

# Aqueous solutions of nonelectrolytes

## A molecular thermodynamics perspective

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**Abstract** The liquid state is one of the three principal states of matter and arguably the most important one, the main reasons being the following: (I) the majority of chemical synthesis reactions are liquid-state reactions; (II) separation processes, such as distillation, extraction, and fractional crystallization, are based on vapor–liquid equilibria, liquid–liquid equilibria, and solid–liquid equilibria, respectively, all involving multicomponent mixtures/solutions; (III) when focusing on *water* as solvent, we note that it is the most abundant substance on the surface of the earth, and being the principal constituent (about 70% by weight) of all living organisms, it is essential for life as we know it. Thus, it is not surprising at all that experimental as well as theoretical work on nonelectrolyte solutions in general, and on aqueous solutions of nonelectrolytes in particular, have held prominent positions in (bio-)physical chemistry for more than a century. The insights thereby gained have contributed decisively to build the *formal* structure of chemical thermodynamics and have paved the way for the development of practically useful real-solution *models* needed in *chemical engineering*. In this review, first the thermodynamic formalism relevant for solubility studies as well as a critical discussion of some popular *approximations* will be presented concisely. *Estimation methods* for auxiliary quantities, such as virial coefficients and partial molar volumes at infinite dilution, will be briefly indicated, followed by a summary of *rational*

*strategies* for data reduction and data correlation. Finally, a few eclectically chosen results obtained for dilute aqueous solutions of nonelectrolytes will be linked to *hydrophobic effects*, which are generally accepted to play an important role in a wide variety of biological processes.

**Keywords** Aqueous solutions · Thermodynamics · Enthalpy changes on solution · Heat capacity changes on solution · Hydrophobic effects

### Introduction

More than 60 years ago, Hildebrand and Scott [1] pointed out that “*the entire history of chemistry bears witness to the extraordinary importance of the phenomena of solubility.*” Indeed, *solubility* has remained one of the most important topics in chemistry [2, 3], and solubility data [4] are required in quite diverse areas of the pure and applied sciences, for instance in chemical engineering, geochemistry, environmental science, biophysical chemistry and biophysics, pharmacology, biomedical technology and so forth. In particular the study of the solubility of nonelectrolytes in liquids has been of immense value for the development of the general discipline of mixture thermodynamics. For instance, by introducing idealized solution models, such as the one based on the Lewis–Randall (LR) rule, or the one based on Henry’s law (HL) [3, 5, 6], new classes of thermodynamic functions known as excess functions may be introduced which greatly facilitate the discussion of liquid mixtures and solutions. When the focus is on *water as solvent* [7, 8], we note that (I) water is the most abundant substance on the surface of the earth, (II) it is the only substance that occurs naturally in all three states of matter, and (III) it sustains life as we know it. In fact,

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water is the principal constituent of all living organisms, making up about 70% by weight, or more, for most. Water is important for the structure, the stability and the function of biomolecules, that is to say it has a controlling influence on biochemical processes [9, 10]. Considering all the solubility-related topics indicated above, it is hardly surprising that for more than a century experimental as well as theoretical investigations of solution properties and phase equilibria involving solutions in general, and aqueous solutions in particular, have held prominent positions in (bio-)physical chemistry. The scientific insights gained thereby are invaluable, and besides contributing decisively to the creation of the *formal* structure of chemical thermodynamics they have paved the way for the development of practically useful *models* describing solution behavior in chemical engineering applications [3, 11, 12].

Chemical thermodynamics is a highly formalized scientific discipline of enormous generality. It provides a mathematical framework which yields *exact* relations between macroscopically observable thermodynamic equilibrium properties of matter, establishes rigorous equations applying to phase equilibria, and restricts the behavior of any natural process. While this aspect alone is already of the greatest practical value, in conjunction with appropriate molecular-based models of material behavior, that is to say by using concepts from statistical mechanics, experimentally determined thermodynamic quantities contribute decisively toward a better understanding of molecular interactions. A plenary lecture provides an opportunity to survey a reasonably large area of any scientific discipline and to reflect on it from the perspective of many years of research. As indicated in the title of this review, the field covered here is *aqueous solutions of nonelectrolytes*, a vast topic to which I have contributed for about 35 years. The coverage throughout will be necessarily brief, and for more details the interested reader should consult the pertinent literature listed. My choices for references are illustrative and not comprehensive, simply reflecting my preferences and idiosyncrasies.

The first part of this review will be devoted to the concise presentation of the thermodynamic formalism relevant for solubility studies, while the following section will focus on various popular approximations to the exact relations obtained so far. These approximations are indispensable when practical application of the thermodynamic relations is the goal. In particular, some current estimation techniques for auxiliary quantities, such as virial coefficients and partial molar volumes at infinite dilution, as well as rational strategies for data reduction, data correlation, and prediction will be included [5, 6, 13–15]. Finally, in the next section a few eclectically chosen experimental results obtained for aqueous solutions of nonelectrolytes will be presented, with the solubility of supercritical solutes, i.e., gases, occupying the center stage. Almost inevitably, pride

of place will be given the Henry fugacity (also known as Henry's law constant) [6, 13, 14], which is certainly one of the most often used, yet also one of the most misunderstood quantities in physical chemistry. Together with some closely related derived quantities it is linked to *hydrophobic hydration* and *hydrophobic interaction*, which are generally accepted to play an important role in a wide variety of biological processes, such as protein folding and the self-assembly of amphiphiles into membranes [9, 10, 16–29].

## Thermodynamic fundamentals

When discussing solutions and solubility, say, the solubility of a gas in a liquid at a given temperature  $T$  and pressure  $P$ , one is either interested in *single-phase properties*, such as partial molar volume or partial molar heat capacity, or in quantities which characterize the equilibrium *solubility* itself, for instance the amount of substance  $i$ , the *solute*, dissolved in a given amount of *solvent*  $j$  in the presence of both *coexisting phases*. As already stated in the introduction to this review, only vapor–liquid equilibria (VLE) will be discussed in some detail, and liquid–liquid equilibria (LLE) and solid–liquid equilibria (SLE) will not be considered at all. We only note that experimental LLE and SLE determinations are usually performed under *isobaric* conditions, while VLE experiments are preferably based on *isothermal* measurements.

A general criterion for any phase equilibrium in *PVT*-systems ( $V$  denotes the molar volume) of uniform temperature and pressure is the equality of the chemical potential  $\mu_i^\pi$  of each constituent component  $i$  in all coexisting phases  $\pi$ , or equivalently, the equality of the fugacity  $f_i^\pi$  of each constituent component  $i$  in all coexisting phases  $\pi$  [3, 30]. Specifically, for VLE, where  $\pi$  may designate either vapor (V) or liquid (L), we thus obtain

$$f_i^V(T, P, \{x_i^V\}) = f_i^L(T, P, \{x_i^L\}), \quad i = 1, 2, \dots, N \quad (1)$$

where  $N$  is the number of components,  $\{x_i^V\}$  is the set of vapor-phase mole fractions,  $\{x_i^L\}$  is the set of liquid-phase mole fractions, and  $\sum x_i^\pi = 1$ . For simplicity, however, from now on only *binary systems* will be considered where  $i = 1$  or 2.

The link with any experimental VLE data may be established by two *entirely equivalent* formal approaches presented below [3, 5, 6, 14, 30].

In the first, the equilibrium condition Eq. 1 is rewritten in terms of the fugacity coefficient of component  $i$  in solution in phase  $\pi = V$  or  $\pi = L$ , which quantity is defined by

$$\phi_i^\pi(T, P, \{x_i^\pi\}) = f_i^\pi(T, P, \{x_i^\pi\})/x_i^\pi P \quad (2)$$

Adopting the widely used notation  $x_i^V = y_i$ , and  $x_i^L = x_i$ , the condition for VLE in a binary system may now be expressed as

$$y_i \phi_i^V(T, P, y_i) = x_i \phi_i^L(T, P, x_i), \quad i = 1, 2 \tag{3}$$

For obvious reasons, this approach is known as the  $(\phi, \phi)$  method.

Perfectly general equations, valid for both fluid phases V and L, allow the calculation of the component fugacity coefficients at any desired pressure or amount-of-substance density  $\rho = 1/V$  from *PVT* equations-of-state (EOS) for the mixture/solution. The proviso is, of course, that the EOS is valid over the entire range of integration. In terms of a *volume-explicit* EOS  $Z \equiv PV/RT = Z(T, P, \{x_i^\pi\})$ , where  $Z$  is the compression factor,  $V$  is the molar volume, and  $R$  is the gas constant,

$$\ln \phi_i = \int_0^P \left[ (\partial(nZ)/\partial n_i)_{T,P,n_j} - 1 \right] \frac{dP}{P}, \quad \text{constant } T, \{x_i^\pi\} \tag{4}$$

Here,  $n_i$  is the amount of substance  $i$ , and  $n = \sum n_i$ . When a *pressure-explicit* EOS  $Z = Z(T, V, \{x_i^\pi\})$  is used, we obtain

$$\ln \phi_i = \int_V^\infty \left[ (\partial(nZ)/\partial n_i)_{T,nV,n_j} - 1 \right] \frac{dV}{V} - \ln Z, \quad \text{constant } T, \{x_i^\pi\} \tag{5}$$

Since the majority of the EOS in use is pressure-explicit rather than volume-explicit, the most important exception being the volume-explicit virial EOS, Eq. 5 is more useful in VLE problems than Eq. 4.

In the second approach, while the component fugacities in the vapor phase are again expressed in terms of fugacity coefficients, the liquid-phase fugacities of the components are expressed in terms of appropriately normalized liquid-phase activity coefficients.

When ideal-solution behavior is based on the *Lewis-Randall rule*

$$f_i^{LR}(T, P, x_i) = x_i f_i^{L*}(T, P), \quad 0 \leq x_i \leq 1 \tag{6}$$

and the corresponding activity coefficients are given by

$$\gamma_i^{LR}(T, P, x_i) \equiv f_i^L / f_i^{LR} = f_i^L(T, P, x_i) / x_i f_i^{L*}(T, P), \quad i = 1, 2 \tag{7}$$

Here, the superscript asterisk denotes, as always, a *pure-substance* property:

$$f_i^{L*}(T, P) = P \phi_i^{L*}(T, P) \tag{8}$$

is the fugacity of pure component  $i$  in either a real or a hypothetical liquid state at  $(T, P)$  of the liquid solution, and  $\phi_i^{L*}(T, P)$  is its fugacity coefficient. The activity

coefficients are said to be normalized *symmetrically* when the defining Eq. 7 applies for *all* components, and

$$\gamma_i^{LR} \rightarrow 1 \quad \text{as } x_i \rightarrow 1, \text{ constant } T, P \tag{9}$$

This approach is also known, somewhat loosely, to be based on *Raoult's law*.

Ideal-solution behavior based on *Henry's law* is characterized by

$$f_i^{HL}(T, P, x_i) = x_i h_{i,j}(T, P), \quad 0 \leq x_i \leq 1 \tag{10}$$

and the corresponding activity coefficients are given by

$$\gamma_i^{HL}(T, P, x_i) \equiv f_i^L / f_i^{HL} = f_i^L(T, P, x_i) / x_i h_{i,j}(T, P), \quad i = 1, 2; i \neq j \tag{11}$$

Here,  $h_{i,j}(T, P)$  denotes the *Henry fugacity* of component  $i$  dissolved in liquid  $j$  at  $(T, P)$  of the liquid solution [14]. This quantity is also known as Henry's law constant. The value of the Henry fugacity depends not only on  $T$  and  $P$  but also on the identity of solute  $i$  and solvent  $j$  (the other component), whence the double subscript has been added. The activity coefficients are said to be normalized *unsymmetrically* when for the solvent ( $i = 1$ ) the defining Eq. 7 applies, and for the solute ( $i = 2$ ) the defining Eq. 11 applies, and

$$\gamma_1^{LR} \rightarrow 1 \quad \text{as } x_1 \rightarrow 1, \text{ constant } T, P \tag{12a}$$

$$\gamma_2^{HL} \rightarrow 1 \quad \text{as } x_2 \rightarrow 0, \text{ constant } T, P \tag{12b}$$

Since the limiting value of the ratio  $f_i^\pi / x_i^\pi$  for  $x_i^\pi \rightarrow 0$  at constant  $T$  and  $P$  is known from experiment to be finite, by de l'Hôpital's rule

$$\lim_{x_i^\pi \rightarrow 0} \left( \frac{f_i^\pi}{x_i^\pi} \right) = \left( \frac{df_i^\pi}{dx_i^\pi} \right)_{x_i^\pi=0} = h_{ij}^\pi(T, P), \quad \text{constant } T, P \tag{13}$$

Equation 13 defines the *Henry fugacity* of  $i$  dissolved in  $j$  for any phase  $\pi$  (L or V). It shows that  $f_i^\pi$  becomes zero at  $x_i^\pi = 0$  and identifies the limiting slope of the curve  $f_i^\pi$  vs.  $x_i^\pi$  as the Henry fugacity. *Henry's law* is a *limiting* law and is *approximately* valid for *small* values of  $x_i^\pi$ .

The limiting behavior at the other end of the composition range, i.e. for  $x_i^\pi \rightarrow 1$ , follows from application of the isothermal-isobaric Gibbs–Duhem equation. At constant  $T$  and  $P$  one obtains

$$\lim_{x_i^\pi \rightarrow 1} \left( \frac{f_i^\pi}{x_i^\pi} \right) = \left( \frac{df_i^\pi}{dx_i^\pi} \right)_{x_i^\pi=1} = f_i^{\pi*}(T, P), \quad \text{constant } T, P \tag{14}$$

where  $f_i^{\pi*}(T, P)$  is the fugacity of pure component  $i$  at  $(T, P)$  of the solution and in the *same* physical state. Equation 14 is valid in any phase  $\pi$  (L or V) and shows that in the limit  $x_i^\pi \rightarrow 1$  both  $f_i^\pi$  and its derivative with respect to  $x_i^\pi$  become equal to the fugacity of pure  $i$ . The *Lewis-*

Randall rule is a limiting law and is approximately valid for values of  $x_i^\pi$  near unity.

We note that while Eqs. 13 and 14 are formally similar, for real systems in general  $h_{ij}^\pi(T, P) \neq f_i^{\pi*}(T, P)$ . The ideal-solution model based on the Lewis-Randall rule, i.e., Eq. 6, is preferably used when component  $i$  can exist as a pure liquid at the temperature of the solution. Whenever a component cannot exist as a pure liquid at the temperature of the solution, a situation encountered in solutions of gases (supercritical solutes) in liquids, the alternative ideal-solution model based on Henry's law, i.e., Eq. 10, may be advantageously used for that component (the solute).

The condition for phase equilibrium (VLE) may now be recast either into

$$\phi_i^V(T, P, y_i)y_iP = \gamma_i^{\text{LR}}(T, P, x_i)x_i f_i^{\text{L}*}(T, P) \quad (15)$$

or, equivalently, into

$$\phi_i^V(T, P, y_i)y_iP = \gamma_i^{\text{HL}}(T, P, x_i)x_i h_{i,j}(T, P) \quad (16)$$

where the superscript  $\pi = \text{L}$  of the Henry fugacity has been dropped for convenience. These two approaches are known as the  $(\phi, \gamma)$  methods.

At this juncture, several points should be emphasized; for details see [5, 6, 14, 15, 31–33]. Since the conventions introduced above are all equivalent, the various quantities associated with them are, of course, related. For instance, comparison of Eq. 7 with Eq. 10 shows that ( $i, j = 1, 2; i \neq j$ )

$$\frac{\gamma_i^{\text{LR}}(T, P, x_i)}{\gamma_i^{\text{HL}}(T, P, x_i)} = \frac{h_{i,j}(T, P)}{f_i^{\text{L}*}(T, P)} \quad (17)$$

Thus, in the limit  $x_i \rightarrow 0$  one obtains for the activity coefficient at infinite dilution in the symmetric (LR) convention

$$\gamma_i^{\text{LR}\infty} = h_{i,j}/f_i^{\text{L}*} \quad (18)$$

whence

$$\gamma_i^{\text{HL}} = \gamma_i^{\text{LR}}/\gamma_i^{\text{LR}\infty} \quad (19)$$

For the sake of a more compact notation, the specifications  $(T, P, x_i)$  etc. have been omitted.

By definition, for component  $i$  in solution in any phase  $\pi$ , Eq. 2 applies, whence according to Eq. 13 the important, generally valid relation

$$\begin{aligned} \phi_i^{\pi\infty}(T, P) &= \lim_{x_i^\pi \rightarrow 0} \phi_i^\pi(T, P, x_i^\pi) = \frac{1}{P} \lim_{x_i^\pi \rightarrow 0} \left\{ \frac{f_i^\pi(T, P, x_i^\pi)}{x_i^\pi} \right\} \\ &= \frac{h_{i,j}^\pi(T, P)}{P}, \quad \text{constant } T \text{ and } P \end{aligned} \quad (20)$$

is obtained [6, 14, 31–33], where  $\phi_i^{\pi\infty}(T, P)$  is the fugacity coefficient of component  $i$  at infinite dilution in the phase  $\pi$ . Evidently, Eq. 20 will yield the thermodynamically correct limiting value of the Henry fugacity  $h_{2,1}(T, P_{s,1})$  as solvent critical conditions (critical temperature  $T_{c,1}$ ,

critical pressure  $P_{c,1}$ , and critical molar volume  $V_{c,1}$ ) are approached [5, 6, 14, 31–36]:

$$\lim_{\substack{T \rightarrow T_{c,1} \\ P \rightarrow P_{c,1}}} h_{2,1}(T, P_{s,1}) = P_{c,1} \phi_2^{V\infty}(T_{c,1}, P_{c,1}) \quad (21)$$

where use was made of the equilibrium condition prevailing at the critical point, that is

$$\phi_2^{V\infty}(T_{c,1}, P_{c,1}) = \phi_2^{\text{L}\infty}(T_{c,1}, P_{c,1}) \quad (22)$$

A considerably more elaborate derivation was presented by Beutier and Renon [37]. Equation 21 conclusively shows that Hayduk and Buckley's assertion [38] that the solubilities of gases in a given solvent tend to coincide at a temperature near the solvent's critical is untenable.

The following equations show some rigorous links between a thermodynamic description of a liquid solution/mixture based on activity coefficients and a thermodynamic description based on fugacity coefficients and hence on an EOS. For instance,

$$\gamma_i^{\text{LR}} = \phi_i^{\text{L}}/\phi_i^{\text{L}*} \quad (23)$$

$$\gamma_i^{\text{HL}} = \phi_i^{\text{L}}/\phi_i^{\text{L}\infty} \quad (24)$$

and

$$\gamma_i^{\text{LR}\infty} = \phi_i^{\text{L}\infty}/\phi_i^{\text{L}*} \quad (25)$$

Finally, I emphasize the close connection with residual quantities in  $(T, P, x)$ -space [6, 14]. Note that,

$$\ln \phi_i^{\text{L}*}(T, P) = G_i^{\text{R,L}*}(T, P)/RT \quad (26)$$

where  $G_i^{\text{R,L}*}$  is the residual molar Gibbs energy of pure liquid component  $i$ , and

$$\ln \phi_i^{\text{L}\infty}(T, P) = \mu_i^{\text{R,L}\infty}(T, P)/RT \quad (27)$$

where  $\mu_i^{\text{R,L}\infty}$  is the residual chemical potential of component  $i$  at infinite dilution in the liquid phase.

Equations 3, 15, and 16 may each serve as a rigorous thermodynamic basis for the treatment of VLE. The decision as to which approach should be adopted is by and large a matter of taste and convenience. VLE involving fairly simple fluids may conveniently be treated in terms of the  $(\phi, \phi)$  approach, Eq. 3, because the use of a single EOS valid for both phases V and L has some computational advantage and a certain aesthetic appeal. However, the emphasis is on "fairly simple," since no generally satisfactory EOS for dense fluids of practical, that is to say, chemical engineering importance has as yet been developed. At low to moderate pressures and for mixtures where the critical temperature  $T_{c,i}$  of each component is larger than the experimental temperature, and when the interest is on the composition dependence of the various thermodynamic quantities over the entire composition range  $0 \leq x_i \leq 1$ , VLE data reduction,

VLE calculations and VLE predictions are preferably based on the classical LR ( $\phi$ ,  $\gamma$ ) formalism, Eq. 15, with the symmetric convention for the activity coefficients. However, when we consider a binary system for which component 2, designated the *solute*, is *supercritical*, no experimental vapor pressure of the solute exists, and thus its fugacity  $f_2^{L*}(T, P)$  as a *real*, pure liquid at the temperature of interest does not exist. An alternative approach is required, the most *natural* choice being the use of the HL ( $\phi$ ,  $\gamma$ ) formalism, Eq. 16, for the solute, while for the solvent, component 1, the LR formalism, Eq. 15, is maintained (unsymmetric convention for the activity coefficients). It has the unquestioned advantage that the Henry fugacity  $h_{2,1}$ , and hence  $\gamma_2^{\text{HL}}$ , are unambiguously accessible according to an *experimental* procedure as outlined below; these quantities may be obtained, at least in principle, to any desired degree of accuracy. Since the HL formulation for the component fugacity of the solute,

$$f_2^L(T, P, x_2) = \gamma_2^{\text{HL}}(T, P, x_2)x_2h_{2,1}(T, P) \quad (28)$$

is of central importance in the discussion of *dilute* solutions, it is also frequently used when  $T_{c,i} > T$ , i.e., for subcritical VLE at *high* dilution. We note that rigorous extensions to mixed solvents are rather complex. The ensuing problems have been discussed in depth by Van Ness and Abbott [39].

The Henry fugacity of solute 2 dissolved in liquid solvent 1 is defined by Eq. 14 with  $\pi = \text{L}$ . For VLE, because of the phase equilibrium criteria Eqs. 1 and 2

$$f_2^L = f_2^V = \phi_2^V y_2 P \quad (29)$$

where all quantities refer to the *actual* VLE conditions. Equation 29 in conjunction with Eq. 28 provides a convenient experimental basis for the determination of  $h_{2,1}$  through isothermal extrapolation  $x_2 \rightarrow 0$ . Here,  $\phi_2^V(T, P, y_2)$  must be calculated with a suitable vapor-phase EOS (see Eqs. 4 and 5, and the appropriate section below). Because the equilibrium composition varies with varying total pressure, for *each* composition  $\gamma_2^{\text{HL}}$  and  $h_{2,1}$  refer to a *different* pressure. For the reduction, correlation and further use of solubility data, it is advantageous to select at each temperature the vapor pressure  $P_{s,1}(T)$  of the solvent as reference pressure (the subscript *s* *always* indicates saturation conditions). Thus, Eqs. 28 and 29 lead to

$$h_{2,1}(T, P_{s,1}) = \frac{\phi_2^V(T, P, y_2)y_2P}{x_2} \frac{1}{\gamma_2^{\text{HL}}(T, P_{s,1}, x_2)} \times \exp \left\{ - \int_{P_{s,1}}^P \frac{V_2^L(T, P, x_2)}{RT} dP \right\} \quad (30)$$

where  $V_2^L(T, P, x_2)$  is the partial molar volume of the solute at mole fraction  $x_2$  in the liquid phase. The exponential,

known as a *Poynting factor*, represents the combined contribution of the pressure dependence of the activity coefficient and the Henry fugacity. At low to moderate pressures, and at temperatures well below the critical temperature  $T_{c,1}$  of the solvent, it typically differs from unity by only a few parts per thousand. Evidently, at the vapor pressure  $P_{s,1}(T)$  of the solvent, the Henry fugacity pertaining to the *liquid phase* is rigorously accessible from *isothermal* VLE measurements at decreasing pressure  $P \rightarrow P_{s,1}$ , where also  $x_2 \rightarrow 0$  and  $y_2 \rightarrow 0$ . It is the intercept of a plot of  $\phi_2^V(T, P, y_2)y_2P/x_2$  against  $x_2$ . Once the Henry fugacity has been obtained through extrapolation to  $P_{s,1}$ , Eq. 30 in conjunction with the experimental VLE results at pressures  $P > P_{s,1}$  may be used to obtain constant-temperature, constant-pressure *activity coefficients*  $\gamma_i^{\text{HL}}(T, P_{s,1}, x_2)$ . Their composition dependence may be represented by any appropriate correlating equation compatible with the number and the precision of the experimental results. Equation 30 is the *key equation* in the classical *sequential* approach to gas-solubility *data reduction* (supercritical solute), and is most frequently adopted [5, 6, 14, 40]. It simply reflects the focusing of *interest on the solute* in a composition range very close to pure solvent, though “very close” varies from system to system. It makes little use of the information thermodynamics supplies on the VLE equilibrium equation for the *solvent*, but, of course, for gas-solubility *calculations* it is needed. The resulting expressions are analogous to those used for subcritical, LR-based VLE calculations [30].

To summarize: both the LR and the HL-based approaches outlined above provide adequate prescriptions for data reduction, correlation, and calculation in experimental VLE investigations. In addition, as indicated by Eqs. 26 and 27, the central quantities involved, that is (for a binary system)  $f_1^{L*}$ ,  $f_2^{L*}$ ,  $h_{2,1}$ ,  $\gamma_1^{\text{LR}}$ ,  $\gamma_2^{\text{LR}}$ ,  $\gamma_2^{\text{HL}}$ , are thermodynamic properties pertaining to the *liquid phase*. For instance, LR-based activity coefficients lead to excess molar Gibbs energies

$$G^E = RT \sum_i x_i \ln \gamma_i^{\text{LR}} \quad (31)$$

of the liquid mixture, the temperature dependence of the Henry fugacity is given by

$$\left( \frac{\partial \ln h_{2,1}(T, P)}{\partial T} \right)_P = - \frac{\Delta H_2^\infty(T, P)}{RT^2} \quad (32)$$

and its pressure dependence by

$$\left( \frac{\partial \ln h_{2,1}(T, P)}{\partial P} \right)_T = \frac{V_2^{L\infty}(T, P)}{RT} \quad (33)$$

Here,  $\Delta H_2^\infty \equiv H_2^{L\infty} - H_2^{\text{pg}*}$  is the the molar enthalpy change on solution (enthalpy of solution) with  $H_2^{L\infty}$  denoting the partial molar enthalpy of the solute at infinite dilution in the liquid solvent and  $H_2^{\text{pg}*}$  denoting the molar

enthalpy of the pure solute in the perfect-gas (pg) state.  $V_2^{L\infty}$  is the partial molar volume of the solute at infinite dilution in the liquid solvent 1.

Equation 32 provides the basis for obtaining enthalpies of solution through *van't Hoff analysis* of high-precision solubility data of gases in liquids. Since

$$\left(\frac{\partial \Delta H_2^\infty(T, P)}{\partial T}\right)_P = \Delta C_{P,2}^\infty(T, P) \quad (34)$$

the molar heat capacity change  $\Delta C_{P,2}^\infty \equiv C_{P,2}^{L\infty} - C_{P,2}^{pg*}$  on solution may also be obtained by van't Hoff analysis [5, 6, 8, 13, 14, 40–42]. Here,  $C_{P,2}^{L\infty}$  is the partial molar heat capacity at constant pressure of the solute at infinite dilution in the liquid solvent, and  $C_{P,2}^{pg*}$  is the molar heat capacity at constant pressure of the pure solute in the perfect-gas state.

Equation 33 allows the calculation of the Henry fugacity of solute 2 dissolved in liquid solvent 1 for any desired pressure (*Poynting correction*), which is, perhaps, the main reason why reliable  $V_2^{L\infty}$  data are so much in demand. The analogous equation for the LR activity coefficients ( $i = 1$  or  $2$ ) reads

$$\left(\frac{\partial \ln \gamma_i^{LR}(T, P, x_i)}{\partial P}\right)_{T, x_i} = \frac{V_i^L(T, P, x_i) - V_i^{L*}(T, P)}{RT} \quad (35)$$

and the pressure dependence of the HL activity coefficient is given by

$$\left(\frac{\partial \ln \gamma_2^{HL}(T, P, x_2)}{\partial P}\right)_{T, x_2} = \frac{V_2^L(T, P, x_2) - V_2^{L\infty}(T, P)}{RT} \quad (36)$$

The most important application of VLE relations is in the design of separation processes for the chemical industry. A frequently used measure of the tendency of a given component to distribute itself between the coexisting equilibrium phases is the *vapor–liquid distribution coefficient* or *K value* of solute 2 in solvent 1. It is defined by

$$K_{2,1}(T, P) \equiv \left(\frac{y_2}{x_2}\right)_{\text{equil}} \quad (37)$$

and thus *always* refers to the actual  $T$  and  $P$  at phase equilibrium. With the help of Eq. 3, the *general* expression

$$K_{2,1}(T, P) = \frac{\phi_2^L(T, P, x_2)}{\phi_2^V(T, P, y_2)} \quad (38)$$

is obtained, which provides the link to EOS-based calculations. Using Eq. 20, the infinite-dilution limit of this quantity may be profitably expressed as

$$K_{2,1}^\infty(T, P_{s,1}) = \frac{h_{2,1}(T, P_{s,1})}{\phi_2^{V\infty}(T, P_{s,1})P_{s,1}} \quad (39)$$

which in turn leads to an important relation with the *Ostwald coefficient*  $L_{2,1}^\infty(T, P_{s,1})$  of solute 2 at infinite dilution in solvent 1:

$$K_{2,1}^\infty(T, P_{s,1}) = \frac{1}{L_{2,1}^\infty(T, P_{s,1})} \frac{V_{s,1}^{V*}}{V_{s,1}^{L*}} \quad (40)$$

Here,  $V_{s,1}^{V*}$  and  $V_{s,1}^{L*}$  are the molar volumes of pure saturated vapor and liquid, respectively, and

$$L_{2,1}^\infty(T, P_{s,1}) = \lim_{P \rightarrow P_{s,1}} L_{2,1}(T, P) = \lim_{P \rightarrow P_{s,1}} \left(\frac{\rho_2^L}{\rho_2^V}\right)_{\text{equil}} \quad (41)$$

$L_{2,1}(T, P)$  is the Ostwald coefficient at  $P > P_{s,1}$ ,  $\rho_2 = n_2 / [(n_1 + n_2)V] = x_2/V = x_2\rho$  with the appropriate superscript L or V, is the amount-of-substance concentration (amount-of-substance density) of solute 2 in either the liquid-phase solution or in the coexisting vapor-phase solution at  $T$  and equilibrium pressure  $P$ ,  $V$  is the molar volume of the solution, the amounts of solvent and solute are denoted by  $n_1$  and  $n_2$ , respectively, and  $\sum \rho_i = \rho = 1/V$  is the total amount-of-substance density of the solution. Thus, in contradistinction to the Henry fugacity, which is a *single-phase quantity*, the Ostwald coefficient (like the  $K$ -value) is a *distribution coefficient* pertaining to the solute dissolved in both coexisting phases L and V, and therefore *always refers to the temperature and pressure of the actual VLE* [5, 6, 14, 34–36, 40, 41, 43, 44]. After some algebraic manipulation we obtain

$$L_{2,1}^\infty(T, P_{s,1}) = \frac{RT}{h_{2,1}(T, P_{s,1})V_{s,1}^{L*}} Z_{s,1}^{V*} \phi_2^{V\infty}(T, P_{s,1}) \quad (42)$$

where  $Z_{s,1}^{V*} = P_{s,1}V_{s,1}^{V*}/RT$  is the compression factor of pure saturated solvent vapor.

## Practical implementation and subtleties of approximation

In the preceding section, the thermodynamic formalism as applied to *binary* solutions that contain a supercritical component (gas) has been summarized concisely. This section is devoted to review various approximations to some of the exact relations obtained so far. Indeed, these approximations are essential when practical application is the goal.

Since Henry fugacities and related quantities are usually referred to orthobaric conditions, reliable vapor pressure data are indispensable, as are data on critical temperature, critical pressure and critical volume [45]. For water, Poling et al. recommend  $T_c = 647.14$  K,  $P_c = 22.064$  MPa, and  $V_c = 55.95$  cm<sup>3</sup> mol<sup>-1</sup>.

As pointed out above, when using the classical sequential approach exemplified by Eqs. 13 and 30, a vapor-phase EOS is required for calculating the fugacity coefficient  $\phi_2^V(T, P, y_2)$ . Since the majority of gas-solubility measurements are performed in the low to

moderate pressure domain, virial EOS are frequently used and are superior to cubic EOS. The computational convenience associated with using a volume-explicit virial EOS

$$Z^V(T, P, y_2) \equiv PV^V/RT = 1 + BP/RT \quad (43)$$

in conjunction with Eq. 4 leads to the widely used expression for the fugacity coefficient of component  $i$  in a binary vapor mixture

$$\ln\phi_i^V = \frac{P}{RT} (B_{ii} + y_j^2\delta_{12}), \quad i, j = 1, 2, \quad i \neq j \quad (44)$$

with  $\delta_{12} = 2B_{12} - (B_{11} + B_{22})$ . Here,  $B = y_1B_{11} + y_2B_{22} + y_1y_2\delta_{12}$  is the second virial coefficient of the mixture,  $B_{11}$  and  $B_{22}$  are the second virial coefficients of the pure components, and  $B_{12}$  designates a composition-independent interaction virial coefficient (cross-coefficient). The fugacity coefficient of the solute at infinite dilution in the vapor phase is thus given by

$$\ln\phi_2^{V\infty} = \frac{P}{RT} (2B_{12} - B_{11}) \quad (45)$$

and the fugacity coefficient of pure component 2 by

$$\ln\phi_2^{V*} = \frac{P}{RT} B_{22} \quad (46)$$

The quite popular rule-of-thumb  $\phi_2^V(T, P, y_2) = \phi_2^{V*}(T, P)$  may frequently be rather unsatisfactory: for the evaluation of  $\phi_2^{V\infty}$  it only holds if  $B_{12} = (B_{11} + B_{22})/2$ .

Frequently, experimental results [46, 47] on second virial coefficients for mixtures are not available, and even for pure water vapor the situation below about 400 K is not entirely satisfactory and subject to intensive research [48]. Thus, one depends heavily on semiempirical estimation methods, which are predominantly based on the *extended corresponding states theorem*. One of the most popular and reliable methods is due to Tsonopoulos and Dymond [49] which, since its inception in 1974, has been revised and extended several times. In order to estimate second virial cross-coefficients  $B_{ij}$ , appropriate semiempirical *combining rules* have to be used to obtain the characteristic parameters pertaining to the unlike interaction from the pure-substance quantities. Almost inevitably, these combining rules incorporate a binary interaction parameter  $k_{ij}$  (usually much smaller than 1) which improves on the geometric-mean approximation for the *pseudo-critical* temperature:

$$T_{c,ij} = (1 - k_{ij})(T_{c,i}T_{c,j})^{1/2} \quad (47)$$

It is, in fact, the most crucial combining rule for the prediction of  $B_{ij}$ . Experiment-based optimized values of  $k_{ij}$  for quite a few mixtures have been reported in the literature, together with appropriate correlations, each valid for a given type of mixture. For instance, for

binaries where both components belong to essentially nonpolar hydrocarbons, or rare gases or simple molecular gases,  $k_{ij}$  may be estimated from [45]

$$k_{ij} = 1 - \frac{8(V_{c,i}V_{c,j})^{1/2}}{(V_{c,i}^{1/3} + V_{c,j}^{1/3})^3} \quad (48)$$

In the key relation Eq. 30, the influence of composition upon the liquid-phase fugacity has been separated formally from the influence of pressure (see Eqs. 33 and 36). However, a rigorous evaluation of the Poynting integral would require detailed knowledge of the composition dependence as well as the pressure dependence of the *partial molar volume*  $V_2^L(T, P, x_2)$  at each temperature of interest. However, such comprehensive information will rarely be available, whence for the great majority of solutions approximations at various levels of sophistication must be introduced to render VLE data reduction tractable. The situation becomes particularly demanding at high pressures and/or when the critical region is approached, where the Poynting corrections become significant.

With solubility experiments, the focus is on the thermodynamics at *high* dilution, and typical gas-solubility measurements do *not* cover large composition ranges. At pressures reasonably close to  $P_{s,1}$ , and thus at *very* small mole fractions  $x_2$ , and at temperatures well below the critical temperature of the solvent, to an excellent approximation  $V_2^L(T, P, x_2)$  of Eq. 30 may be replaced by a pressure-independent partial molar volume at infinite dilution  $V_2^{L\infty}(T, P_{s,1})$ . Since inevitable experimental scatter often tends to obscure the composition dependence of any activity coefficient  $\gamma_2^{\text{HL}}(T, P_{s,1}, x_2)$  for  $x_2 \rightarrow 0$ , we may now assume  $\gamma_2^{\text{HL}} \cong 1$ , independent of composition. These approximations lead to the *Krichevsky–Kasarnovsky* equation

$$\ln h_{2,1}(T, P_{s,1}) = \ln \left( \frac{\phi_2^V(T, P, y_2)y_2P}{x_2} \right) - \frac{(P - P_{s,1})V_2^{L\infty}(T, P_{s,1})}{RT} \quad (49)$$

Evidently, the partial molar volume of the solute at infinite dilution is important in the reduction and correlation of accurate solubility measurements. The preferred experimental methods for determining  $V_2^{L\infty}$  are either precision dilatometry or precision densimetry or magnetic float methods [50–53]. However, experimental results on  $V_2^{L\infty}$  of gases dissolved in liquids are not plentiful, whence reliable semi-empirical estimation methods are required. For instance, partial molar volumes of gases at infinite dilution in non-aqueous solvents will usually be predicted to within about  $\pm 10\%$  by the Handa–Benson correlation

$$\frac{P_{c,2}V_2^{L\infty}}{RT_{c,2}} = 0.088 + 2.763 \frac{TP_{c,2}}{T_{c,2}\Pi_{s,1}^{L*}} \quad (50)$$

where

$$\Pi_{s,1}^{L*} = \frac{T\alpha_{P,s,1}^{L*}}{\beta_{T,s,1}^{L*}} - P_{s,1} \quad (51)$$

is the internal pressure,  $\alpha_{P,s,1}^{L*}$  is the isobaric expansivity, and  $\beta_{T,s,1}^{L*}$  is the isothermal compressibility, respectively, of the pure, saturated liquid solvent. Scaled particle theory (SPT) has been used successfully by Pierotti [54], among others, to calculate  $V_2^{L\infty}$  of non-polar and polar gases in non-polar and polar solvents including water. The SPT expressions for this quantity are well known and may easily be found in the literature. As emphasized by Wilhelm and Battino [55, 56], the use of self-consistent molecular parameters, that is of *effective* Lennard–Jones (6, 12) parameters, is of central importance. The correlational and predictive powers of the SPT-based approach can be substantially improved by introducing the concept of *temperature-dependent effective size parameters* as suggested by Wilhelm [57], and more recently by Schulze and Prausnitz [58].

The development of new experimental techniques to VLE in general, and as applied to dilute solutions in particular, continues unabated. These efforts are stimulated not only by theory-related aspects, but also by a growing awareness of the practical value of highly accurate thermodynamic data. Those potentially interested in building precision equipment are referred to reviews, for instance, by Raal and Ramjugernath [59], Richon and de Loos [60], Wilhelm [14], Maurer and Pérez-Salado Kamps [61], Matouš et al. [62], Raal and Ramjugernath [63], and Dohnal [64].

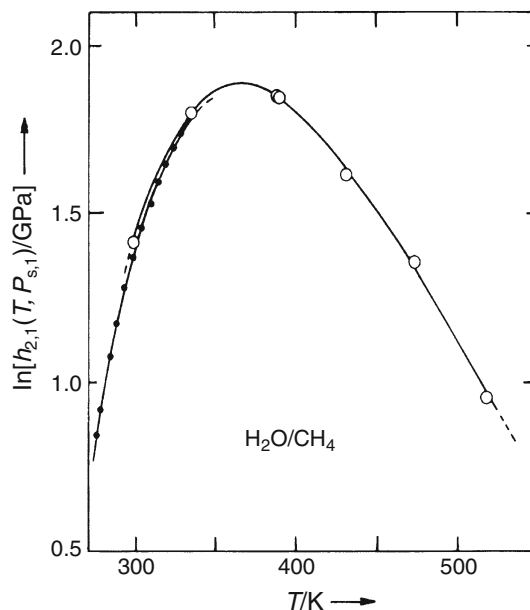
Once experimental Henry fugacities for a specific binary solution have been determined over a reasonably large temperature range, the question arises as to their most satisfactory mathematical representation as a function of temperature. Depending on the choice of variables, that is  $T$  or  $T^{-1}$ , for expanding the enthalpy of solution, either the *Clarke–Glew* equation [65]

$$\ln[h_{2,1}(T, P_{s,1})/\text{Pa}] = A_0 + A_1(T/\text{K})^{-1} + A_2\ln(T/\text{K}) + \sum_{i=3}^n A_i(T/\text{K})^{i-2} \quad (52)$$

or the *Benson–Krause* (BK) equation [66]

$$\ln[h_{2,1}(T, P_{s,1})/\text{Pa}] = \sum_{i=0}^m a_i(T/\text{K})^{-i} \quad (53)$$

is obtained. On the basis of the ability to fit high-precision Henry fugacity data over large temperature ranges, and of simplicity, the BK power series in  $T^{-1}$  appears to be superior.



**Fig. 1** Plot of  $\ln[h_{2,1}(T, P_{s,1})/\text{GPa}]$  against temperature  $T$  for methane dissolved in liquid water.  $h_{2,1}(T, P_{s,1})$  denotes the Henry fugacity (Henry’s law constant) at temperature  $T$  and vapor pressure  $P_{s,1}(T)$ . *Filled circles*, experimental results of Rettich et al. [40]; the average percentage deviation of the Henry fugacity from the value calculated via the correlating BK function (see text) is about  $\pm 0.05\%$ ; *open circles*, experimental results of Crovetto et al. [67]; the average percentage deviation of the Henry fugacity from the value calculated via the correlating BK function (see text) is about  $\pm 2\%$

At this juncture I would like to emphasize that the frequently found sweeping statement “the solubility of a gas in a liquid decreases with increasing temperature” is misleading/incorrect when the entire liquid range between the triple point and the critical point of the solvent is considered. For many systems, the following behavior is well documented: at low temperatures near the solvent triple point,  $h_{2,1}(T, P_{s,1})$  first *increases* with increasing temperature, then goes through a *maximum* to *decrease* toward the *exact* limiting value given by Eq. 21. As an example, Fig. 1 shows a plot of  $h_{2,1}(T, P_{s,1})$  plotted against temperature for methane dissolved in liquid water [40, 67], a solution which plays an important role in discussions of hydrophobicity. When the critical point of the solvent is approached along the coexistence curve, for *volatile* solutes the limiting temperature derivative of the Henry fugacity is given by [68, 69]

$$\lim_{\substack{T \rightarrow T_{c,1} \\ P \rightarrow P_{c,1}}} \frac{d \ln[h_{2,1}(T, P_{s,1})/\text{Pa}]}{dT} = -\infty \quad (54)$$

During the last 20 years or so, several equations for presenting the temperature dependence of the Henry fugacity between the triple point temperature and the critical temperature of the solvent were developed to incorporate the thermodynamically correct limiting behavior indicated by



Eqs. 21 and 54. For details I refer to [14] and the original literature cited therein.

Until the mid-eighties, high-precision measurements of Henry fugacities over temperature ranges large enough to permit reliable *van't Hoff analysis* constituted the only source of information on *partial molar enthalpy changes on solution*  $\Delta H_2^\infty(T, P_{s,1})$ , see Eq. 32, and a fortiori on *partial molar heat capacity changes on solution*  $\Delta C_{P,2}^\infty(T, P_{s,1})$ , see Eq. 34. Since the experimental Henry fugacities at different temperatures refer to different saturation pressures  $P_{s,1} = P_{s,1}(T)$ , Eqs. 32 and 34 have to be augmented accordingly, as detailed by Wilhelm [6, 11, 13, 42] and in earlier references quoted therein. For instance, selecting a BK-type fitting equation to represent the temperature dependence of the  $h_{2,1}(T, P_{s,1})$  data, we obtain

$$\frac{\Delta H_2^\infty(T, P_{s,1})}{RT} = \sum_{i=1}^m ia_i(T/K)^{-i} + \frac{V_2^{L\infty}}{R} \frac{dP_{s,1}}{dT} \quad (55)$$

These supplemental terms (here it is only one term, the second term on the right-hand side of Eq. 55) containing  $V_2^{L\infty}$  and its derivatives with respect to  $T$  and  $P$  together with  $dP_{s,1}/dT$  and  $d^2P_{s,1}/dT^2$  and so forth—now referred to in the literature [69, 70] as *Wilhelm terms*—have been long overlooked. Their contributions increase rapidly with increasing temperature. 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, and the partial molar enthalpy at infinite dilution,  $H_2^{L\infty}$ , will diverge in exactly the same manner. The important experiments of Wood and collaborators confirm these expectations [53, 71–74].

In [42], we recently presented a comprehensive compilation and comparison, at  $T = 298.15$  K and  $P_{s,1} = 3.1691$  kPa, of partial molar enthalpy changes on solution,  $\Delta H_2^\infty(T, P_{s,1})$  and partial molar heat capacity changes on solution,  $\Delta C_{P,2}^\infty(T, P_{s,1})$ , for 32 gases in liquid water (in a few cases the solutes were, in fact, subcritical vapors, i.e.,  $298.15$  K  $< T_c$ , 2). The comparison was between results obtained via *van't Hoff analysis* of high-precision solubility data and *calorimetrically* determined values, which is also contained here, in Table 1, for argon, oxygen, and methane in water.

When measured over a sufficiently large temperature range, calorimetry-based  $\Delta H_2^\infty(T, P_{s,1})$  may in turn be used to to *calculate*  $\Delta C_{P,2}^\infty(T, P_{s,1})$  according to

$$\Delta C_{P,2}^\infty(T, P_{s,1}) = \frac{d\Delta H_2^\infty(T, P_{s,1})}{dT} - \left[ V_2^{L\infty} - T \left( \frac{\partial V_2^{L\infty}}{\partial T} \right)_P \right] \frac{dP_{s,1}}{dT} \quad (56)$$

However, in the temperature regions considered so far the second term on the right-hand side of Eq. 56 is usually

**Table 1** Partial molar enthalpy changes on solution  $\Delta H_2^\infty(T, P_{s,1})$  and partial molar heat capacity on solution  $\Delta C_{P,2}^\infty(T, P_{s,1})$  of argon, oxygen and methane dissolved in liquid water at  $T = 298.15$  K and  $P_{s,1} = 3.1691$  kPa: comparison of values obtained via *van't Hoff analysis* of high-precision gas solubility data with values obtained by calorimetric methods

Gas	$10^{-3}\Delta H_2^\infty(T, P_{s,1})/(\text{J mol}^{-1})$		$\Delta C_{P,2}^\infty(T, P_{s,1})/(\text{JK}^{-1}\text{mol}^{-1})$	
	van't Hoff	Calorimetry	van't Hoff	Calorimetry
Ar	-11.95 [66]	-12.01 [76]	186 [66]	200 [76]
	-11.92 [70]	-11.94 [77]	195 [70]	189 [72]
	-11.96 [75]		192 [75]	
O <sub>2</sub>	-12.19 [66]	-12.06 [79]	192 [66]	205 [76]
	-12.01 [78]	-12.03 [80]	196 [78]	
	-11.97 [41]	-12.00 [76]	200 [41]	
CH <sub>4</sub>	-13.19 [40]	-13.06 [76]	237 [40]	242 [76]
		-13.18 [81]		218 [83]
		-13.12 [82]		209 [82]
			212 [74]	

smaller than the experimental imprecision, whence the approximate equation

$$\Delta C_{P,2}^\infty(T, P_{s,1}) \approx \frac{d\Delta H_2^\infty(T, P_{s,1})}{dT} \quad (57)$$

is entirely satisfactory.

Direct calorimetric determinations of the high-dilution partial molar enthalpy change on solution of a gas in a liquid have been carried out by only a limited number of researchers, essentially because of the experimental difficulties associated with accurately measuring small heat effects in very dilute solutions (typically, mole fraction solubilities at 0.1 MPa gas pressure are about  $10^{-4}$ – $10^{-5}$ ). A fortiori this is the case for *directly* measured heat capacities of gases dissolved in water: there exist only *seven sets* of such data, all originating from the laboratory of R. H. Wood at the University of Delaware in Newark, Delaware, USA. Wood and collaborators [72, 73] determined the *apparent* molar heat capacities of four inert solutes, i.e., of aqueous argon, xenon [73], methane [74], and ethene [73] (and of aqueous CO<sub>2</sub>, H<sub>2</sub>S, and NH<sub>3</sub> [74]) over very large temperature ranges with sophisticatedly constructed flow calorimeters. Although these calorimetric measurements were all performed at elevated pressures between, roughly, 17 and 32 MPa, the mole fractions of the dissolved gases are small enough to make the apparent molar heat capacities *approximately equal* to the partial molar heat capacities at infinite dilution within experimental error (at temperatures below ca. 500 K). Evidently, much more experimental calorimetric work on simple aqueous solutions would be desirable.

The large partial molar heat capacity changes  $\Delta C_{p,2}^\infty(T, P_{s,1})$  observed when nonpolar molecules are dissolved in water are widely regarded as *the* signature of hydrophobicity, and have been connected with some unspecified ordering of the water molecules around the solute (exemplified by the famous “iceberg model” of Frank and Evans [84]). The picture that emerges from structural studies, using the method of neutron diffraction and isotopic substitution, on aqueous solutions of methane [85] is the following: the solute is surrounded by a relatively strong first coordination shell containing about 19 water molecules which are oriented tangentially to the CH<sub>4</sub> molecule, with no evidence of a second coordination shell. There is reasonably good agreement between these observations and those deduced from theoretical model calculations and computer simulations [86], though the interaction between the apolar molecules and water appears to be much shorter-ranged than suggested by the model calculations. At elevated temperatures, these pseudo-clathrate cages should gradually disappear, and concomitantly the partial molar heat capacity  $C_{p,2}^{L,\infty}$  at constant pressure of solute 2 at infinite dilution in liquid water should diminish, though it will increase again, and eventually diverge to  $+\infty$  when the critical point of water is approached from *lower* temperatures.

Comparing thermodynamically rigorous van't Hoff-derived enthalpy changes (*one* differentiation level with respect to temperature) and heat capacity changes (*two* differentiation levels with respect to temperature), both referring to infinitely dilute solutions of gases in water, with high-precision calorimetric results constitutes a severe quality test of solubility data. In general, the agreement between these two approaches was found to be entirely satisfactory, as shown by Wilhelm [13, 14] and by Wilhelm and Battino [42]: it was usually within the combined experimental errors. What better tribute to both experimental ingenuity and state-of-the-art data treatment can one wish for!

### Concluding remarks

Chemical thermodynamics of solutions in general, and of aqueous solutions in particular, continue to be exciting, developing fields which, combined with advances in the statistical-mechanical treatment of solutions and increasingly sophisticated computer simulations, provide new insights and stimulating connections at a microscopic level. The major driving forces for progress in instrumentation are the desire to increase the application range, to increase precision and accuracy, to improve on the speed of measurement, and to facilitate application [5, 11,

12, 87]. In this review, I have concisely presented the thermodynamic formalism relevant to the study of dilute solutions of nonelectrolytes, the focus being on aqueous solutions. Two intimately related topics have been dealt with prominently:

- adequate discussion of solution behavior in terms of the *Henry fugacity* (also known as Henry's law constant) and related quantities, such as *activity coefficients* and *fugacity coefficients*;
- reconciliation of results for caloric quantities (e.g.  $\Delta H_2^\circ$  and  $\Delta C_{p,2}^\circ$ ) derived from solubility measurements via *van't Hoff analysis* with those measured directly with *calorimeters*.

They both present the state of the art to the potential experimentalist. Finally, I would like to point out that cross-fertilization with neighboring disciplines has always been a potent stimulus in science. This is particularly true for research on the solubility of gases in liquid water, which contributes greatly to our understanding of hydrophobic effects which play a central role in biology. The increasing number of investigations with a strong biophysical and/or biomedical flavor is thus not surprising.

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