

# **Theory, Techniques and Results**



## CHAPTER 1

# *Thermodynamics of Nonelectrolyte Solubility*

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*Magic means rather different things to different people.*

Brigadier Donald Ffellowes in “*The Kings of the Sea*”, by S.E. Lanier,  
*The Magazine of Fantasy & Science Fiction*, November 1968.

## 1.1 Introduction

The liquid state is one of the three principal states of matter. The majority of chemical synthesis reactions are carried out in the liquid state, and separation processes usually involve liquid/fluid states, *i.e.* solutions. Thus, not surprisingly, for a century and a half experimental investigations of physical properties of solutions and of phase equilibria involving solutions (vapour–liquid equilibrium: VLE; liquid–liquid equilibrium: LLE; solid–liquid equilibrium: SLE; solid–vapour equilibrium: SVE) have held a prominent position in physical chemistry. The scientific insights gained in these studies can hardly be overrated, and have been of immense value for the development of the highly formalized, general discipline of mixture thermodynamics, for instance by providing idealized solution models, such as the one based on the Lewis–Randall (LR) rule, or the one based on Henry’s law (HL). In addition to its profound theoretical interest, this topic includes many important practical, industrial applications in chemical process design, in the environmental sciences, in geochemistry, in biomedical technology and so forth. Water is the most abundant liquid on the earth, and because it sustains life as we know it, it is also the most important liquid solvent. The preponderance of scientific papers dealing with aqueous solutions is thus not surprising. We note that the study of the solubility in water of the rare gases and of simple hydrocarbons have provided fundamental information on hydrophobic effects that are thought to be of pivotal importance for the formation and stability of higher order structures of biological substances, such as proteins, nucleic acids, and cell membranes.

Evidently, this short review cannot possibly be comprehensive, and I shall focus on just a few topics which reflect my current research interests and idiosyncrasies. For instance, VLE with supercritical solutes, that is the solubility of gases in liquids, will be discussed in some detail, and so will the van't Hoff type analysis of high-precision solubility data. SLE and SVE will not be considered at all. Almost inevitably, pride of place will be given to the Henry fugacity,<sup>1</sup> or Henry's law constant, which is one of most misunderstood thermodynamic quantities. The goal is to clarify some points often overlooked, and to dispel misconceptions frequently encountered in the literature.

## 1.2 Thermodynamics

In this section I will present a brief overview of classical thermodynamics applicable to nonelectrolyte solutions in general,<sup>2</sup> and to solutions of gases in liquids in particular.<sup>1,3-6</sup> When discussing solutions, one is either interested in *single-phase properties*, such as partial molar volumes, 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*. The equations governing VLE and LLE will be considered first. For details see refs. 1 and 2.

A general criterion for phase equilibrium at temperature  $T$  and pressure  $P$  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 component in all coexisting phases. Thus, for the specific case of VLE ( $\pi = V$  or L),

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

where  $N$  is the number of components present, each with mole fraction  $x_i^V$  in the vapour phase and  $x_i^L$  in the liquid phase. Similarly, for LLE ( $\pi = L'$  or L'')

$$f_i^{L'}(T, P, \{x_i^{L'}\}) = f_i^{L''}(T, P, \{x_i^{L''}\}), \quad i = 1, 2, \dots, N \quad (2)$$

From now on, however, I shall confine attention to *binary* systems, where  $i = 1$  or 2.

Two entirely *equivalent* formal procedures are commonly used to establish the link with experimental reality:

(I) When using the fugacity coefficient of component  $i$  in solution in phase  $\pi$ , which quantity is defined by

$$\phi_i^\pi(T, P, \{x_i^\pi\}) = f_i^\pi(T, P, \{x_i^\pi\})/x_i^\pi P \quad (3)$$

and adopting the convenient notation  $x_i^V = y_i$ ,  $x_i^L = x_i$ , and dropping the superscript L where unambiguously permissible, the condition for thermodynamic equilibrium (VLE) may be expressed as

$$y_i \phi_i^V(T, P, y_i) = x_i \phi_i^L(T, P, x_i) \quad (4)$$

and for LLE as

$$x'_i \phi_i^{\text{L}'}(T, P, x'_i) = x''_i \phi_i^{\text{L}''}(T, P, x''_i) \quad (5)$$

This approach is called, for obvious reasons, the  $(\phi, \phi)$  method.

(II) In the second procedure, the component fugacities in the vapour phase are again expressed in terms of fugacity coefficients, whereas the liquid-phase fugacities of the components are expressed in terms of appropriately normalized liquid-phase activity coefficients.

When based on the LR rule the convention is called *symmetric*, and the corresponding activity coefficient is given by

$$\gamma_i^{\text{LR}}(T, P, x_i) = f_i^{\text{L}}(T, P, x_i) / x_i f_i^{\text{L}*}(T, P) \quad (6)$$

where the superscript asterisk denotes, as always, a pure substance property:  $f_i^{\text{L}*}(T, P) = P \phi_i^{\text{L}*}(T, P)$  is the *fugacity of pure component i* in either a real or a hypothetical liquid state at  $(T, P)$  of the liquid solution, and  $\phi_i^{\text{L}*}(T, P)$  is its fugacity coefficient.

When based on HL the convention is called *unsymmetric*, and leads to

$$\gamma_i^{\text{HL}}(T, P, x_i) = f_i^{\text{L}}(T, P, x_i) / x_i h_{i,j}(T, P) \quad (7)$$

where  $h_{i,j}(T, P)$  is the *Henry fugacity of i dissolved in liquid j* at  $(T, P)$  of the liquid solution.<sup>1</sup> This quantity is also known as Henry's law constant. It is defined for any phase  $\pi$  (L or V) by

$$\lim_{x_i^\pi \rightarrow 0} (f_i^\pi / x_i^\pi) = (df_i^\pi / dx_i^\pi)_{x_i^\pi=0} = h_{i,j}^\pi(T, P) \quad (8)$$

where all the operations are at *constant T and P*.

The VLE conditions may thus be recast into

$$\phi_i^{\text{V}}(T, P, y_i) y_i P = \gamma_i^{\text{LR}}(T, P, x_i) x_i f_i^{\text{L}*}(T, P) \quad (9)$$

or, equivalently, into

$$\phi_i^{\text{V}}(T, P, y_i) y_i P = \gamma_i^{\text{HL}}(T, P, x_i) x_i h_{i,j}(T, P) \quad (10)$$

where the superscript  $\pi = \text{L}$  of the Henry fugacity has been dropped for convenience. This approach is called the  $(\phi, \gamma)$  method.

For LLE we may write either

$$x'_i \gamma_i^{\text{LR}}(T, P, x'_i) = x''_i \gamma_i^{\text{LR}}(T, P, x''_i) \quad (11)$$

or equivalently

$$x'_i \gamma_i^{\text{HL}}(T, P, x'_i) = x''_i \gamma_i^{\text{HL}}(T, P, x''_i) \quad (12)$$

For VLE, there exists in principle a third procedure in which the component fugacities in the liquid phase *as well as* in the vapour phase are expressed in terms of activity coefficients ( $\gamma_i^{\text{L,LR}}, \gamma_i^{\text{V,LR}}, \gamma_i^{\text{L,HL}}, \gamma_i^{\text{V,HL}}$ ). However, to the best of my knowledge, it has never been utilized.

By definition, for component  $i$  in solution in *any* phase  $\pi$ , Equation (3) applies, hence according to Equation (8) the important, *generally valid* relation

$$\begin{aligned}\phi_i^{\pi\infty}(T, P) &= \lim_{x_i^\pi \rightarrow 0} \phi_i^\pi(T, P, x_i^\pi) \\ &= \frac{1}{P} \lim_{x_i^\pi \rightarrow 0} [f_i^\pi(T, P, x_i^\pi)/x_i^\pi] \\ &= h_{i,j}^\pi(T, P)/P\end{aligned}\quad (13)$$

is obtained,<sup>1,4-6</sup> where  $\phi_i^{\pi\infty}(T, P)$  is the fugacity coefficient of  $i$  at infinite dilution in the phase  $\pi$ .

As this juncture, several points should be emphasized. While

$$f_i^{\text{L}*}(T, P)/P = \phi_i^{\text{L}*}(T, P) = \exp\left(G_i^{\text{R,L}*}(T, P)/RT\right)\quad (14)$$

is a property, at  $(T, P)$ , of *pure liquid*  $i$  ( $G_i^{\text{R,L}*}$  denotes the residual molar Gibbs energy), the Henry fugacity defined by Equation (8) for the liquid solution phase ( $\pi = \text{L}$ ) is a *liquid-phase* property which depends on  $(T, P)$  and the chemical identity of *both* solute  $i$  and solvent  $j$  (hence the double subscript!):<sup>1,4-6</sup>

$$h_{i,j}(T, P)/P = \phi_i^{\text{L}\infty}(T, P) = \exp\left(\mu_i^{\text{R,L}\infty}(T, P)/RT\right)\quad (15)$$

Here,  $\phi_i^{\text{L}\infty}$  is the fugacity coefficient of component  $i$  at infinite dilution in the liquid solvent  $j$ , and  $\mu_i^{\text{R,L}\infty}$  is the corresponding residual chemical potential.

The various quantities corresponding to the two conventions introduced above are, of course, related. For instance,

$$\gamma_i^{\text{LR}} = \phi_i^{\text{L}}/\phi_i^{\text{L}*}\quad (16)$$

$$\gamma_i^{\text{HL}} = \phi_i^{\text{L}}/\phi_i^{\text{L}\infty}\quad (17)$$

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

where  $\gamma_i^{\text{LR}\infty}$  denotes the activity coefficient at infinite dilution. For details see ref. 1 and the literature cited therein.

Equations (4), (9), and (10) may each serve as a rigorous thermodynamic basis for the treatment of VLE. The decision as to which approach should be adopted for solving actual problems is by and large a matter of taste and/or convenience, yet is subject to important practical constraints.

VLE involving fairly simple fluids may conveniently be treated in terms of the  $(\phi, \phi)$  approach, Equation (4), because the use of a single equation of state (EOS) valid for *both* phases V and L has some computational advantage and a certain aesthetic appeal. However, since no generally satisfactory EOS for dense fluids of practical, that is technical, importance has as yet been developed, this approach is rather limited. The situation is further aggravated by the

sensitivity of results on the so-called mixing rules and combining rules,<sup>7,8</sup> which have always an empirical flavour.

At low to moderate pressures, data reduction and VLE calculations are preferably based upon the classical  $(\phi, \gamma)$  formalism expressed by Equations (9) and (10). Here, an EOS is required only for the low-density vapour phase for which satisfactory models based on virial coefficients are available, while for the liquid phase a suitable activity coefficient model is introduced.

For LLE, similar comments apply: in the majority of cases the  $(\gamma, \gamma)$  method is used.

Gas solubilities are usually measured at isothermal conditions. Since the equilibrium composition varies with total pressure, for each composition the quantities  $\phi_i^V$ ,  $\phi_i^L$ ,  $\gamma_i^{LR}$ ,  $\gamma_i^{HL}$ ,  $f_i^*$ , and  $h_{2,1}$  refer to a *different* pressure. For the reduction and correlation of solubility data it is customary and advantageous to select for each temperature the vapour pressure  $P_{s,1}(T)$  of the solvent as reference pressure (the subscript s always indicates saturation condition). For temperatures well below the critical temperature of the solvent, the respective correction terms, known as *Poynting integrals*, are usually quite small.<sup>1-3,7,9,10</sup> If so desired, conversion to any other reference pressure is, in principle, straightforward.

According to Equation (8), the Henry fugacity of solute 2 dissolved in liquid solvent 1 is defined by

$$h_{2,1} = \lim_{x_2 \rightarrow 0} (f_2^L/x_2) \quad (19)$$

For VLE, because of the phase equilibrium criterion (1),  $f_2^L$  may be set equal to the fugacity of the solute in the coexisting vapour phase, that is

$$f_2^L = f_2^V = \phi_2^V y_2 P \quad (20)$$

At the vapour pressure  $P_{s,1}$ , the Henry fugacity pertaining to the *liquid phase* is thus rigorously accessible from *isothermal* VLE measurements at decreasing total pressure  $P \rightarrow P_{s,1}$  according to

$$h_{2,1}(T, P_{s,1}) = \lim_{x_2 \rightarrow 0} [\phi_2^V(T, P, y_2) y_2 P/x_2] \quad (21)$$

Entirely equivalent expressions relating the Henry fugacity to limiting slopes, (see Equation (8)), may be derived. We note that from the VLE measurements at  $P > P_{s,1}$  the liquid-phase activity coefficient  $\gamma_2^{HL}$  may be extracted, though frequently experimental imprecision precludes obtaining reliable results.

Another versatile and widely used measure of the solubility of a gas in a liquid is the *Ostwald coefficient*.<sup>1,3,9-11</sup> It is defined by

$$L_{2,1}(T, P) = (\rho_2^L/\rho_2^V)_{\text{equil}} \quad (22)$$

where  $\rho_2 = n_2/v = x_2/V = x_2\rho$ , with the appropriate superscript L or V, is the amount-of-substance concentration of solute 2 in either the liquid-phase solution or in the *coexisting* vapour-phase solution at  $T$  and equilibrium pressure  $P$ .

The amounts of solvent 1 and solute 2 are denoted by  $n_1$  and  $n_2$ , respectively,  $v = (n_1 + n_2)V$ ,  $V = \rho^{-1}$  is the molar volume of the solution (L or V), and  $\rho$  is the (total) molar density of the solution. Thus in contradistinction to the Henry fugacity, the Ostwald coefficient is a *distribution coefficient* pertaining to the solute dissolved in the coexisting phases L and V. It therefore *always* refers to  $T$  and  $P$  of the *actual* VLE. After some algebraic manipulation one can show that<sup>12</sup>

$$\begin{aligned} L_{2,1}^\infty(T, P_{s,1}) &= \lim_{P \rightarrow P_{s,1}} L_{2,1}(T, P) \\ &= \frac{RT}{h_{2,1}(T, P_{s,1})V_{s,1}^{L*}} Z_{s,1}^{V*} \phi_2^{V\infty}(T, P_{s,1}) \end{aligned} \quad (23)$$

where  $Z_{s,1}^{V*} = P_{s,1}V_{s,1}^{V*}/RT$  is the compression factor of pure saturated solvent vapour,  $V_{s,1}^{V*}$  is the molar volume of pure saturated solvent vapour,  $V_{s,1}^{L*}$  is the molar volume of pure saturated liquid solvent, and  $\phi_2^{V\infty}$  is the fugacity coefficient of the solute in the vapour phase at infinite dilution. When correlating solubility data over wide temperature ranges up to the critical point, it might be advantageous to use  $L_{2,1}^\infty$  instead of  $h_{2,1}$ .<sup>13,14</sup>

The most important application of VLE relations is in the design of zseparation processes. A frequently used measure of the tendency of a given component to distribute itself in one or the other equilibrium phase is the *vapour-liquid distribution coefficient* or *K-value* of solute 2 in solvent 1,  $K_{2,1}(T, P) = (y_2/x_2)_{\text{equil}}$ . Using Equation (4) the *general* expression

$$K_{2,1}(T, P) = \phi_2^L(T, P, x_2)/\phi_2^V(T, P, y_2) \quad (24)$$

is obtained, which establishes the link with EOS calculations. The infinite-dilution limit of this quantity may thus also be expressed as<sup>1,6,13</sup>

$$K_{2,1}^\infty(T, P_{s,1}) = h_{2,1}(T, P_{s,1})/P_{s,1}\phi_2^{V\infty}(T, P_{s,1}) \quad (25)$$

$$K_{2,1}^\infty(T, P_{s,1}) = \gamma_2^{\text{LR}\infty}(T, P_{s,1})\phi_2^{L*}(T, P_{s,1})/\phi_2^{V\infty}(T, P_{s,1}) \quad (26)$$

or

$$K_{2,1}^\infty(T, P_{s,1}) = V_{s,1}^{V*}/V_{s,1}^{L*}L_{2,1}^\infty(T, P_{s,1}) \quad (27)$$

Infinite-dilution quantities are usually used for selecting selective solvents for extractive distillation or extraction ( $\gamma_i^{\text{LR}\infty}$  is needed) or gas absorption ( $h_{ij}$  is needed) (see, for instance, ref. 15).

### 1.3 Subtleties of Approximation

Taking into account the pressure dependence of  $h_{ij}(T, P)$  and  $\gamma_2^{\text{HL}}(T, P, x_2)$ ,<sup>1,3</sup> the equilibrium criterion Equation (10) may be recast into the *key equation* for *isothermal* VLE data treatment (data reduction and correlation) within the

unsymmetric convention:

$$\ln \gamma_2^{\text{HL}}(T, P_{s,1}, x_2) = \ln \left( \frac{\phi_2^{\text{V}}(T, P, y_2) y_2 P}{x_2 h_{2,1}(T, P_{s,1})} \right) - \int_{P_{s,1}}^P \frac{V_2^{\text{L}}(T, P, x_2)}{RT} dP \quad (28)$$

This equation provides the rigorous basis for the determination of the activity coefficients  $\gamma_2^{\text{HL}}$  from *isothermal* solubility data measured at various total pressures  $P$ . The argument of the logarithmic term on the right-hand side of Equation (28) is a dimensionless group containing the experimental data, the Henry fugacity already extracted therefrom *via* Equation (21), and the vapour-phase fugacity coefficient of the solute which must be either known from independent experiments or calculated from a suitable EOS, say, the virial equation. In order to evaluate the second term on the right-hand side, *i.e.* the Poynting integral, information is needed on the pressure dependence as well as the composition dependence of the partial molar volume  $V_2^{\text{L}}$  of the solute in the liquid phase. Each data point thus yields a constant-temperature, constant-pressure activity coefficient  $\gamma_2^{\text{HL}}(T, P_{s,1}, x_2)$ , which may be represented as a function of composition by any appropriate correlating equation compatible with the number and the precision of the experimental results. This is, then, the reward for exacting and tedious experimental work on the solubility of a gas in a liquid: the *Henry fugacity*  $h_{2,1}(T, P_{s,1})$  and a *correlating equation for*  $\gamma_2^{\text{HL}}(T, P_{s,1}, x_2)$ . This classical sequential approach is almost universally adopted in this field and simply reflects the focusing of interest on the solute in a composition range close to pure solvent.

In the key relation (28), the influence of composition on the liquid-phase fugacity has been separated formally from the influence of pressure. However, rigorous evaluation of the Poynting integral would require detailed knowledge of the pressure dependence *and* the composition dependence of the partial molar volume at each temperature of interest. Such comprehensive information is rarely available, whence for the great majority of solutions approximations at various levels of sophistication must be introduced to make the problem tractable.<sup>1,3</sup> The situation becomes particularly unsatisfactory at high pressures and/or when the critical region is approached, where Poynting corrections become significant. In fact, theoretical models predict that the partial molar volume of the solute is proportional to the compressibility of the solvent near its critical point,<sup>16</sup> with the effects of this divergence being already felt relatively far from the critical point.<sup>17</sup> The pioneering experiments of Wood and collaborators<sup>18,19</sup> have fully confirmed these expectations.

With few exceptions, typical gas-solubility measurements do not cover large composition ranges, while at the same time experimental scatter often tends to obscure the composition dependence of any derived activity coefficient. Thus, practicality usually dictates very simple correlating equations for  $\gamma_2^{\text{HL}}$  containing rarely more than one adjustable parameter. Using a two-suffix *Margules* equation and approximating  $V_2^{\text{L}}(T, P, x_2)$  by a pressure-independent

partial molar volume at infinite dilution  $V_2^{L\infty}(T, P_{s,1})$ , the *Krichevsky–Ilinskaya* equation<sup>20</sup> is obtained:

$$\ln\left(\frac{\phi_2^V(T, P, y_2)y_2P}{x_2h_{2,1}(T, P_{s,1})}\right) - \frac{(P - P_{s,1})V_2^{L\infty}(T, P_{s,1})}{RT} = A(x_1^2 - 1) \quad (29)$$

where  $A = A(T, P_{s,1})$  is a system-specific parameter. The error introduced by assuming  $V_2^{L\infty}$  to be pressure-independent may be estimated, for instance, *via* a *modified Tait* equation.<sup>3,21</sup> If one now assumes  $\gamma_2^{\text{HL}} = 1$ , independent of composition, the *Krichevsky–Kasarnovsky* equation<sup>22</sup> is obtained:

$$\ln\left(\frac{\phi_2^V(T, P, y_2)y_2P}{x_2h_{2,1}(T, P_{s,1})}\right) = \frac{(P - P_{s,1})V_2^{L\infty}(T, P_{s,1})}{RT} \quad (30)$$

It has frequently been used for the determination of  $V_2^{L\infty}$  from gas-solubility measurements at elevated pressures. However, the solubility may then be already appreciable and hence the underlying assumptions too severe. Values of  $V_2^{L\infty}$  obtained in this way should always be regarded with caution and may be unreliable.

The next popular simplification neglects the Poynting term, which leads to

$$\phi_2^V(T, P, y_2)y_2P = x_2h_{2,1}(T, P_{s,1}) \quad (31)$$

And finally, with the assumption  $\phi_2^V = 1$ , that is the vapour phase is regarded as a perfect-gas mixture, the simplest and most familiar version of HL,

$$P_2 = x_2h_{2,1}(T, P_{s,1}) \quad (32)$$

is obtained, where  $P_2 = y_2P$  is the partial pressure of the gaseous solute.

Evidently, the partial molar volume of the solute in the liquid solution is of importance in the reduction and correlation of accurate gas-solubility measurements. The preferred experimental methods for its determination are either precision dilatometry or precision densimetry.<sup>18,19,23–28</sup> For a survey of estimation methods see refs. 1, 3, and 4. Of special note is the capability of semi-empirical versions of scaled particle theory<sup>29,30</sup> to predict  $V_2^{L\infty}(T, P_{s,1})$  reasonably well, even for aqueous solutions, where the minima found experimentally for argon and oxygen dissolved in water,<sup>18,25,26</sup> respectively, are semi-quantitatively reproduced.<sup>10,31</sup>

$$V_2^{L\infty}(T, P_{s,1}) = V_{\text{cav}} + \kappa_{T,s,1}^{L*}(\mu_{\text{int}} + RT) \quad (33)$$

Here,  $V_{\text{cav}}$  is the partial molar volume associated with cavity formation,  $\kappa_{T,s,1}^{L*}$  the isothermal compressibility of the pure liquid solvent at saturation, and  $\mu_{\text{int}}$  the partial molar Gibbs energy of interaction. For many solvents, a self-consistent set of *effective* Lennard–Jones (6,12) parameters has been given by Wilhelm and Battino.<sup>32</sup> The correlational and predictive powers of this method can be substantially improved by introducing the concept of *temperature-dependent* size parameters.<sup>33,34</sup>

As pointed out above, when using the classical sequential approach exemplified by Equations (21) and (28), a vapour-phase EOS is required for

calculating  $\phi_2^V(T, P, y_2)$ . The majority of gas-solubility measurements lie in the low to moderate pressure domain, whence the virial EOS, either explicit in pressure or in molar volume, is most convenient. The computational convenience associated with a volume-explicit EOS leads to the widely used approximation for the mixture compression factor at fairly *low pressures*,

$$\begin{aligned} Z^V(T, P, y_2) &= PV^V/RT \\ &= 1 + (RT)^{-1}P(y_1B_{11} + y_2B_{22} + y_1y_2\delta_{12}) \end{aligned} \quad (34)$$

where the second virial coefficients with identical subscripts refer to pure components 1 and 2, respectively, and

$$\delta_{12} = 2B_{12} - (B_{11} + B_{22}) \quad (35)$$

$B_{12}$  designates a composition-independent interaction virial coefficient (cross-coefficient). The corresponding expression for the vapour-phase fugacity coefficient is

$$\ln \phi_i^V = \frac{P}{RT} (B_{ii} + y_j^2 \delta_{12}), \quad i, j = 1, 2, \quad i \neq j \quad (36)$$

The fugacity coefficient of the solute at infinite dilution in the vapour phase is thus given by

$$\ln \phi_2^{V\infty} = \frac{P}{RT} (2B_{12} - B_{11}) \quad (37)$$

and the fugacity coefficient of pure component  $i$  by

$$\ln \phi_i^{V*} = PB_{ii}/RT \quad (38)$$

The quite popular rule of thumb,  $\phi_2^V(T, P, y_2) = \phi_2^{V*}(T, P)$ , is in general inapplicable for the evaluation of  $\phi_2^{V\infty}$  since it requires  $B_{12} = (B_{11} + B_{22})/2$ .

Frequently, experimental results on second virial coefficients and/or second interaction virial coefficients<sup>35</sup> are not available. In particular this is the case at low reduced temperatures, where adsorption is significant. Even for water vapour, perhaps the best investigated fluid, the situation below about 400 K is not entirely satisfactory and subject to intensive research.<sup>36,37</sup> Important contributions come from flow calorimetric measurements of the isothermal Joule–Thomson coefficient, which have the advantage that adsorption errors are avoided, and measurements can be made at considerably lower pressures and temperatures than in conventional  $(P, V, T)$  methods.<sup>38</sup> Thus one has to rely quite heavily on semi-empirical correlation methods, which are almost all based on the *extended corresponding states theorem*. One of the most popular and reliable methods is that originally due to Tsonopoulos,<sup>39</sup> which since its inception in 1974 has been revised and extended several times:<sup>40</sup>

$$\begin{aligned} B_{ii,r}(T_r) &\equiv B_{ii}P_{c,i}/RT_{c,i} = B^{(0)}(T_r) + \omega_i B^{(1)}(T_r) \\ &\quad + \hat{a}_i B^{(2)}(T_r) + \hat{b}_i B^{(3)}(T_r) \end{aligned} \quad (39)$$

Here,  $B_{i,r}(T_r)$  is the reduced second virial coefficient of pure substance  $i$  at a reduced temperature  $T_r = T/T_{c,i}$ ,  $T_{c,i}$  is the critical temperature,  $P_{c,i}$  is the critical pressure, and  $\omega_i$  is the acentric factor. The  $B^{(l)}(T_r)$  are the universal *Tsonopoulos functions*, and  $\hat{a}_i$  and  $\hat{b}_i$  are quantities for specific compound classes, such as ketones, alkylhalides, 1-alkanols, *etc.* For hydrogen-bonded substances both parameters  $\hat{a}_i$  and  $\hat{b}_i$  must be used. For instance, for the normal 1-alkanols (except methanol)  $\hat{a}_i = 0.0878$  and  $\hat{b}_i$  appears to be a function of the reduced dipole moment  $\mu_{i,r}$  defined by<sup>41</sup>

$$\mu_{i,r} = (N_L \mu_i^2 / 4\pi\epsilon_0 V_{c,i} k_B T_{c,i})^{1/2} \quad (40)$$

Here,  $N_L$  is Avogadro's constant,  $\mu_i$  is the numerical value of the permanent molecular dipole moment of substance  $i$ ,  $\epsilon_0$  is the permittivity of vacuum,  $V_{c,i}$  is the critical molar volume, and  $k_B$  is Boltzmann's constant.

If one wishes to use Equation (39) to calculate the reduced second virial cross-coefficient  $B_{ij,r}(T_r) = B_{ij} P_{c,ij} / RT_{c,ij}$  at a reduced temperature  $T_r = T/T_{c,ij}$ , appropriate combination rules have to be devised to obtain the characteristic interaction parameters  $T_{c,ij}$ ,  $P_{c,ij}$ ,  $V_{c,ij}$ ,  $\omega_{ij}$ ,  $\hat{a}_{ij}$ , and  $\hat{b}_{ij}$  to replace the corresponding pure-substance quantities. For details see the original literature and refs. 1, 7, and 8.

Evidently, property estimation methods and correlation methods based on generalized corresponding states approaches require reliable data on critical properties and acentric factors. Since Henry fugacities and related quantities of interest are usually referred to orthobaric conditions, reliable vapour pressure data are indispensable and must be judiciously selected. A valuable source for all these quantities is the book by Poling *et al.*<sup>42</sup> For the most important solvent, water, the International Association for the Properties of Water and Steam (IAPWS) recommends<sup>43</sup>  $T_c = 647.096$  K,  $P_c = 22.064$  MPa, and  $\rho_c = 322$  kg · m<sup>-3</sup>. The molar mass of the international standard water with respect to isotopic composition (Vienna Standard Mean Ocean Water, VSMOW) is  $18.015268 \times 10^{-3}$  kg · mol<sup>-1</sup>. An equation representing the vapour pressure of liquid water at most temperatures within current experimental uncertainty (*ca.*  $\pm 0.025\%$ ) has been given by Wagner and Pruss<sup>44</sup> in the form of a six-constant Wagner-type vapour pressure equation.

Once experimental Henry fugacities for a specific solvent-solute 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, essentially empirical fitting equations have to be used, subject however, to some important thermodynamic constraints. Depending on the choice of variables, that is  $T$  or  $T^{-1}$ , for expanding the enthalpy of solution, either the *Clarke–Glew* equation<sup>45</sup>

$$\begin{aligned} \ln[h_{2,1}(T, P_{s,1})/Pa] = & A_0 + A_1(T/K)^{-1} \\ & + A_2 \ln(T/K) + \sum_{i=3}^n A_i(T/K)^{i-2} \end{aligned} \quad (41)$$

or the *Benson–Krause* (BK) equation<sup>46,47</sup>

$$\ln [h_{2,1}(T, P_{s,1})/\text{Pa}] = \sum_{i=0}^m a_i (T/\text{K})^{-i} \quad (42)$$

is obtained. Note that the three-term version of Equation (41) is the well-known *Valentiner* equation.<sup>48</sup> On the basis of the ability to fit accurate  $h_{2,1}$  data over reasonably large temperature ranges, and of simplicity, the BK power series in  $T^{-1}$  appears to be superior.

In some (elementary) chemistry textbooks there appears to be some confusion concerning the qualitative dependence of solubility on temperature. In fact, the sweeping claim that “the solubility of a gas in a liquid decreases with increasing temperature” is misleading/incorrect when the entire liquid range between the triple point ( $T_{t,1}$ ) and the critical point of the solvent is considered. For many systems, the following behaviour is well documented: at low temperatures near  $T_{t,1}$ , the solubility expressed as, say, mole fraction solubility  $x_2$  of gas dissolved at a convenient low partial pressure (traditionally,  $P_2 = 1 \text{ atm} = 101.325 \text{ kPa}$ ), first *decreases* with increasing temperature, then passes through a *minimum* to *increase* steeply when the solvent critical temperature is approached. Such a behaviour is, of course, also reflected by the temperature dependence of the Henry fugacity, that is to say,  $h_{2,1}(T, P_{s,1})$  first *increases* with increasing temperature, then goes through a *maximum* to *decrease* steeply, when  $T_{c,1}$  is approached, as found, respectively, for argon, krypton, oxygen, methane, *etc.* dissolved in water.<sup>1,9,49</sup>

Any correlation for  $h_{2,1}(T, P_{s,1})$  extending up to the critical region *must* incorporate the thermodynamically correct *limiting behaviour* of the Henry fugacity for  $T \rightarrow T_{c,1}$  and  $P_{s,1} \rightarrow P_{c,1}$ :<sup>1,4-6,13</sup>

$$\lim_{T \rightarrow T_{c,1}} h_{2,1}(T, P_{s,1}) = P_{c,1} \phi_2^{V\infty}(T_{c,1}, P_{c,1}) \quad (43)$$

This *exact* limiting value follows directly from the generally valid Equation (13) and the equilibrium condition prevailing at the critical point, that is

$$\phi_2^{V\infty}(T_{c,1}, P_{c,1}) = \phi_2^{L\infty}(T_{c,1}, P_{c,1}) \quad (44)$$

No elaborate derivation is necessary.<sup>50</sup> Equation (43) also shows that Hayduk’s assertion<sup>51</sup> that the solubilities of gases in a given solvent tend to coincide at a temperature near the solvent’s critical is not true.

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  $-\infty$ .<sup>52,53</sup>

During the last 15 years or so, a number of equations for presenting the temperature dependence of  $h_{2,1}(T, P_{s,1})$  between the triple point temperature and the critical temperature of the solvent were developed to incorporate the thermodynamically correct limiting behaviour indicated above. For details I refer to refs. 1 and 13, and the original literature.<sup>54-57</sup>

Until recently, precision measurements of Henry fugacities over temperature ranges sufficiently large to permit *van't Hoff analysis* of the solubility data, constituted the only reliable source of information on partial molar enthalpy changes on solution,  $\Delta H_2^\infty(T, P_{s,1}) = H_2^{L\infty} - H_2^{pg*}$ , and *a fortiori* on partial molar heat capacity changes on solution,  $\Delta C_{P,2}^\infty(T, P_{s,1}) = C_{P,2}^{L\infty} - C_{P,2}^{pg*}$ , of sparingly soluble gases in liquids. Here,  $H_2^{L\infty}$  is the partial molar enthalpy of the solute at infinite dilution in the liquid solvent,  $C_{P,2}^{L\infty}$  is the partial molar heat capacity at constant pressure of the solute at infinite dilution in the liquid solvent, and  $H_2^{pg*}$  and  $C_{P,2}^{pg*}$  are, respectively, the molar enthalpy and the molar heat capacity at constant pressure of the pure solute in the perfect-gas state (pg). If the BK equation is selected for the correlation of experimental Henry fugacities with temperature,

$$\frac{\Delta H_2^\infty(T, P_{s,1})}{RT} = \sum_{i=1}^m ia_i(T/K)^{-i} + \frac{V_2^{L\infty}}{R} \frac{dP_{s,1}}{dT} \quad (45)$$

and

$$\begin{aligned} \frac{\Delta C_{P,2}^\infty(T, P_{s,1})}{R} = & - \sum_{i=2}^m i(i-1)a_i(T/K)^{-i} + 2 \frac{T}{R} \frac{dV_2^{L\infty}}{dT} \frac{dP_{s,1}}{dT} \\ & - \frac{T}{R} \left( \frac{\partial V_2^{L\infty}}{\partial P} \right)_T \left( \frac{dP_{s,1}}{dT} \right)^2 + \frac{TV_2^{L\infty}}{R} \frac{d^2P_{s,1}}{dT^2} \end{aligned} \quad (46)$$

are obtained.<sup>1,58</sup> Until recently, the supplemental terms in Equations (45) and (46) containing the slope ( $dP_{s,1}/dT$ ) and the curvature ( $d^2P_{s,1}/dT^2$ ) of the orthobaric curve – now referred to in the literature<sup>53,54</sup> as *Wilhelm terms* – have been overlooked. Their contributions increase rapidly with increasing temperature. In fact,  $V_2^{L\infty}$  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. Since  $C_{P,2}^{L\infty} = (\partial H_2^{L\infty}/\partial T)_P$ , the partial molar heat capacity at constant pressure at infinite dilution will diverge as  $(\partial \kappa_{T,s,1}^*/\partial T)_P$ , *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 experiments of Wood *et al.* confirm these expectations.<sup>18,19,59,60</sup>

In ref. 1, I have presented a comprehensive comparison of enthalpy changes on solution,  $\Delta H_2^{L\infty}$ , and heat capacity changes on solution  $\Delta C_{P,2}^{L\infty}$ , obtained from van't Hoff analysis of *high-precision solubility data* with calorimetrically determined values. Besides our own results<sup>9,10,31,61</sup> on Ar, O<sub>2</sub>, CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, and C<sub>3</sub>H<sub>8</sub> dissolved in liquid water, those of Krause and Benson<sup>54</sup> on the rare gases He through Xe have been included. The calorimetrically determined enthalpy changes on solution were obtained either at the Thermochemistry Laboratory in Lund, Sweden, or in the Chemistry Department of the University of Colorado in Boulder, USA.<sup>62–69</sup> With the exception of one set of *direct* heat capacity measurements on argon dissolved in water,<sup>59</sup> all heat capacity changes

on solution were obtained from the temperature dependence of the enthalpy changes on solution, *i.e.*  $\Delta C_{p,2}^{\infty} = (\partial \Delta H_2^{\infty} / \partial T)_p$ .

Evidently, comparing van't Hoff derived enthalpy changes (*one* differentiation level) and heat capacity changes (*two* differentiation levels) with directly obtained high-quality calorimetric results is a severe test of solubility data. In general, the agreement was found to be completely satisfactory, that is it was usually within the combined experimental error. What better tribute to both experimental ingenuity and state-of-the-art data treatment can one wish for?

## 1.4 Concluding Remarks

Chemical thermodynamics of solutions continues to be a developing field. The major impetus comes from continuing advances in instrumentation leading to increased precision, accuracy and speed of measurements, and from increasing ranges of application (higher temperatures, higher pressures, smaller concentrations).<sup>70</sup> This is paralleled by advances in the statistical-mechanical treatment of solutions, and by increasingly sophisticated computer simulations which provide new insights and stimulating connections at a microscopic level. In this review, I have concisely presented the thermodynamic formalism relevant to the study of dilute solutions of nonelectrolytes. Two intimately related topics have been dealt with prominently: (a) adequate discussion of solution behaviour in terms of the *Henry fugacity* and related *activity coefficients*, and (b) *reconciliation* of results for caloric quantities derived from solubility measurements, that is *via van't Hoff analysis*, with those measured directly with *calorimeters*. Though outside the scope of this article, I would like to point out the increasing number of solubility studies with a strong biophysical and/or biomedical flavour. While my own perception of their importance may not be shared by all, it appears safe to state that they will greatly stimulate applied research in the coming decade: cross-fertilization is becoming increasingly important.

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