i(i-1)A_i(T/\mathrm{K})^{-i} + 2\frac{T}{R}\frac{\mathrm{d}V_2^{L\infty}}{\mathrm{d}T}\frac{\mathrm{d}P_{s,1}}{\mathrm{d}T} - \frac{T}{R}\left(\frac{\partial V_2^{L\infty}}{\partial P}\right)_T\left(\frac{\mathrm{d}P_{s,1}}{\mathrm{d}T}\right)^2 + \frac{TV_2^{L\infty}}{R}\frac{\mathrm{d}^2P_{s,1}}{\mathrm{d}T^2}. \quad (12)$$

Until recently, the remaining terms on the rhs of Eqs. (8) through (12) [9–11] containing $V_2^{L\infty}$ and its

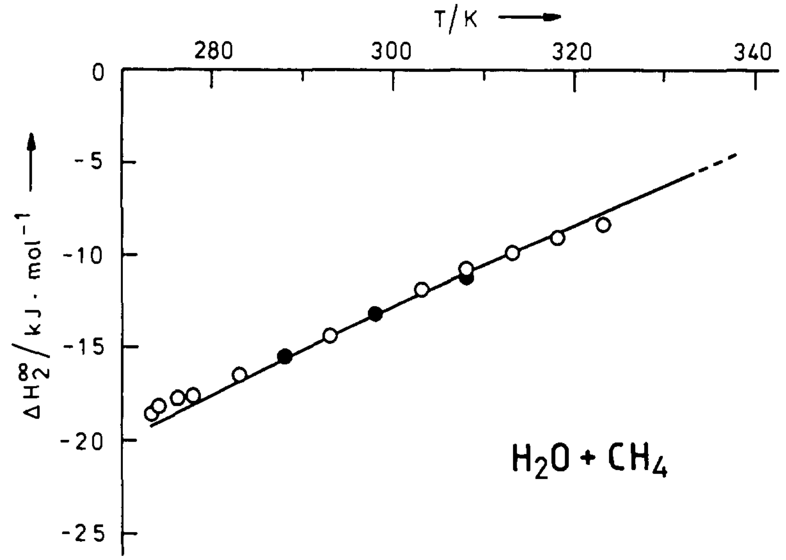

Fig. 2. Partial molar enthalpy change on solution, $\Delta H_2^\infty(T, P_{s,1})$, of methane in liquid water from 273.15 to 333.15 K: — - Rettich et al. [41]; ○ - Naghibi et al.[70]; and • - Dec and Gill [68,69]. At this scale, the results of Olofsson et al. [67] cannot be distinguished from those of Refs. [68–70], see Table 1.

derivatives with respect to T and P together with $dP_{s,1}/dT$ and $d^2P_{s,1}/dT^2$ – now referred to in the literature [61,62] as Wilhelm terms – have been overlooked. As I have pointed out repeatedly, at temperatures well below the critical temperature of the solvent, the magnitude of these terms will often be smaller than the experimental error of the measurements, and may thus be neglected. However, their contributions increase rapidly with increasing temperature because of the increase of $dP_{s,1}/dT$ and $d^2P_{s,1}/dT^2$, and, of course, of $V_2^{L\infty}$, $dV_2^{L\infty}/dT$ and $|(\partial V_2^{L\infty}/\partial P)_T|$. In fact, the partial molar volume of a gas at infinite dilution in a liquid solvent *diverges* to $+\infty$ at the critical point of the solvent. The effects of this divergence are felt relatively far from the critical point [63]. Using a lattice gas model, in 1972 Wheeler [64] showed that for such a system $V_2^{L\infty}$ will tend to $+\infty$, proportional to the isothermal compressibility of the pure solvent $\beta_{T,s,1}^{L^*}$. The partial molar enthalpy at infinite dilution will diverge at the solvent critical point to $+\infty$ in exactly the same manner. Since $C_{P,2}^{L\infty} = (\partial H_2^{L\infty}/\partial T)_P$, the partial molar heat capacity at infinite dilution will diverge as $(\partial \beta_{T,s,1}^{L^*}/\partial T)_P$, i.e. $C_{P,2}^{L\infty}$ will tend to $+\infty$ as $T_{c,1}$ is *approached from lower temperatures*, and to $-\infty$ as $T_{c,1}$ is *approached from higher temperatures* (at $P = P_{c,1}$). The important recent experiments of Wood et al. confirm these expectations [25,40,65,66].

Little experimental information is available on $(\partial V_2^{L\infty}/\partial P)_T$, appearing in Eqs. (10) and (12). It diverges to $-\infty$ as $T \rightarrow T_{c,1}$ and $P \rightarrow P_{c,1}$, but at temperatures well removed from the critical temperature of the solvent this quantity is very small. For instance, from the work of Wood et al. on argon in water [40], we estimated $(\partial V_2^{L\infty}/\partial P)_T = -0.003 \mathrm{cm^3 bar^{-1} mol^{-1}}$ at 367 K and -0.006 cm^3 bar^{-1} mol^{-1} at 428 K for this system [44].

In Fig. 2, our results [41] on the partial molar enthalpy change on solution of methane in water, obtained via Eq. (11), are compared with values determined calorimetrically [67–70]: excellent agreement is observed over the entire temperature range of measurements. Using our data, the extrapolated minimum-solubility temperature, i.e. the temperature where the curve $H_{2,1}(T, P_{s,1})$ vs. T shows a maximum, is ca. 362 K, which has indeed been observed by Crovetto et al. [71] as shown in Fig. 3 (their solubility measurements are considerably less precise, with average deviations of about ±2%, but cover a much larger temperature range). Qualitatively similar behavior is also observed with other solvent–solute pairs:

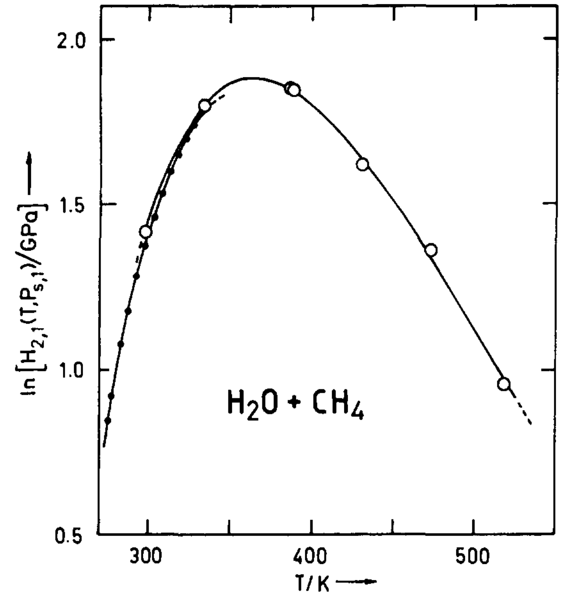

Fig. 3. Plot of ln $[H_{2,1}(T, P_{s,1})/\mathrm{GPa}]$ against temperature T for methane dissolved in liquid water: ● – Rettich et al. [41] (average percentage deviation of the Henry fugacity from the correlating function is about ±0.05%); and ○ – Crovetto et al. [71] (average percentage deviation of the Henry fugacity from the correlating function is about ±2%).

after passing through a maximum, $H_{2,1}(T, P_{s,1})$ decreases to the finite limiting value at $T = T_{c,1}$ and $P_{s,1} = P_{c,1}$ given by Eq. (5) with negative infinite limiting slope. In recent years, several semiempirical correlations for $H_{2,1}(T, P_{s,1})$ over large temperature ranges up to the critical temperature of the solvent, trying to incorporate the thermodynamically correct limiting behavior, have been suggested, with the focus being on aqueous solutions. Here, I note only the contributions of Krause and Benson [62]:

$$T_r^2 \ln[H_{2,1}(T, P_{s,1})/\mathrm{Pa}] = T_r^2 b_0 + b_1(1 - T_r)^{1/3} + b_2(1 - T_r)^{2/3}, \qquad (13)$$

where $T_r = T/T_{c,1}$; and Harvey and Levelt-Sengers [72]:

$$T\ln[H_{2,1}(T, P_{s,1})/f^*_{s,1}] = A + B(\rho^{L^*}_{s,1} - \rho^*_{c,1}) + CT\rho^{L^*}_{s,1}\exp[(273.15\,\mathrm{K} - T)\tau^{-1}], \qquad (14)$$

where $f^*_{s,1}$ is the fugacity of the solvent at saturation, $\rho^{L^*}_{s,1}$ is the molar density of pure saturated solvent, $\rho^*_{c,1}$ is its critical molar density and τ is a constant varying little with the systems (≈ 50 K). My own contribution of 1991 [5] involves the Ostwald coefficient $L^\infty_{2,1}$ at infinite dilution. The following expression was expected to be asymptotically valid in the neighborhood of the critical point of the solvent:

$$T\ln L^\infty_{2,1} = b(\rho^{L^*}_{s,1} - \rho^*_{c,1}). \qquad (15)$$

However, since $L^\infty_{2,1}$ is related to the infinite dilution distribution coefficient $K^\infty_{2,1} = \lim_{x_2 \to 0}(y_2/x_2)_{\mathrm{equil}}$ according to

$$L^\infty_{2,1} = \frac{\rho^{L^*}_{s,1}}{\rho^{V^*}_{s,1}} \frac{1}{K^\infty_{2,1}}, \qquad (16)$$

the density dependence of $\ln(\rho^{L^*}_{s,1}/\rho^{V^*}_{s,1})$ and $-\ln K^\infty_{2,1}$ partially compensate each other (here, $\rho^{V^*}_{s,1}$ is the molar density of saturated vapor). This, and a preliminary survey of existing literature data, led me to suggest that the linear relation Eq. (15) may, in general, hold over a significantly larger range of orthobaric densities than the analogous expression given by Harvey et al. [73] involving $K^\infty_{2,1}$ instead. My contention was recently corroborated by Chialvo et al. [74].

Table 1 contains a comparison of $\Delta H^\infty_2(T, P_{s,1})$ and $\Delta C^\infty_{P,2}(T, P_{s,1})$ for several gases dissolved in liquid water obtained from van't Hoff analysis of high-precision solubility measurements [cf. Eqs. (8)–(10)] with calorimetrically determined values. Besides our own results on solutions of Ar, O_2, CH_4, C_2H_6 and C_2H_4 [41,44,75], I have also included those of Krause and Benson on the rare gases He through Xe dissolved in water [62]. Essentially, these authors now use our method of data reduction first presented in 1981 [41], but include a very small empirical third-order correction term which presumably takes into account the impact of the third virial coefficients pertaining to the vapor phase and, perhaps, the variation of the Henry's Law activity coefficient γ^{HL}_2 with composition. The calorimetrically determined partial molar enthalpy changes on solution were all obtained by one of the two above-mentioned types of flow microcalorimeters [23,24]. With the exception of one set of *direct* heat capacity measurements on argon dissolved in water [25], all partial molar heat capacity changes on solution were obtained from the temperature dependence of the enthalpy of solution, i.e. from $\Delta C^\infty_{P,2} = (\partial \Delta H^\infty_2/\partial T)_P$.

Table 1

Partial molar enthalpy changes on solution $\Delta H_2^\infty(T, P_{s,1})$ and partial molar heat capacity changes on solution $\Delta C_{P,2}^\infty(T, P_{s,1})$ of several gases dissolved in liquid water at 298.15 K and $P_{s,1} = 3.1691$kPa: comparison of values obtained via van't Hoff analysis of high-precision gas solubility measurements [see Eqs. (8) and (10)] with those obtained by calorimetric methods

Gas	$\Delta H_2^\infty(T, P_{s,1})$/ kJ mol^{-1}		$\Delta C_{P,2}^\infty(T, P_{s,1})$/ J K^{-1} mol^{-1}	
	solubility	calorimetry	solubility	calorimetry
He	−0.54 [a]	−0.65 [e]	122 [a]	135 [e]
		−0.52 [f]		
Ne	−3.64 [a]	−3.64 [e]	143 [a]	145 [e]
		−3.95 [f]		
Ar	−11.92 [a]	−12.01 [e]	195 [a]	200 [e]
	−11.96 [b]	−11.94 [f]	192 [b]	189 [l]
Kr	−15.34 [a]	−15.29 [e]	218 [a]	220 [e]
		−15.28 [f]		
Xe	−19.06 [a]	−18.87 [e]	250 [a]	250 [e]
		−19.10 [f]		
O_2	−12.02 [c]	−12.06 [g]	200 [c]	205 [e]
		−12.03 [h]		
		−12.00 [e]		
CH_4	−13.19 [c]	−13.06 [e]	237 [c]	242 [e]
		−13.18 [i]		209 [j]
		−13.12 [j]		218 [m]
C_2H_6	−19.50 [c]	−19.30 [e]	270 [c]	317 [e]
		−19.52 [i]		273 [k]
		−19.43 [k]		284 [m]
C_2H_4	−16.28 [d]	−16.46 [i]	238 [d]	237 [m]

[a] Krause and Benson [62]: all their enthalpy-of-solution data have the wrong sign.

[b] Rettich et al. [44].

[c] Rettich et al. [41].

[d] Rettich et al. [75].

[e] Olofsson et al. [67].

[f] Dec and Gill [76].

[g] Gill and Wadsö [23].

[h] Dec and Gill [24].

[i] Dec and Gill [68].

[j] Naghibi et al. [70].

[k] Naghibi et al. [77].

[l] Biggerstaff et al. [25]. This is the only directly obtained value. All the other $\Delta C_{P,2}^\infty$ values have been obtained from the temperature dependence of the enthalpy of solution, i.e. from $\Delta C_{P,2}^\infty = (\partial \Delta H_2^\infty / \partial T)_P$.

[m] Dec and Gill [69].

By way of example, I illustrate here the imprecision of the caloric data by reporting twice the estimated standard deviation, 2σ, for a few representative systems. For the partial molar enthalpy changes on solution $\Delta H_2^\infty(T, P_{s,1})$ obtained from VLE experiments, 2σ/(kJ mol^{-1}) varies from ±0.08 for He/H_2O to ±0.04 for Xe/H_2O and ±0.04 for CH_4/H_2O (all at 298.15 K). The corresponding values for the calorimetrically obtained enthalpies of solution are, respectively, ±0.04, ±0.12 and ±0.07. Similarly, for the partial molar heat capacity changes on solution $\Delta C_{P,2}^\infty(T, P_{s,1})$ at 298.15 K for the same three systems in the same sequence, the imprecision 2σ/(J K mol^{-1}) of the results based upon VLE measurements is ±7, ±3 and ±3, respectively, while for the calorimetrically determined heat capacity changes obtained from the temperature dependence of $\Delta H_2^\infty(T, P_{s,1})$ it amounts to ±7, ±9 and ±3. The imprecision of the *directly* measured $\Delta C_{p,2}^\infty$ of argon in water [25] is ±20 J K^{-1} mol^{-1}. To fully appreciate the quality of the VLE data, please note that they have to survive one (for ΔH_2^∞) or two differentiation steps (for $\Delta C_{P,2}^\infty$)!

For the sake of brevity, I have limited the comparison to 298.15 K, yet essentially the same picture emerges at other temperature too (see Fig. 2): in general, the agreement is outstanding, i.e. usually within the combined experimental error, and may be taken as a tribute to both experimental ingenuity and state-of-the-art data treatment.

Acknowledgements

It is a pleasure to acknowledge the many years of fruitful scientific collaboration with Prof. R. Battino, now Emeritus at Wright State University, Dayton, OH, and several colleagues, post-doctoral fellows and students. The original experimental VLE work with the RBW high-precision gas-solubility apparatus was supported by the Public Health Service of the United States of America via a grant from the National Institute of General Medical Sciences.

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