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Solubility of gases in liquids: a critical review

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Abstract - Selected theoretical and experimental aspects of vapor-liquid equilibria involving supercritical (noncondensable) components are reviewed. The focus is on the rigorous thermodynamic basis on which high-precision methods for the determination of Henry coefficients have to rest. A condensed outline of current theories and correlations for the prediction of auxiliary quantities, such as virial coefficients and partial molar volumes, is presented. Finally, attention is given to recent work on relatively simple aqueous solutions of nonelectrolytes, which may contribute towards a better understanding of hydrophobic effects.

INTRODUCTION

The years since 1970 have been marked by intense activity in the field of solutions of nonelectrolytes in general, and of the solubility of gases in liquids in particular. The wealth of new and precise experimental data (often a consequence of novel designs of apparatus), the development of refined solution theories, and the recognition of the central role in science of effective communication and dissemination of data, are documented representatively by Refs.(1-32). This activity can be traced to requirements originating in rather diverse areas of the pure and applied sciences. For instance, chemical process design often needs reliable estimates of vapor-liquid equilibria (VLE) for mixtures containing one or more components at rather low concentrations (trace components), which are either supercritical (noncondensable) or only slightly subcritical. Other areas, where gas solubility data are frequently needed, are geochemistry, environmental science (pollution control) and biomedical technology. Since life cannot exist without water, studies of simple aqueous solutions, in particular of the rare gases and of hydrocarbons, have held a prominent position in biophysics. Perhaps most important, studies on such model systems have provided information on hydrophobic effects, which are thought to be of importance in complex biological processes. By way of example we list a few application-oriented topics of recent interest: strongly enhanced solubility of oxygen in perfluorinated hydrocarbons (33) as compared to the solubility in the parent hydrocarbons - these substances are chemically inert enough to be used as blood substitutes and as gas carriers in liquid breathing (34,35); solubility of gases in long-chain alcohols (36) and its relation to anesthetic potency (37, 38); solubility of Freons in water (39), and of oxygen and ozone in water (waste water treatment) (40,41); removal of CO_2 and H_2S from sour natural or synthetic gases by mixed-solvent absorption (gas sweetening) (42-44); solubility of hydrogen and other light gases in high molecular weight solvents (45,46), which is of importance for a number of engineering processes such as hydrofining of oil and coal, and enhanced oil recovery; solubility of gases in aqueous solutions of surfactants (solubilization) (47).

Given this wide scope it is not surprising that the subject of gas solubility in liquids has such a vast literature, as evidenced by the various representative reviews, state-of-the-art reports and data compilations cited above. Because of this diversity, a certain variation of experimental as well as theoretical methods used in each of these areas is almost inevitable, and makes it impossible to cover all of them in one short review. Far from being exhaustive, this article will therefore focus on just a few selected areas with the bias reflecting current research interests of the author. First, a rigorous discussion of the thermodynamic fundamentals relevant to the solubility of gases in liquids will be presented. This will be followed by an appraisal of recent experimental developments and of advances pertinent to data reduction and correlation. A condensed outline of current methods for the prediction of important auxiliary quantities, such as virial coefficients and partial molar volumes, will be included. The last section will be devoted almost entirely to recent work on relatively simple aqueous solutions of nonelectrolytes (with special attention to hydrophobic effects).

In a loose way, the expression "solution of gas(es) in liquid(s)" is usually meant to characterize VLE in multicomponent mixtures where one or more of the components are *supercritical* or only *slightly* subcritical at the experimental temperature, and where the liquid-phase mole fraction x_2 of the "gas" is *much smaller* than that of the solvent. At room temperature and at a partial pressure of "gas" of about 100 kPa, mole fraction solubility values for gases like Ar, N_2 or CH_4 dissolved in liquids such as benzene, methanol or water are roughly between 10^{-4} and 10^{-2}. Clearly, some arbitrariness is involved and such a classification is to be taken as a mere heuristic convenience to deal with corresponding VLE data, i.e. with "gas-solubility data". Most of what follows will concern the solubility of a *pure gas* in a *pure liquid*. Gas solubilities in mixed solvents, though undoubtedly of considerable practical as well as theoretical interest, will only be touched upon. Further, problems associated with solutions of chemically reacting gases will not be treated to any extent. Those with a specific interest in these topics are referred to Refs. (1,20,23,48-53).

THERMODYNAMICS

When discussing equilibria of phases containing more than one component, it is frequently convenient to distinguish between a mixture or a solution, and a *dilute solution*. In a mixture all components are on equal footing; thermodynamically they are all treated in the same manner, that is to say symmetrically. On the other hand in a dilute solution, one (or several) of the components is/are present in great excess and form(s) the *solvent* or *mixed solvent*, while the remaining component(s) at usually rather low mole fraction(s) is/are classified as *solute(s)*. In general, the thermodynamic treatment of dilute solutions focuses on the solute(s), that is to say it will be asymmetric. These statements will be quantified below. There is nothing fundamental in this distinction between a dilute solution and a mixture, and although *not always* stated explicitly, thermodynamic analysis of gas-solvent systems proceeds essentially along the lines as for other phase equilibrium problems. It seems thus permissible to present here only a rather condensed treatment and to refer for details to the appropriate reviews (22,31) and monographs (1,20,24), in particular to the excellent recent book by Van Ness and Abbott (24), which contains a section on the reduction and correlation of gas-solubility data.

Consider a PvT-system with uniform temperature T and pressure P containing K components in each phase. The fundamental relations characterizing phase equilibrium between two phases are those which equate the chemical potential of each component i = 1, ... , K in one phase to its chemical potential in the other. This equilibrium condition may be replaced advantageously by the rigorously equivalent criterion of *equality of the component fugacities* f_i. For VLE this can be expressed in compact notation as

$$f_i^V(T,P,\{x^V\}) = f_i^L(T,P,\{x^L\}) , \qquad i = 1,\dots,K, \tag{1}$$

where the superscripts V and L indicate the vapor phase and the liquid phase, respectively, $\{x^V\}$ denotes the set of (K-1) independent vapor-phase mole fractions $\{x_1^V, \dots , x_{K-1}^V\}$, and $\{x^L\}$ denotes the set of (K-1) independent liquid-phase mole fractions. As indicated in Eq.(1) the fugacities depend on temperature, pressure and composition. Two methods are commonly used to establish the link with experimental practice. In the first, the equilibrium condition is rewritten in terms of the *fugacity coefficients*

$$\phi_i(T,P,\{x\}) \equiv f_i/(x_i P) \tag{2}$$

in *both* phases L and V. In the second method the fugacities in the vapor phase are again expressed in terms of ϕ_i^V , while the *liquid-phase* fugacities are expressed in terms of liquid-phase *activity coefficients*

$$\gamma_i^L(T,P,\{x^L\}) \equiv f_i^L/(x_i^L f_i^{\circ L}) , \tag{3}$$

where $f_i^{\circ L}$ is an appropriate standard-state fugacity. Setting $\{y\} \equiv \{x^V\}$ and dropping the superscript L where permissible, Eq.(1) may be recast in the following two *entirely equivalent* ways:

$$y_i\phi_i^V(T,P,\{y\}) = x_i\phi_i^L(T,P,\{x\}) \qquad i = 1,\dots,K , \tag{4}$$

$$y_i\phi_i^V(T,P,\{y\})P = x_i\gamma_i(T,P,\{x\})f_i^\circ(T,P) \qquad i = 1,\dots,K . \tag{5}$$

Each equation may serve as a rigorous basis for the treatment of VLE problems. Note that both Eqs.(4) and (5) in fact represent K highly complex equations relating 2K variables (T,P,{x},{y}). Hence - in accord with the phase rule - K variables have to be specified to allow solution for the remaining K unknowns. The decision as to what approach should be preferred is by and large a matter of convenience and of taste. For high pressure VLE involving fairly simple substances, the use of a single equation of state (EOS) valid for *both* phases has often computational advantages and a certain aesthetic appeal, and thus Eq.(4) may be selected. Eq.(5) is the one most frequently used in the thermodynamic analysis of VLE (data reduction or VLE calculations) at low to moderate pressures. In this case, an EOS is required *only* for the *low-density vapor* phase (often the virial EOS is useful), while for the *liquid* phase usually an adequate *activity coefficient* model (or more precisely an analytical expression for the excess molar Gibbs energy G^E as a function of the x_i) is introduced; see however also Refs. (54,55) for numerical methods. Since the emphasis of this review is on gas solubilities at rather low pressures and temperatures well below the critical temperature $T_{c,1}$ of the solvent (see Note a), only the (γ,ϕ)-method, Eq.(5), will be considered; the

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Note a: Throughout this article, a subscript c will denote a "critical quantity", and reduced quantities $Q_r \equiv Q/Q_c$ will be designated by a subscript r. A subscript s indicates "orthobaric (i.e. saturation) conditions". Superscripts ° identify either "standard-state quantities" or "perfect-gas-state quantities", * is reserved for "pure-substance quantities", and $^\infty$ indicates "infinite dilution".

(ϕ,ϕ)-method will not be pursued further. In what follows now on *binary systems*, component 1 will always be the subcritical solvent and component 2 will be the dissolved gas (usually, but not necessarily a supercritical fluid).

So far nothing has been decided as to the choice of standard states, which is in fact again largely a matter of convenience. Two *conventions* are in common use. One is based on ideal behavior in the sense of the *Lewis-Randall rule*, that is to say for *all* components we identify f_i° with f_i^*, the fugacity of the pure component i in either a real or hypothetical liquid state at (T,P) of the solution. Thus, reality is compared with the behavior of the model fluid "ideal solution (Lewis-Randall)", where

$$f_i^{id} = x_i f_i^*(T,P) \,, \qquad i = 1 \text{ or } 2 \,. \tag{6}$$

The other convention distinguishes between the solvent and the solute and is based on ideal behavior of the latter in the sense of *Henry's law*, that is to say for component 1 (solvent) $f_1^\circ = f_1^*$, whereas for component 2 (solute) f_2° is identified with the *Henry coefficient* $H_{2,1}$, all at (T,P) of the solution. Thus, reality is compared with the behavior of the model fluid "ideal-dilute solution (Henry)", where

$$\left.\begin{aligned} f_1^{id} &= x_1 f_1^*(T,P) \\ f_2^{id} &= x_2 H_{2,1}(T,P) \end{aligned}\right\} \tag{7}$$

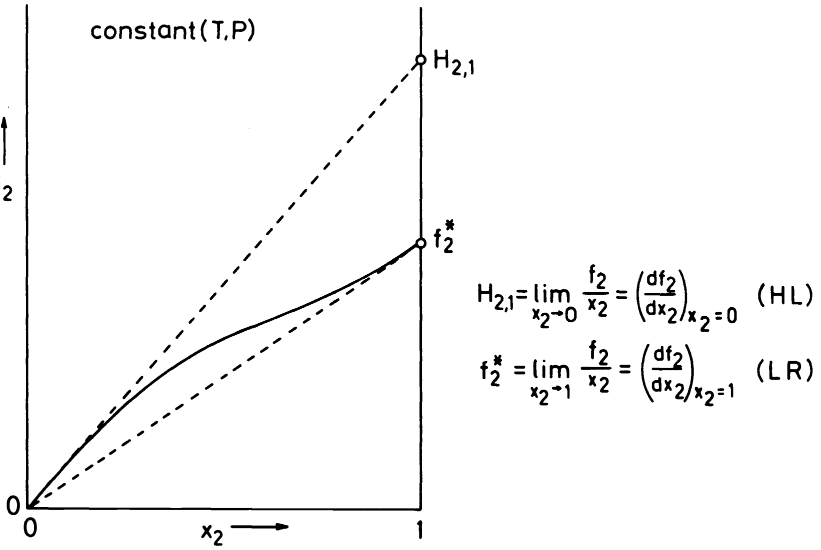

Fig. 1. Composition dependence of component fugacity f_2 in a binary solution at constant (T,P). f_2^* is the fugacity of pure substance 2 and $H_{2,1}$ is the Henry coefficient. The dashed lines represent Henry's law (HL) and the Lewis-Randall rule (LR), respectively.

Corresponding to these two conventions, the liquid-phase activity coefficients are normalized either *symmetrically*

$$\left.\begin{aligned} \gamma_1 &\rightarrow 1 \quad \text{as} \quad x_1 \rightarrow 1 \\ \gamma_2 &\rightarrow 1 \quad \text{as} \quad x_2 \rightarrow 1 \end{aligned}\right\} \qquad (8)$$

or *unsymmetrically*

$$\left.\begin{aligned} \gamma_1 &\rightarrow 1 \quad \text{as} \quad x_1 \rightarrow 1 \\ \gamma_2' &\rightarrow 1 \quad \text{as} \quad x_2 \rightarrow 0 \end{aligned}\right\} \qquad (9)$$

The prime in Eq.(9) is to serve as a reminder that the unsymmetric convention of normalization has been used, that is to say $\gamma_1 = f_1/(x_1 f_1^*)$ and $\gamma_2' = f_2/(x_2 H_{2,1})$. We reiterate that the numerical value of the activity coefficient depends on the selected standard state and has no significance whatsoever unless the value of f_i° is specified concomitantly. The two choices of convention for the standard states are shown in Fig. 1. Note that for a supercritical component 2 no experimental value for the liquid-state fugacity of pure 2 exists, and that f_2 is known from experiment only for $x_2 < 1$.

The *symmetric convention* is the most natural one for mixtures where *all* $T_{c,i} > T$, and where the interest is on the composition dependence of the various thermodynamic quantities in the whole range $0 \leq x \leq 1$. When $T_{c,2} < T$ and/or when the interest is on the thermodynamics of component 2 in the dilute region, the *unsymmetric convention* is usually selected. It has the advantage that the Henry coefficient and hence γ_2' are unambiguously defined according to an *experimental procedure* (as indicated in Fig. 1); these quantities may be obtained, at least in principle, to any desired degree of accuracy. However, as an alternative in the case $T_{c,2} < T$ one may obtain the fugacity of pure solute in a *hypothetical* liquid state through essentially *arbitrary* extrapolation of the function

$$\ln f = x_1 \ln(f_1/x_1) + x_2 \ln(f_2/x_2) \, , \qquad \text{constant } (T, P) \qquad (10)$$

to $x_2 = 1$: f is the mixture fugacity, and $\ln(f_i/x_i)$ is the partial molar quantity associated with $\ln f$. The resulting pure-component fugacity f_2^* may then be adopted as an arbitrary standard-state fugacity for the solute and the symmetric convention may be applied. We note that for each extrapolation recipe a corresponding *different* set of liquid-phase activity coefficients ensues (56), each satisfying $\gamma_2 f_2^{*L} = f_2^L/x_2$.

The various quantities corresponding to these conventions are, of course, related. At constant (T,P)

$$\ln f_2^* = \ln H_{2,1} - \ln \gamma_2^\infty \, , \qquad (11)$$

$$\ln \gamma_2 = \ln \gamma_2' + \ln \gamma_2^\infty \, , \qquad (12)$$

where the activity coefficient at infinite dilution is given by

$$\ln \gamma_2^\infty = \lim_{x_2 \to 0} (\ln \gamma_2) = - \lim_{x_2 \to 1} (\ln \gamma_2') \, . \qquad (13)$$

The equilibrium criteria for VLE, Eqs.(4,5), provide relations at temperature T and equilibrium pressure P of the solution. For *isothermal conditions*, P varies with x_2, and hence for each composition ϕ_i, γ_1 and γ_2', f_1^* and $H_{2,1}$ will refer to a *different* pressure and not to a fixed reference pressure. Thus the pressure dependence of these quantities must be known and the pertinent formulae are summarized below. For the reduction (or correlation) of gas-solubility data it is advantageous to choose the vapor pressure $P_{s,1}$ of the solvent as the constant reference pressure. Conversion to any other reference pressure is - at least in principle - straightforward. The fugacity of the pure solvent at (T,P) is related to its vapor pressure by

$$f_1^{*L}(T,P) = f_1^{*L}(T,P_{s,1})\mathcal{P}_1(T,P) = P_{s,1}\phi_{s,1}^{*V}\mathcal{P}_1(T,P) \ , \tag{14}$$

$$\mathcal{P}_1(T,P) \equiv \exp\left\{\int_{P_{s,1}}^{P}\frac{V_1^{*L}(T,P)}{RT}\,dP\right\} \ . \tag{15}$$

Here, $\phi_{s,1}^{*V} \equiv \phi_1^{*V}(T,P_{s,1})$ is the fugacity coefficient of pure saturated solvent vapor, V_1^{*L} is the molar volume of pure liquid, and $\mathcal{P}_1(T,P)$ is called the Poynting correction. For the Henry coefficient we obtain

$$H_{2,1}(T,P) = H_{2,1}(T,P_{s,1})\mathcal{P}_2(T,P) \ , \tag{16}$$

$$\mathcal{P}_2(T,P) \equiv \exp\left\{\int_{P_{s,1}}^{P}\frac{V_2^{\infty L}(T,P)}{RT}\,dP\right\} \ , \tag{17}$$

where $V_2^{\infty L}$ is the partial molar volume of dissolved gas at infinite dilution. The appropriate relations for the activity coefficients are

$$\gamma_1(T,P,x_2) = \gamma_1(T,P_{s,1},x_2)\exp\left\{\int_{P_{s,1}}^{P}\frac{V_1^{L}(T,P,x_2) - V_1^{*L}(T,P)}{RT}\,dP\right\} \ , \tag{18}$$

$$\gamma_2'(T,P,x_2) = \gamma_2'(T,P_{s,1},x_2)\exp\left\{\int_{P_{s,1}}^{P}\frac{V_2^{L}(T,P,x_2) - V_2^{\infty L}(T,P)}{RT}\,dP\right\} \ , \tag{19}$$

where $V_i^L(T,P,x_2)$ is the partial molar volume of component i (= 1 or 2) at mole fraction x_2. As concerns the fugacity coefficient ϕ_i of species i,we present two perfectly general equations valid for V as well as for L, which allow its determination either in terms of a *pressure-explicit* or a *volume (density)-explicit EOS*, provided of course, that the EOS are valid over the entire ranges of integration. When a pressure-explicit EOS $P/\rho RT \equiv Z = Z(T,\rho,\{x\})$ is used

$$\ln\phi_i = \int_0^{\rho}\left[\left(\frac{\partial nZ}{\partial n_i}\right)_{T,\rho/n,n_j} - 1\right]\rho^{-1}\,d\rho - \ln Z \ , \quad \text{constant } (T,\{x\}) \ . \tag{20}$$

Here $\rho \equiv V^{-1}$ is the molar density of the mixture, n_i is the amount of substance i, $n = \sum n_i$, and Z is the compressibility factor of the mixture. The corresponding expression for a volume (density)-explicit EOS $Z = Z(T,P,\{x\})$ is

$$\ln \phi_i = \int_0^P (Z_i - 1)P^{-1}dP\ , \qquad \text{constant } (T,\{x\})\ , \tag{21}$$

where $Z_i \equiv PV_i/RT$ and $V_i \equiv (\partial nV/\partial n_i)_{T,P,n_{j\neq i}}$ is the partial molar volume of i in the solution. Since the majority of EOS are pressure-explicit rather than volume-explicit, Eq.(20) is more useful in VLE problems than Eq.(21). The appropriate formulae for the pure-substance fugacity coefficients ϕ_i^* are, with obvious notation,

$$\ln \phi_i^* = \int_0^{\rho_i^*} (Z_i^* - 1)(\rho_i^*)^{-1}d\rho_i^* + Z_i^* - 1 - \ln Z_i^*\ , \quad \text{constant } T \tag{22}$$

and

$$\ln \phi_i^* = \int_0^P (Z_i^* - 1)P^{-1}dP\ , \qquad \text{constant } T\ . \tag{23}$$

We now have at hand the thermodynamic formalism for a rigorous discussion of the *reduction* and *correlation* of gas-solubility data on the basis of the (γ,ϕ)-approach in the unsymmetrical version (22,24,31). *Isothermal* conditions are assumed throughout and the vapor pressure $P_{s,1}$ of pure solvent is always chosen as the *reference pressure*. For the solute the equilibrium criterion Eq.(5) may be replaced by

$$y_2\phi_2^V(T,P,y_2)P = x_2\gamma_2'(T,P_{s,1},x_2)H_{2,1}(T,P_{s,1})\exp\left\{\int_{P_{s,1}}^P \frac{V_2^L(T,P,x_2)}{RT}dP\right\}\ , \tag{24}$$

where use was made of Eqs.(16,17,19). Analogously, for the solvent we now have

$$y_1\phi_1^V(T,P,y_2)P = x_1\gamma_1(T,P_{s,1},x_2)P_{s,1}\phi_{s,1}^*\exp\left\{\int_{P_{s,1}}^P \frac{V_1^L(T,P,x_2)}{RT}dP\right\}\ . \tag{25}$$

Note that both γ_1 and γ_2' of Eqs.(24,25) are constant-pressure activity coefficients which, at fixed temperature, depend only on liquid-phase composition. They are by definition independent of the system pressure. Their advantages have been discussed in detail by Prausnitz (1). In particular, they satisfy the isothermal-isobaric Gibbs-Duhem equation

$$x_1 d\ln\gamma_1(T,P_{s,1},x_2) + x_2 d\ln\gamma_2'(T,P_{s,1},x_2) = 0\ . \tag{26}$$

At the vapor pressure $P_{s,1}$ of the solvent, the Henry coefficient is rigorously accessible through determination of the limiting value of experimental (VLE) ratios of the fugacity of the solute over the corresponding mole fraction (see Fig. 1):

$$H_{2,1}(T,P_{s,1}) = \lim_{x_2\to 0}(f_2^L/x_2) = \lim_{x_2\to 0}\frac{y_2\phi_2^V(T,P,y_2)P}{x_2}\ . \tag{27}$$

Thus, according to the prescription Eq.(27), $H_{2,1}(T,P_{s,1})$ is obtained as the *intercept* in a graph of $(y_2\phi_2^V P/x_2)$ against x_2 at constant T. Since for $x_2 \to 0$ also $y_2 \to 0$, application of de l'Hôpital's rule (see Fig. 1) yields several entirely equivalent expressions for the Henry coefficient (24,31), relating it to *limiting slopes*. For instance

$$H_{2,1}(T,P_{s,1}) = \lim_{x_2\to 0}(df_2^L/dx_2) = \phi_2^{\infty V} P_{s,1} \lim_{x_2\to 0}(dy_2/dx_2) \; , \tag{28}$$

which is perhaps the most useful version. Here $\phi_2^{\infty V}$ is the fugacity coefficient of component 2 at infinite dilution in the vapor phase.

Determination of the Henry coefficient is only the first step in a comprehensive reduction of gas-solubility data. Since actual solubility measurements are sometimes performed at several *different* pressures $P > P_{s,1}$ and hence at different *finite* mole fractions x_2, they contain not only information on $H_{2,1}$, but also on the composition dependence of the activity coefficient. The influence of total pressure upon liquid-phase fugacities has been separated formally from the influence of composition through Eqs.(24,25), whence extraction of constant-pressure activity coefficients becomes feasible. The *key relation* for the determination of $\{\gamma_2'(T,P_{s,1},x_2)\}$ at constant T is a more compact and convenient form (31) of Eq.(24),

$$\ln\left(\frac{y_2\phi_2^V(T,P,y_2)P}{x_2H_{2,1}(T,P_{s,1})}\right) - \int_{P_{s,1}}^{P}\frac{V_2^L(T,P,x_2)}{RT}\,dP = \ln\gamma_2'(T,P_{s,1},x_2) \; . \tag{29}$$

The argument of the logarithmic term on the lhs of Eq.(29) is a dimensionless group containing the experimental isothermal data, the Henry coefficient $H_{2,1}(T,P_{s,1})$ already extracted therefrom, and the vapor-phase fugacity coefficient of the solute, which must be calculated from a suitable EOS, see Eqs.(20,21). To proceed further, that is to say in order to evaluate the integral in Eq.(29), information is needed on the composition dependence *as well as* the pressure dependence of the partial molar volume V_2^L in the liquid phase. These two terms may then be combined to yield constant - pressure activity coefficients for each data point, which in turn may be correlated with x_2 by any appropriate correlating equation. This is, then, the reward for exacting and tedious experimental work on the solubility of a gas in a liquid: the Henry coefficient $H_{2,1}(T,P_{s,1})$ and a correlating equation for $\gamma_2'(T,P_{s,1},x_2)$.

A final caveat concerns the extension of the methods just described to multisolute/multisolvent systems. The activity coefficient of any supercritical component may again be based on either the Henry coefficient or the fugacity of the pure solute in a hypothetical liquid state. Both approaches are thermodynamically equivalent, though implementation of the unsymmetric formalism leads to somewhat more complex equations. The ensuing problems have been discussed in depth by Van Ness and Abbott (49), see also Ref.(24). Let it here suffice to present the general situation for a ternary solution in which a supercritical component 3 (the gas) is dissolved in a mixture of two solvents 1 and 2. For this case Fig. 2 shows schematically the surface

$$\ln f = \sum_{i=1}^{3} x_i \ln(f_i/x_i) \tag{30}$$

as a function of the composition at constant T and P. The two curves $\ln f = \ln f(x_3;x_2=0)$ and $\ln f = \ln f(x_3;x_1=0)$ characterize the constituent binary solutions [3,1] and [3,2]. For component 3 dissolved in solvent i, $H_{3,i}(T,P)$ is by definition the limiting value at constant T and P of the partial molar quantity $\ln(f_3/x_3)$ as $x_3\to 0$, and is thus given by the intercept on the $x_3 = 1$ axis of the tangent drawn at $(x_3 = 0, x_i = 1)$. For the gas dissolved in a binary mixed solvent [1+2] with composition (x_1, x_2), $\ln H_{3,[1+2]}(T,P)$ is obtained analogously. The curve results now from the intersection of the $\ln f$ surface with the vertical plane characterizing the constant composition ratio x_1/x_2, and the tangent is drawn at $(x_3 = 0, x_1, x_2 = 1 - x_1)$, yielding the Henry coefficient again as the intercept on the $x_3 = 1$ axis. In the limit $x_3 \to 0$

$$\ln H_{3,[1+2]} \equiv \lim_{x_3 \to 0}\left(\ln \frac{f_3}{x_3}\right) = \ln f_{[1+2]} + \lim_{x_3 \to 0}\left(\frac{\partial \ln f}{\partial x_3}\right)_{T,P,x_1/x_2} , \qquad (31)$$

where $\ln f_{[1+2]}$ is the fugacity of the binary (solute-free) solvent mixture [1+2]. Evidently, $H_{3,[1+2]}$ depends on the composition of the mixed solvent [1+2] , and has of course the limiting values $H_{3,1}$ for $x_1 = 1$ and $H_{3,2}$ for $x_2 = 1$.

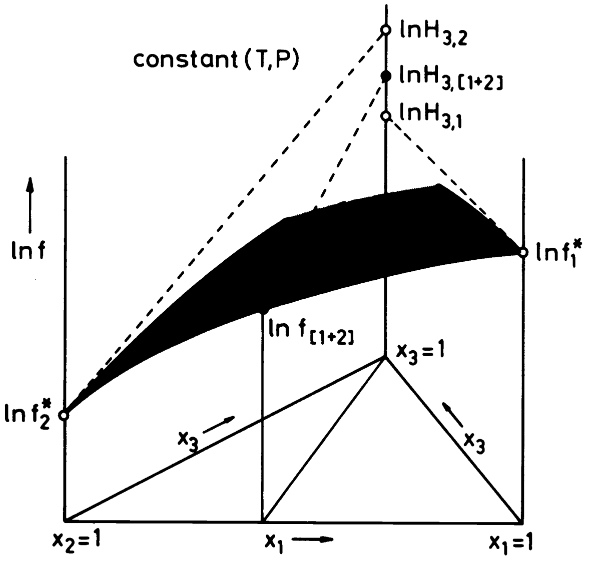

Fig. 2. Schematic representation of the $\ln f$ surface for a ternary solution of a gas, 3 , in the mixed solvent [1+2]: the Henry coefficient in the pure solvent i (= 1 or 2) is $H_{3,i}$, and in the mixed solvent it is $H_{3,[1+2]}$.

While the solubility of gases in mixed solvents is important in many industrial applications, relatively few experimental data are available. Thus, heavy use is made of prediction schemes which endeavor to correlate the multisolvent quantity $\ln H_{gas,[1+2+3+\ldots]}$ with the much more frequently known $\ln H_{gas,i}$ characterizing the solubility of the particular gas in solvent i= 1,2,3 etc. In addition to work already cited, Refs. (57-60) further illustrate activities in this area.

We conclude this introduction to the thermodynamics of mixtures containing supercritical components with a section devoted entirely to various approximations to the exact relations obtained so far. These approximations are indispensable when application to experimental reality is desired. Additional details will be given together with the discussion of experimental techniques. Consider for instance the key relation Eq.(29). Though thermodynamically rigorous and fairly straightforward, this formalism for separating the influence of composition upon the liquid-phase fugacity from the influence of pressure is marred by the following (22,31):

(a) Rigorous evaluation of the Poynting term would require detailed knowledge of the pressure dependence as well as the composition dependence of the partial molar volume, and this at each temperature of interest. Such comprehensive information will be available only in very few cases; for the great majority of solutions, however, approximations at various levels of sophistication must be introduced (1,22,24,31,61,62) to make the problem tractable. Similar comments apply to Eqs.(14),(16) etc. The situation is particularly unsatisfactory at high pressures and when approaching the critical region, where the Poynting corrections become significant.

(b) Frequently, the calculation of ϕ_2^V cannot be based on experimental results, say second and third virial coefficients (63), but must use semi-empirical correlations, the reliability of which may not always be high. This may impede satisfactory reduction of data obtained at elevated pressures (64,65).

(c) With few exceptions, typical gas solubility measurements *do not* cover large composition ranges. At the same time, experimental scatter often tends to obscure the composition dependence of the derived constant-pressure activity coefficients. Thus for purely practical reasons, the correlating equations for γ_2' usually contain only few adjustable parameters, that is to say very rarely more than two (1,66).

Against this background several *popular approximations* to the key relation Eq.(29) will be given in order of decreasing restrictiveness. The assumption $\phi_2^V = 1$ (the vapor phase behaves as an ideal-gas mixture), together with $\gamma_2'(T,P_{s.1},x_2) = 1$ (usually quite reasonable for small solubilities) and ignoring the Poynting term (acceptable for pressures $P \approx P_{s,1}$ well below the critical region) leads to the simplest and most *familiar* relation

$$P_2 \equiv y_2 P = x_2 H_{2,1} \quad , \tag{32}$$

which is often called "*Henry's law*". A series of similar approximations to Eq.(25) results in "*Raoult's law*" for the solvent,

$$P_1 \equiv y_1 P = x_1 P_{s,1} \quad . \tag{33}$$

If only the simplification concerning the vapor phase is relaxed, we obtain for the solute

$$y_2 \phi_2^V(T,P,y_2) P = x_2 H_{2,1} \quad . \tag{34}$$

Adding the Poynting term with $V_2^L(T,P,x_2) = V_2^{\infty L}(T,P_{s,1})$, yet still retaining $\gamma_2' = 1$, independent of composition, yields

$$\ln\left(\frac{y_2 \phi_2^V(T,P,y_2) P}{x_2 H_{2,1}(T,P_{s,1})}\right) = \frac{(P - P_{s,1}) V_2^{\infty L}(T,P_{s,1})}{RT} \quad . \tag{35}$$

This expression is known as the *Krichevsky-Kasarnovsky equation* (67). For a long time it has been used for the determination of $V_2^{\infty L}$ from gas solubility measurements at elevated pressures and accounts, in fact, for a large portion of the existing data. However, the mole fraction solubility may then be already appreciable and hence the assumptions $\gamma_2' = 1$ and $V_2^L = V_2^{\infty L}$ too severe. Values for $V_2^{\infty L}$ obtained in this way should always be regarded with caution and may be unreliable (68,69). The *preferred* experimental method for determining $V_2^{\infty L}$ is either precision densimetry (70) or dilatometry (71) at very small mole fractions.

As concerns the modeling of the composition dependence of γ_2', the correlating equation has to be compatible with the number and the precision of the experimental data points. Because of the interconvertability of symmetrically and unsymmetrically normalized activity coefficients, Eqs.(11) through (13), the selection of such correlations usually follows rather closely the well established recipes for the symmetrically normalized activity coefficients. The simplest possibility corresponds to the two-suffix Margules equation, that is to say for the constant-pressure activity coefficients at $P_{s,1}$ and T we obtain

$$\ln\gamma_1 = Ax_2^2 \quad , \quad \ln\gamma_2' = A(x_1^2 - 1) \quad . \tag{36}$$

Insertion into Eq.(29) and maintaining the same level of approximation with respect to V_2^L gives

$$\ln\left(\frac{y_2\phi_2^V(T,P,y_2)P}{x_2H_{2,1}(T,P_{s,1})}\right) - \frac{(P-P_{s,1})V_2^{\infty L}(T,P_{s,1})}{RT} = A(x_1^2 - 1) \ , \tag{37}$$

which is known as the *Krichevsky-Ilinskaya equation* (72,73). There can be little doubt that even Eq.(37) is not particularly realistic at high pressures and/or high solubility. However, we emphasize again that an indispensible prerequisite for the use of more elaborate correlating equations is the availability of experimental data on the *composition dependence* of the partial molar volume as well as on its *pressure dependence*.

The magnitude of the Poynting correction, evaluated with a generally applicable liquid-phase EOS, is indicated by the following specific example. Consider a fictitious liquid, at 298.15 K, with molar volume V_s^{*L} = 120 cm^{3}mol^{-1} and isothermal compressibility $\beta_{T,s}^{*L} = 10^{-9}$Pa^{-1}, and let the pressure dependence of V^{*L} be accounted for by the *modified Tait equation* (22, 26,31,74), which is satisfactory for pressures up to several tens of megapascals. Upon insertion into Eq.(15) and integration

$$\mathcal{P}_{\mathrm{MTE}} = \exp\left\{\frac{V_s^{*L}}{RT}\,\frac{\left(1 + m\beta_{T,s}^{*L}\Delta P\right)^{\frac{m-1}{m}} - 1}{(m-1)\beta_{T,s}^{*L}}\right\} \ , \tag{38}$$

where $\Delta P = P - P_s$, and m is a pressure-independent parameter. For many organic liquids experimental values cluster around m = 10, with very small temperature dependence (74,75). For an applied pressure ΔP = 0.2 MPa we obtain $\mathcal{P}_{\mathrm{MTE}}$= 1.01, and for ΔP = 2 MPa the result is $\mathcal{P}_{\mathrm{MTE}}$= 1.10, quite a significant correction. Qualitatively similar comments apply for the solute.

Whatever method for determining $H_{2,1}(T,P_{s,1})$ is selected, say for instance recipes Eq.(27) or Eq.(28), evaluation from an experimental isothermal data set requires a vapor-phase EOS for calculating the fugacity coefficient. The majority of gas solubility measurements are in the low to moderate pressure domain, say with P not exceeding several megapascals. Hence for many systems the virial equation

$$Z^V \equiv P/\rho^V RT = 1 + B\rho^V + C(\rho^V)^2 + \cdots \tag{39}$$

is convenient (26,31), and often yields entirely satisfactory results even when truncated after the term which is linear in molar density ρ^V. For a mixture of K components, each with mole fraction y_i

$$B(T,\{y\}) = \sum_i^K \sum_j^K y_i y_j B_{ij}(T) \quad , \tag{40}$$

$$C(T,\{y\}) = \sum_{i}^{K}\sum_{j}^{K}\sum_{k}^{K} y_i\, y_j\, y_k\, C_{ijk}(T) \quad \text{etc.} \tag{41}$$

Coefficients with identical subscripts refer to pure substances, whereas mixed subscripts designate composition-independent interaction virial coefficients (or cross-coefficients) characterizing the molecular interaction between molecules of species i with those of species j (B_{ij}), of species i with those of species j and k (C_{ijk}) and so forth. They are functions of temperature only. Insertion of Eqs.(39-41) into Eq.(20) yields for a two-component mixture

$$\ln\phi_2^V = 2\rho^V(y_2B_{22} + y_1B_{12}) + \frac{3}{2}(\rho^V)^2\left(y_2^2C_{222} + 2y_1y_2C_{122} + y_1^2C_{112}\right) - \ln Z^V, \tag{42}$$

$$\ln\phi_2^{\infty V} = 2\rho_1^{*V}B_{12} + \frac{3}{2}(\rho_1^{*V})^2C_{112} - \ln Z_1^{*V}. \tag{43}$$

Unfortunately, experimental information on third virial coefficients is rather limited and one has to rely heavily on correlation methods, such as those advanced by Chueh and Prausnitz (76), or more recently by De Santis and Grande (77), and Orbey and Vera (78). This, and the computational convenience associated with a volume-explicit rather than a pressure-explicit EOS, leads to the widely used approximation for *low* pressures

$$Z^V = 1 + BP/RT\ , \tag{44}$$

where B of the mixture is again given by Eq.(40). The corresponding expression for the fugacity coefficient is now

$$\ln\phi_2^V = \frac{P}{RT}(B_{22} + y_1^2\delta_{12})\ , \tag{45}$$

$$\ln\phi_2^{\infty V} = \frac{P}{RT}(2B_{12} - B_{11})\ , \tag{46}$$

where $\delta_{12} \equiv 2B_{12} - (B_{11} + B_{22})$. We emphasize that the quite popular rule of thumb

$$\phi_2^V(T,P,y_2) = \phi_2^{*V}(T,P) \tag{47}$$

may frequently be a rather unsatisfactory assumption (22), and is in general inapplicable for the evaluation of $\phi_2^{\infty V}$. Eq.(47) can be justified only if the vapor phase is an ideal solution.

EXPERIMENT

Advances in experimental technique for the determination of Henry coefficients may be classified as follows:

(a) novel designs of apparatus which significantly improve experimental precision and accuracy;

(b) designs which increase the accessible pressure and temperature ranges of already existing instruments;

(c) efforts towards simplifying and accelerating data acquisition.

In this article only recent contributions to (a) will be considered. Some of the older, more popular types of apparatus have been reviewed in detail by Battino and Clever (79) in 1966, and a decade later in 1975 (8); see also Refs.(6,13,17,21,25).

The most significant recent advance belonging to group (a) is undoubtedly due to Benson and Krause (BK) (80,81). They use an *analytical* method in which the composition of the liquid phase and of the vapor phase in equilibrium is determined via classical PvT measurements. The precision (and accuracy) which may be achieved with BK-type equipment surpasses that of any previous design, including the one of Cook and Hanson (82). A schematic representation of the experimental situation (31,81,83-85) is provided by Fig. 3. The flow diagram contains the essential parts of the apparatus as well as the auxiliary thermodynamic quantities, which have to be either measured separately, or extracted from the literature, or estimated. The average random error of $H_{2,1}(T,P_{s,1})$ obtained in this way is usually about ±0.05 %. The method's reliability has been impressively demonstrated by the reported interlab accord on oxygen solubility in water: between 275 and 328 K, the difference between the data reported by Benson et al. (81) and those reported by Rettich et al. (83-85) amounted to about 0.1 %.

As shown in Fig. 3, the essential parts of this apparatus are a degassing device (86), an equilibrator (81,83), an extractor (same design as for degassing), the Töpler pump (87) for transferring the dry gas to the manometric system, the high-precision manometric system itself (PvT-measurements) and, of course, powerful thermostats (temperature drift $\leq \pm$ 0.003 K during 24 h) and platinum resistance thermometers. Quantities measured are the temperature at equilibrium, and the amounts of gas n_2^L and n_2^V contained in precisely known volumes of the liquid solution, v^L, and of the vapor phase, v^V. As was shown in Ref.(83), Henry coefficients of sparingly soluble gases may be obtained according to

$$H_{2,1}(T,P_{s,1}) = \lim_{x_2\to 0}\left[h_{2,1}Z^V(T,P,y_2)\phi_2^V(T,P,y_2)\right], \tag{48}$$

$$h_{2,1} = (n_2^V/n_2^L)(\hat{v}^L/v^V)RT/V_1^{*L} , \tag{49}$$

$$\hat{v}^L \simeq v^L - n_2^L(V_2^{\infty L} - V_2^{*L}) . \tag{50}$$

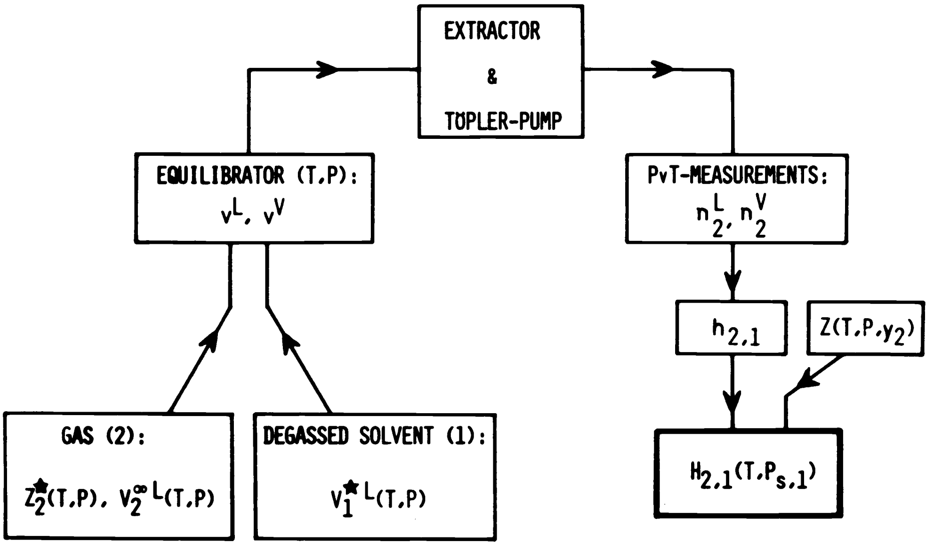

Fig. 3. Determination (schematic) of Henry coefficients $H_{2,1}(T,P_{s,1})$ with a BK-type apparatus (81,83). Auxiliary quantities needed for rigorous data reduction are also shown (31,83-85).

Note that the total equilibrium pressure P does not appear explicitely in Eq.(48). It has to be known, however, for the evaluation of the correction term $Z^V\phi_2^V$, and is obtained by an iterative procedure described in detail in Ref.(83).

As already indicated above, for gaseous mixtures at low pressures the virial EOS in its volume-explicit form is convenient. While there is often sufficient information on the pure-substance virial coefficients B_{ii}, experimental results on the cross-coefficients B_{12} are frequently lacking (63). Cross-coefficients may be estimated with reasonable confidence by several well-established correlations, such as the Hayden-O'Connell method (88) or the Pitzer-Curl-Tsonopoulos corresponding-states method (89,90). When using the latter, the reduced pure-substance virial coefficient at a reduced temperature T_r is given by

$$\frac{BP_c}{RT_c} = B^{(0)}(T_r) + \omega B^{(1)}(T_r) \ , \tag{51}$$

where $B^{(0)}$ and $B^{(1)}$ are polynomials in T_r^{-1} , and ω is the acentric factor. It is assumed that the same relation holds for the cross-coefficient B_{12}, but with characteristic parameters (interaction parameters) $T_{c,12}$, $P_{c,12}$ and ω_{12} replacing the pure-substance quantities T_c, P_c and ω , to which they are related by conventional recipes known as *combining rules*. Specifically, the reduced temperature is now $T_{r,12} \equiv T/T_{c,12}$, and

$$T_{c,12} = (1 - k_{12})(T_{c,1}T_{c,2})^{1/2} \ , \tag{52a}$$

$$P_{c,12} = 4T_{c,12}(P_{c,1}V_{c,1}/T_{c,1} + P_{c,2}V_{c,2}/T_{c,2})(V_{c,1}^{1/3} + V_{c,2}^{1/3})^{-3} \ , \tag{52b}$$

$$\omega_{12} = (\omega_1 + \omega_2)/2 \ . \tag{52c}$$

The quantity k_{12} is another binary interaction parameter (usually much smaller than unity). It is similar to the binary interaction parameters used in the more fundamental combining rules for unlike energy parameters of two-parameter pair potentials (26,91,92). Mixture compressibility factor Z^V and component fugacity coefficient ϕ_2^V may then be calculated by Eqs.(40,44,45). Alternatively, one may use any appropriate analytical EOS to obtain $Z^V\phi_2^V$. Examples for calculations of this kind have been presented in Refs.(93) and (94). In the former, a modified Redlich-Kwong equation is used, while the latter utilizes a perturbed-hard-sphere EOS similar to that introduced by Carnahan and Starling (95).

In our method (31,83-85) of determining $H_{2,1}(T,P_{s,1})$, the partial molar volume at infinite dilution has to be known. Recent measurements with a vibrating-tube densimeter (70) yielded $V_2^{\infty L}$ for 20 fluids (about half of them supercritical) dissolved in water; a dilatometric method was used in Ref.(71) to obtain this quantity for several gases (CH_4, C_2H_6 etc.) in n-alkanes and 1-alkanols. $V_2^{\infty L}$ in liquid water is well correlated with $V_{c,2}$, that is to say at 298.15 K our results are represented to within ca. ± 10 % by $V_2^{\infty L}/cm^3mol^{-1} = 10.74 + 0.2683\ V_{c,2}/cm^3mol^{-1}$. For the noncondensables this is comparable to the performance of the Brelvi-O'Connell correlation (96), which should *not* be used at temperatures substantially below the critical temperature of the solute $T_{c,2}$. Scaled particle theory has been used by Pierotti (12,97) and Wilhelm et al. (14), amongst others, to calculate $V_2^{\infty L}$ for nonpolar and polar gases in both nonpolar and polar solvents according to

$$V_2^{\infty L} = V_{CAV} + \beta_{T,s,1}^{*L}(G_{INT} + RT) \ . \tag{53}$$

Here $V_{CAV} = (\partial G_{CAV}/\partial P)_T$, and G_{CAV} and G_{INT} are the partial molar Gibbs energy of cavity formation (98) and interaction (12,14,97,99,100), respectively. Agreement with experiment is satisfactory in most cases. For a review of the literature on $V_2^{\infty L}$ see Handa and Benson (62).

Over limited ranges of T , the temperature dependence of $H_{2,1}(T,P_{s,1})$ is usually adequately represented by either the Clarke-Glew (CG) equation (101)

$$\ln(H_{2,1}/\mathrm{Pa}) = A_0 + A_1(T/K)^{-1} + A_2\ln(T/K) + A_3(T/K) + A_4(T/K)^2 + \cdots \tag{54}$$

or by the BK equation (80,81)

$$\ln(H_{2,1}/\mathrm{Pa}) = \sum_{i=0}^{n} a_i(T/K)^{-i} \, . \tag{55}$$

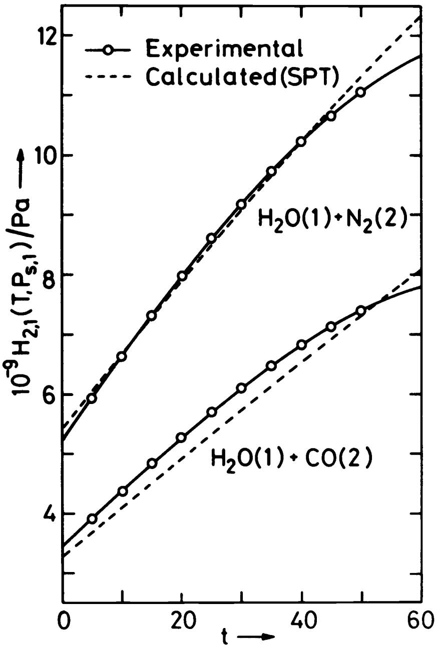

Fig. 4. Henry coefficients $H_{2,1}(T,P_{s,1})$ for (H_2O + N_2) and (H_2O + CO) as functions of temperature: t = T/K - 273.15. O, experimental results; ——, either CG or BK smoothing equations; - - -, obtained via scaled particle theory (84,85).

Fig. 4 shows measured Henry coefficients for CO and N_2 dissolved in water (84,85) as a function of temperature, the correlations provided by the appropriate smoothing equations (CG or BK), and results obtained by application of scaled particle theory in its simplest version (12,14,97,99,100). Substantial improvement of the temperature dependence of $H_{2,1}$ (for instance, reasonably accurate prediction of the usually observed maximum of the curve $H_{2,1}$ vs. T) is possible by introducing the concept of *effective*, hence *temperature-dependent*, hard-sphere diameters (102) into the formalism, as recently shown by Prausnitz et al. (46, 103).

With very few exceptions precision measurements of $H_{2,1}(T,P_{s,1})$ over sufficiently large ranges of temperature constitute the only source of information on enthalpies of solution, ΔH_2°, and *a fortiori* on heat capacity changes upon solution, $\Delta C_{p,2}^\circ = (\partial \Delta H_2^\circ/\partial T)_p$, of sparingly soluble gases in liquids (14,104,105), see also Refs.(26,31). Specifically,

$$\Delta H_2^\circ/RT = \left(H_2^{\infty L} - H_2^{\circ V}\right)/RT = -\frac{T}{H_{2,1}(T,P_{s,1})}\,\frac{dH_{2,1}(T,P_{s,1})}{dT} + \frac{V_2^{\infty L}}{R}\,\frac{dP_{s,1}}{dT}\ , \tag{56}$$

where $H_2^{\infty L}$ is the partial molar enthalpy of the gas at infinite dilution in the solvent, and $H_2^{\circ V}$ is the molar enthalpy of pure component 2 in the ideal-gas state. The first term on the rhs of Eq.(56) is obtained from one of the selected fitting equations. The temperature dependence of the vapor pressure of the solvent may be calculated from any suitable vapor pressure correlation, for instance from the Antoine equation, the Lee-Kesler equation (for nonpolar liquids) (106) or the Scott-Osborne equation (107). For temperatures far below $T_{c,1}$, the second term on the rhs of Eq.(56) will frequently be rather small as compared to the first term. Eq.(56) evidently provides a set of values $\Delta H_2^\circ(T,P_{s,1})$, which yields, by an argument analogous to that used above, the heat capacity change upon solution.

The *Ostwald coefficient* $L_{2,1}$ is another widely used practical measure of the solubility of gas 2 in solvent 1 (108). Let the conventional Ostwald coefficient be defined by

$$L_{2,1}(T,P) \equiv \left(c_2^L/c_2^V\right)_{\text{equil}}\ , \tag{57}$$

where $c_2 \equiv n_2/V$, with the appropriate superscript, is the amount-of-substance concentration (or simply, concentration) of solute 2 either in the liquid-phase solution or in the coexisting vapor-phase solution at (T,P). Its *limiting value* for vanishingly small concentration is denoted by

$$L_{2,1}^\infty \equiv \lim_{\substack{c_2^L\to 0\\ P\to P_{s,1}}} L_{2,1}(T,P) = \lim_{\substack{c_2^L\to 0\\ P\to P_{s,1}}} \left(c_2^L/c_2^V\right)_{\text{equil}}\ . \tag{58}$$

Eq.(57) in conjunction with the equilibrium condition formulated on the basis of Henry's law yields (22), after some algebraic manipulation, the rigorous relation

$$L_{2,1}(T,P) = \frac{RT}{H_{2,1}(T,P)V^L(T,P,x_2)}\ \frac{Z^V(T,P,y_2)\,\phi_2^V(T,P,y_2)}{\gamma_2'(T,P,x_2)}\ , \tag{59}$$

where $V^L(T,P,x_2)$ is the molar volume of the liquid solution. Hence in the limit of $c_2^L \to 0$ we obtain, with $\lim\limits_{c_2^L\to 0} V^L(T,P,x_2) = V_1^{*L}(T,P_{s,1})$,

$$L_{2,1}^\infty = \frac{RT}{H_{2,1}(T,P_{s,1})V_{s,1}^{*L}}\ Z_{s,1}^{*V}\,\phi_2^{\infty V}(T,P_{s,1})\ . \tag{60}$$

At low to moderate pressures Eq.(43) may be applied, whereby

$$Z_{s,1}^{*V}\,\phi_2^{\infty V}(T,P_{s,1}) = \exp\left\{2\rho_{s,1}^{*V}B_{12} + \frac{3}{2}\left(\rho_{s,1}^{*V}\right)^2 C_{112}\right\}\ . \tag{61}$$

Alternatively, we may use the virial equation in its volume-explicit form, whence after series expansion

$$Z_{s,1}^{*V}\,\phi_2^{\infty V}(T,P_{s,1}) = 1 + 2\left(\frac{P_{s,1}}{RT}\right)B_{12} + \left(\frac{P_{s,1}}{RT}\right)^2 B_{11}(2B_{12} - B_{11})\ . \tag{62}$$

As reported by Wilhelm (22), Eq.(60) provides a rigorous expression for the *limiting value* of the Henry coefficient as $T \to T_{c,1}$ and $P_{s,1} \to P_{c,1}$:

$$\lim_{T\to T_{c,1}} H_{2,1}(T,P_{s,1}) = P_{c,1}\,\phi_2^{\infty V}(T_{c,1},P_{c,1})\ , \tag{63}$$

which equation was also given by Beutier and Renon (109). It *must* be incorporated in any rational *wide-temperature range* correlation for $H_{2,1}(T,P_{s,1})$ extending up to the critical region. In particular we note that the empirical extrapolation recipe of Hayduk and Laudie (110) is in variance with Eq.(63).

The Ostwald coefficient is of central importance in the theory of hydrophobic (solvophobic) phenomena. Following Ben-Naim (18), when discussing *pairwise hydrophobic interaction* (HI) we refer to the *indirect* part $\delta G^{HI}(r)$ of the Gibbs energy change $\Delta G(r)$ required to bring the solute particles from fixed positions at infinite separation in water to some close distance r at constant temperature and pressure. In other words, we are interested in the *solvent-induced* contribution augmenting the *direct* part that is due to the solute-solute pair potential $U_{SS}(r)$,

$$\Delta G(r) = U_{SS}(r) + \delta G^{HI}(r) \ . \tag{64}$$

The link with experimentally accessible quantities is established by the *approximate* relation

$$\delta G^{HI}(r = r_{C-C}) = \Delta\mu^{\circ}_{C_2H_6,H_2O} - 2\Delta\mu^{\circ}_{CH_4,H_2O} \ , \tag{65}$$

where $r_{C-C} = 0.1533$ nm is the carbon-carbon distance in ethane and

$$\Delta\mu^{\circ}_{i,H_2O} = -RT\ln L^{\infty}_{i,H_2O} \quad , \quad i = CH_4 \text{ or } C_2H_6 \ . \tag{66}$$

The approximation indicated by Eq.(65) is easily generalized to discuss HI among many solute particles (18,111).

CONCLUDING REMARKS

Quantitative investigation of the solubility of gases in liquids has a long and well established tradition in physical chemistry. Essentially it started in the fifties of the last century with the work of Bunsen (112), and throughout the years many a distinguished scientist has contributed to this subject. One can only marvel about the careful experimental work of some of the early researchers; for instance about Winkler's contributions (113) almost a century ago, which are still quite acceptable (± 1 %) in the majority of cases. The assortment of modern instrumentation accessible to today's experimentalist, however, has now made possible the study of highly dilute binary solutions of gases in liquids with unparalleled precision, accuracy and speed over wide ranges of temperature and pressure. Cross-fertilization with other disciplines, for instance with calorimetry, is becoming increasingly important (104,105). In fact, one of the objectives of this article was to indicate new and active interdisciplinary topics (see the Introduction); while our own perception of their relative importance may not be shared by all, it appears safe to state that they will greatly stimulate applied research in the coming decade.

This review was primarily concerned with the rigorous thermodynamic formalism relevant to VLE involving supercritical compounds, and its rational implementation in high-precision experimental work directed towards the determination of Henry coefficients and related quantities. Alternatives to the classical approach have been indicated, for instance the use of an EOS valid for both the liquid and the vapor phases. This method may gradually become more prominent when relatively simple solutions are considered. Yet as long as the scientist's interest is focused on phenomena involving significantly anisotropic molecules in dilute solutions, in particular in aqueous solutions, the Henry's law approach appears to be naturally superior to the others, and it is hard to imagine its replacement. Little space was devoted to experimental details, and recent theoretical advances have been indicated only briefly. Our understanding of nonpolar, nonassociated liquids and of "simple" solutions has increased considerably during the last decade (7,13,15,17,25,114-118). This is much less so for liquid water, and aqueous solutions even of rather simple solutes, such as hydrocarbons, remain a major challenge to a statistical-mechanical interpretation of solubility phenomena. High-precision measurements of the kind discussed here in the experimental section evidently occupy a key position in the development of new theoretical approaches.

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