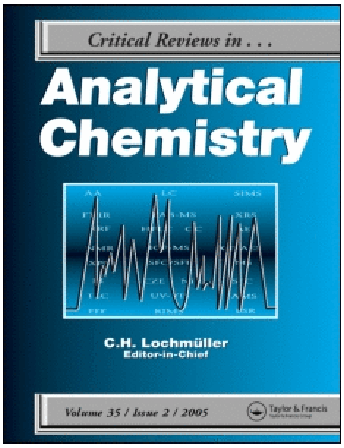

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PRECISION METHODS FOR THE DETERMINATION OF THE SOLUBILITY OF GASES IN LIQUIDS

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I. INTRODUCTION

Quantitative investigation of the solubility of gases in liquids has a long and well-established tradition in physical chemistry. Essentially, it started in the 1850s with the pioneering work of Bunsen "Ueber das Gesetz der Gasabsorption"[1], 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 example, Winkler's contributions[2,3] of almost a century ago are still quite acceptable (±2%) in the majority of cases; the fine work of Szeparowicz on radon solubility in water [4] is still useful; and the impressive, yet relatively little known, work of Horiuti[5] in the 1930s still stands as a major achievement. The years since about 1970 have been marked by renewed and intense activity in the field of solutions of nonelectrolytes in general, and of the solubility of gases in liquids in particular. This has brought about a wealth of new and precise experimental results (usually a consequence of novel designs of apparatus), the development of refined solution theories, and the recognition of the central role in the chemical and engineering sciences of effective communication and dissemination of data. These points are documented by the representative but by no means exhaustive cross-section of literature, References 6 to 56, which includes several of the older major reviews.

Why, now, this marked interest in vapor-liquid equilibria (VLE) involving components near or already above their respective critical temperature? The study of gas solubilities has, in addition to its profound theoretical interest, many important practical applications. In fact, research activities can be traced to requirements originating in surprisingly diverse areas of the pure and applied sciences. For instance, chemical process design often needs reliable estimates of VLE for multicomponent systems containing one or more gases (noncondensables). 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 current application-oriented topics (see also Figure 1): strongly enhanced solubility of oxygen in perfluorinated hydrocarbons[57] 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;[58-60] solubility of gases in selected solvents, for instance, in long-chain alcohols,[61] and its relation to anesthetic potency;[62,63] solubility of Freons and hydrocarbons in water (environmental pollution control),[64,65] and of oxygen and ozone in water (water treatment and waste water treatment);[66,67] removal of CO_2 and H_2S from sour

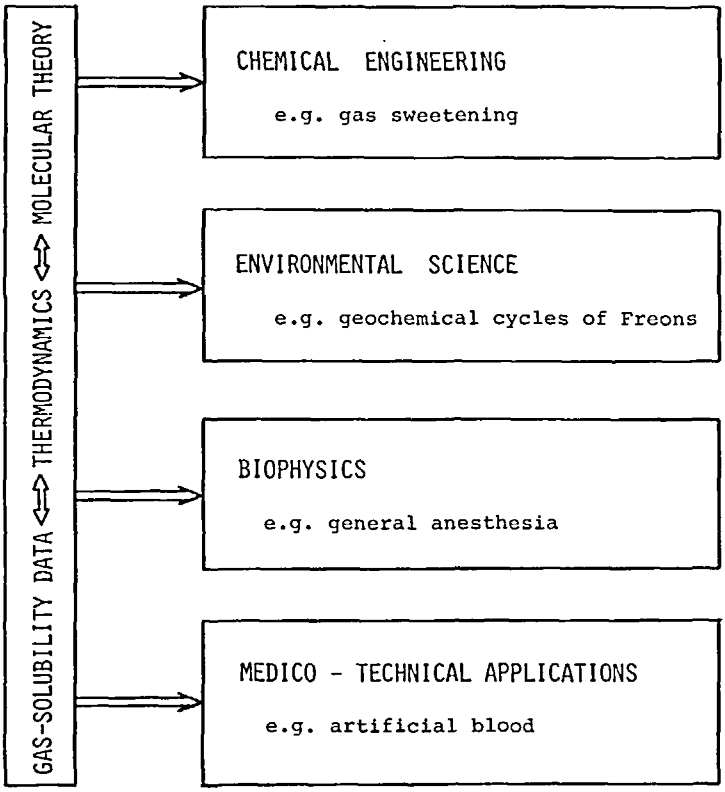

FIGURE 1. Representative examples of topics in the applied sciences where data on the solubility of gases in liquids are needed.

natural or synthetic gases by mixed-solvent absorption (gas sweetening);[68-73] solubility of hydrogen and other light gases in various (high molecular weight) solvents,[74-78] which is of importance for a number of engineering processes such as hydrofining of oil and coal and enhanced oil recovery; and solubility of gases in aqueous solutions of surfactants (solubilization).[79,80]

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 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 the current research interests of the author. First of all, a rigorous discussion of the thermodynamic fundamentals relevant to the solubility of gases in liquids will be presented. This will be followed by a critical examination of current methods for the prediction of important auxiliary quantities, such as virial coefficients and partial molar volumes. The next section will be devoted to the appraisal of several recent designs of precision apparatus and to the presentation and correlation of experimental data. Pride of place will be given to experimental methods characterized by imprecisions of *less* than 0.1%. Finally, a condensed outline of semitheoretical methods for estimating Henry coefficients will be given.

Most of what follows will concern the solubility of a *pure gas* in a *pure liquid*. Gas solubility in mixed solvents, though undoubtedly of considerable practical interest, will only be touched upon, and no salt effects will be discussed. Further, problems associated with solutions of chemically reacting gases will not be treated to any extent, since absorbtion with chemical reaction is an extensive topic by itself. Let it suffice to indicate a few important industrial applications in addition to those already mentioned: oxidation, hydrogenation, halogenation, etc. in the liquid phase; gas-scrubbing to reduce air pollution (SO_2, H_2S, Cl_2, HF, etc.); and biotechnological processes such as aerobic fermentation and sludge oxidation. The characteristic feature of all these processes is the interplay of equilibrium thermodynamics (solubility of gases) on the one hand, and time-dependent processes, that is to say mass transfer (diffusivity) and chemical reaction (rate constant), on the other. Enormous effort and ingenuity have gone into the designs of absorbers, strippers, and reactors. Indeed, the variety of shapes (spray columns, wetted-wall columns, packed columns, turbulent liquid jets, and so forth) simply reflects the need of industry to operate under optimal conditions. Those with a specific interest in one or more of these topics are referred to the pertinent sections of References 11, 32, 40, 44, 45, and 81 to 97.

II. THEORY

A. Thermodynamics of Vapor-Liquid Equilibrium: Fundamentals

As already indicated above, the expression "solution of gas(es) in liquid(s)" is usually meant to characterize, in a rather loose way, VLE in multicomponent systems where one or more of the components are *supercritical* or only *slightly* subcritical, and where the liquid-phase mole fraction 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 common liquids such as *n*-heptane, benzene, ethanol, or water are roughly between 10^{-2} and 10^{-5}. Clearly, some arbitrariness is involved and such a classification is to be taken as a mere heuristic convenience.

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 thus seems permissible to present here only a rather condensed treatment and to refer for details to the appropriate reviews[28,43] and monographs,[11,40,45,98-100] in particular to the excellent recent book by Van Ness and Abbott,[45] 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 of the π phases α, β, and γ, ... The fundamental relations characterizing phase equilibrium are those which equate the *chemical potential* μ_i^α of each component i = 1,2,..., K in phase α to its chemical potential μ_i^β in phase β and so forth. That is to say, we have (π − 1) independent equations:

$$\mu_i^\alpha(T,P,\{x^\alpha\}) = \mu_i^\beta(T,P,\{x^\beta\}) = \ldots = \mu_i^\pi(T,P,\{x^\pi\}) \qquad (1)$$

for each i, where $\{x^\alpha\}$ denotes the set of (K-1) independent mole fractions $\{x_1^\alpha, x_2^\alpha, \ldots, x_{K-1}^\alpha\}$ in phase α; $\{x^\beta\}$ denotes the set of (K-1) independent mole fractions $\{x_1^\beta, x_2^\beta, \ldots, x_{K-1}^\beta\}$ in phase β; etc. $x_i = n_i/n$, $n = \Sigma n_i$, n_i is the amount of substance i, and $\Sigma x_i = 1$. These equations of equilibrium may be replaced advantageously by the rigorously equivalent criterium of *equality of the component fugacities* f_i. For component i in *any* mixed phase, f_i is defined by

$$\left.\begin{aligned} d\mu_i &= RT\,d\ln f_i \\ \lim_{P\to 0}\,[f_i/(x_iP)] &= 1 \end{aligned}\right\} \text{ constant T} \qquad (2)$$

with obvious formulations for a solution and a pure substance. Instead of Equation 1, we now have in compact notation:

$$f_i^{\alpha}(T,P,\{x^{\alpha}\}) = f_i^{\beta}(T,P,\{x^{\beta}\}) = \ldots = f_i^{\pi}(T,P,\{x^{\pi}\}) \qquad (3)$$

For each i. For VLE this is written as

$$f_i^{V}(T,P,\{x^{V}\}) = f_i^{L}(T,P,\{x^{L}\}) \qquad i = 1,\ldots,K \qquad (4)$$

where the superscripts V and L now indicate the vapor phase and the liquid phase, respectively. As indicated, 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* of the components:

$$\phi_i(T,P,\{x\}) \equiv f_i/(x_iP) \qquad (5)$$

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:*

$$\gamma_i^L(T,P,\{x^L\}) \equiv f_i^L/(x_i^L f_i^{oL}) \qquad (6)$$

where f_i^{oL} is an appropriate standard-state fugacity. Setting $\{y\} \equiv \{x^V\}$ and dropping the superscript L where permissible, Equation 4 may be recast in the following two *entirely equivalent* ways:

$$y_i\phi_i^V(T,P,\{y\}) = x_i\phi_i^L(T;P,\{x\}) \qquad i = 1,\ldots,K \qquad (7)$$

and

$$y_i\phi_i^V(T,P,\{y\})P = x_i\gamma_i(T,P,\{x\})f_i^o(T,P) \qquad i = 1,\ldots,K \qquad (8)$$

Each equation may serve as a rigorous basis for the treatment of VLE problems. Note that both Equations 7 and 8 in fact represent K highly complex equations relating 2K variables (T,P,{x},{y}). Hence, in accord with the phase rule:

$$F = K - \pi + 2 \qquad (9)$$

with F being the number of degrees of freedom, K variables have to be specified to allow solution for the remaining K unknowns.

Numerical values for the fugacity coefficients are obtained through use of equation-of-state (EOS) information on the fluid (see below). Hence, the decision as to what approach should be preferred, though in principle a matter of taste, is subject to important *practical constraints.* For high pressure VLE involving fairly simple substances, the use of a single

EOS valid for *both* phases V and L often has computational advantages (and a certain aesthetic appeal), and thus, Equation 7 may be selected. An attractive feature of this approach is that the troublesome problem of specifying liquid-phase standard-state fugacities for supercritical components is altogether avoided. However, the emphasis is on "fairly simple", since no generally satisfactory EOS for dense fluids encountered in practice has been as yet established. In addition, we note that the simultaneous solution of a large number of strongly nonlinear equations is not a trivial problem. The situation is further aggravated by the sensitivity of the results on the so-called "combining rules", which have almost always a strong empirical flavor. We return to some of these problems in Section II.B.

In the thermodynamic analysis of VLE (i.e., *data reduction* or *VLE calculations*) at low to moderate pressures, Equation 8 is most frequently used. Here, an EOS is required *only* for the *low-density vapor phase*, while for the *liquid phase* usually an adequate *activity coefficient* model is introduced, or more precisely, an analytical expression (at constant T and P) for the excess molar Gibbs energy G^E:

$$G^E/RT = \sum_i x_i \ln\gamma_i \tag{10}$$

$$\ln\gamma_i = \left(\frac{\partial(nG^E/RT)}{\partial n_i}\right)_{T,P,n_{j\neq i}} \tag{11}$$

as a function of composition {x}.[101] See, however, References 102 and 103 for numerical methods. The practical advantages of this approach are obvious: properties of the low-density vapor phase can frequently be calculated from a relatively simple EOS, such as the virial equation,[49,104-106] and there exists a variety of semitheoretical methods for modeling G^E, even for strongly nonideal solutions. Perhaps the most useful are known under the heading "group-contribution theories".[49,107-114] The disadvantages of the (γ, ϕ) approach will emerge slowly.

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,* only the (γ, ϕ) method, based on Equation 8, will be considered; the (ϕ, ϕ) method will not be pursued further. We note, however, the intense efforts of many research groups in EOS research.[115-131]

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

$$f_i^{id} = x_i f_i^*(T,P) \qquad i = 1 \text{ or } 2 \tag{12}$$

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

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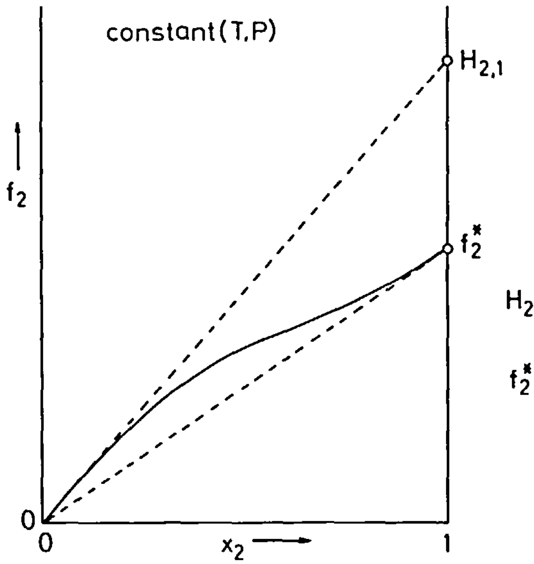
* Throughout this article a subscript c will denote a "critical quantity", and reduced quantities $Q_r = Q/Q_c$ will be designated by a subscript r. A subscript s indicates "orthobaric (i.e., saturation) conditions". Superscripts ° identify either "standard-state quantities" or "perfect-gas-state quantities";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



$$H_{2,1} = \lim_{x_2 \to 0} \frac{f_2}{x_2} = \left(\frac{df_2}{dx_2}\right)_{x_2=0} \quad \text{(HL)}$$

$$f_2^* = \lim_{x_2 \to 1} \frac{f_2}{x_2} = \left(\frac{df_2}{dx_2}\right)_{x_2=1} \quad \text{(LR)}$$

FIGURE 2. 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. (From Wilhelm, E., *Pure Applied Chem.*, 57, 303, 1985. With permission.)

$$\left.\begin{aligned} f_1^{id} &= x_1 f_1^*(T,P) \\ f_2^{id} &= x_2 H_{2,1}(T,P) \end{aligned}\right\} \qquad (13)$$

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

$$\left.\begin{aligned} \gamma_1 &\to 1 \quad \text{as} \quad x_1 \to 1 \\ \gamma_2 &\to 1 \quad \text{as} \quad x_2 \to 1 \end{aligned}\right\} \qquad (14)$$

or *unsymmetrically:*

$$\left.\begin{aligned} \gamma_1 &\to 1 \quad \text{as} \quad x_1 \to 1 \\ \gamma_2' &\to 1 \quad \text{as} \quad x_2 \to 0 \end{aligned}\right\} \qquad (15)$$

The prime in Equation 15 is to serve as a reminder that the unsymmetric convention of normalization has been used, that is to say $\gamma_1 \equiv f_1/(x_1 f_1^*)$ and $\gamma_2' \equiv f_2/(x_2 H_{2,1})$. 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 Figure 2. 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 $0 \leq x_i \leq 1$. 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 Figure 2); 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:

$$\ln f = x_1 \ln(f_1/x_1) + x_2 \ln(f_2/x_2) \qquad \text{constant (T,P)} \tag{16}$$

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^{*L} 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,[132] *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 temperature and pressure:

$$\ln f_2^{*} = \ln H_{2,1} - \ln \gamma_2^{\infty} \tag{17}$$

and

$$\ln \gamma_2 = \ln \gamma_2' + \ln \gamma_2^{\infty} \tag{18}$$

where the activity coefficient at infinite dilution γ_2^{∞} is given by

$$\ln \gamma_2^{\infty} = \lim_{x_2 \to 0} (\ln \gamma_2) = -\lim_{x_2 \to 1} (\ln \gamma_2') \tag{19}$$

The excess molar Gibbs energy $G^{E'}$ based on the unsymmetric normalization of activity coefficients is obtained from

$$G^{E'}/RT = x_1 \ln \gamma_1 + x_2 \ln \gamma_2' \tag{20}$$

According to Equations 10, 17, and 18 it is related to the excess molar Gibbs energy based on the symmetric convention by

$$G^{E}/RT - G^{E'}/RT = x_2 \ln \gamma_2^{\infty} \tag{21}$$

$$= x_2 \ln(H_{2,1}/f_2^{*L}) \tag{22}$$

Because of the unsymmetric normalization, $G^{E'}$ vanishes at infinite dilution with respect to component 2, the gas, but *not* with respect to component 1, the solvent. The situation is illustrated by Figure 3.

The equilibrium criteria for VLE, Equations 7 and 8, apply at temperature T and equilibrium pressure P of the solution. For isothermal conditions, P varies with x_2 and hence for each composition the four quantities ϕ_1, 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 formulas 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

$$f_1^{*L}(T,P) = f_1^{*L}(T,P_{s,1})\mathscr{P}_1(T,P) = P_{s,1}\phi_{s,1}^{*V}\mathscr{P}_1(T,P) \tag{23}$$

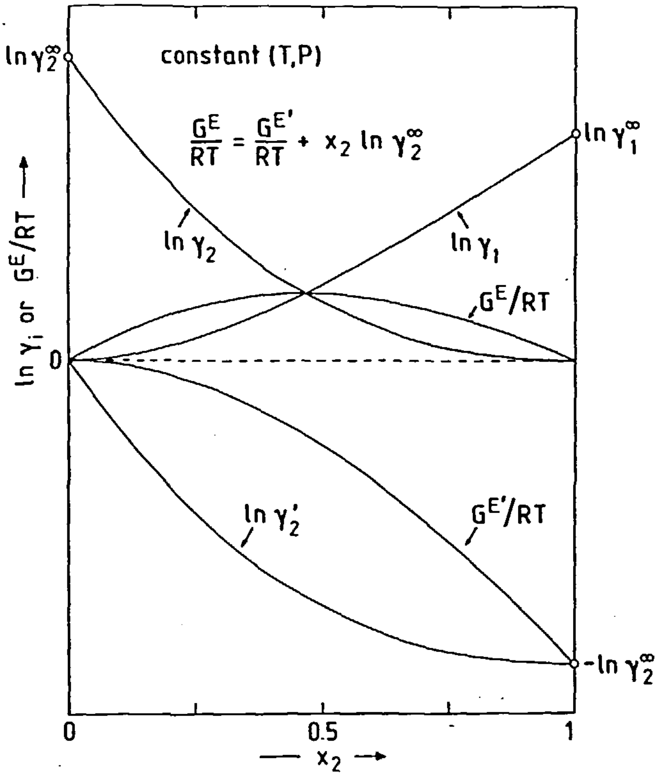


FIGURE 3. Composition dependence of ln γ_i (symmetric normalization of activity coefficients, i = 1 or 2) and ln γ_2' (unsymmetric normalization), and the corresponding dimensionless quantities G^E/RT and $G^{E'}/RT$ of a binary mixture at constant T and P. G^E denotes the excess molar Gibbs energy.

$$\mathcal{P}_1(T,P) \equiv \exp\left\{\int_{P_{s,1}}^{P} \frac{V_1^{*L}(T,P)}{RT}\,dP\right\} \tag{24}$$

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} (T,P) is the molar volume of pure liquid; and $\mathcal{P}_1(T,P)$ is called the Poynting correction. For the Henry coefficient we obtain

$$H_{2,1}(T,P) = H_{2,1}(T,P_{s,1})\mathcal{P}_2(T,P) \tag{25}$$

$$\mathcal{P}_2(T,P) \equiv \exp\left\{\int_{P_{s,1}}^{P} \frac{V_2^{\infty L}(T,P)}{RT}\,dP\right\} \tag{26}$$

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

$$\gamma_1(T,P,x_2) = \gamma_1(T,P_{s,1},x_2)\exp\left\{\int_{P_{s,1}}^{P} \frac{V_1^{L}(T,P,x_2) - V_1^{*L}(T,P)}{RT}\,dP\right\} \tag{27}$$

$$\gamma_2'(T,P,x_2) = \gamma_2'(T,P_{s,1},x_2)\exp\left\{\int_{P_{s,1}}^{P} \frac{V_2^{L}(T,P,x_2) - V_2^{\infty L}(T,P)}{RT}\,dP\right\} \tag{28}$$

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 at any desired density or pressure, either in terms of a *pressure-explicit or a volume (density)-explicit EOS*. The proviso is, 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:

$$\ln \phi_i = \int_0^{\rho} \left[\left(\frac{\partial nZ}{\partial n_i} \right)_{T,\rho/n,n_j} - 1 \right] \rho^{-1} d\rho - \ln Z \qquad \text{constant } (T,\{x\}) \qquad (29)$$

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

$$\ln\phi_i = \int_0^{P} (Z_i - 1)P^{-1}dP \qquad \text{constant } (T,\{x\}) \qquad (30)$$

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 is pressure explicit rather than volume explicit, Equation 24 is more useful in VLE problems than Equation 30. The appropriate formulae for the pure-substance fugacity coefficient ϕ_i^* are, with obvious notation:

$$\ln \phi_i^* = \int_0^{\rho_i^*} (Z_i^* - 1)(\rho_i^*)^{-1} d\rho_i^* + Z_i^* - 1 - \ln Z_i^* \qquad \text{constant } T \qquad (31)$$

and

$$\ln \phi_i^* = \int_0^{P} (Z_i^* - 1)P^{-1}dP \qquad \text{constant } T \qquad (32)$$

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.[43,45,54,56] *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 Equation 8 may be replaced by

$$y_2\phi_2^V(T,P,y_2)P = x_2\gamma_2'(T,P_{s,1},x_2)H_{2,1}(T,P_{s,1})\exp\left\{ \int_{P_{s,1}}^{P} \frac{V_2^L(T,P,x_2)}{RT} dP \right\} \qquad (33)$$

where use was made of Equations 25, 26, and 28. Analogously, for the solvent we now have:

$$y_1\phi_1^V(T,P,y_2)P = x_1\gamma_1(T,P_{s,1},x_2)P_{s,1}\phi_{s,1}^{*V}\exp\left\{ \int_{P_{s,1}}^{P} \frac{V_1^L(T,P,x_2)}{RT} dP \right\} \qquad (34)$$

Note that both γ_1 and γ_2' of Equations 33 and 34 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;[11] see also Van Ness.[133] In particular, they satisfy the isothermal-isobaric Gibbs-Duhem equation:

$$x_1 d\ln\gamma_1(T,P_{s,1},x_2) + x_2 d\ln\gamma_2'(T,P_{s,1},x_2) = 0 \tag{35}$$

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 Figure 2):

$$H_{2,1}(T,P_{s,1}) = \lim_{x_2\to 0}(f_2^L/x_2) = \lim_{x_2\to 0}\frac{y_2\phi_2^V(T,P,y_2)P}{x_2} \tag{36}$$

Thus, according to Equation 36, $H_{2,1}(T,P_{s,1})$ 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 Figure 2) yields several entirely equivalent expressions for the Henry coefficient,[45,54] relating it to *limiting slopes*. For instance

$$H_{2,1}(T,P_{s,1}) = \lim_{x_2\to 0}(df_2^L/dx_2) = \phi_2^{\infty V}(T,P_{s,1})P_{s,1}\lim_{x_2\to 0}(dy_2/dx_2) \tag{37}$$

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 Equations 33 and 34, whence the 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[54,56] of Equation 35:

$$\ln\left(\frac{y_2\phi_2^V(T,P,y_2)P}{x_2H_{2,1}(T,P_{s,1})}\right) - \int_{P_{s,1}}^{P}\frac{V_2^L(T,P,x_2)}{RT}\,dP = \ln\gamma_2'(T,P_{s,1},x_2) \tag{38}$$

The argument of the logarithmic term on the lhs of Equation 38 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 Equations 29 and 30). To proceed further, that is to say in order to evaluate the integral in Equation 38, 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 (or another measure of composition) 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 the constant-pressure activity coefficients* $\gamma_2'(T,P_{s,1},x_2)$.

The sequential approach outlined above is adopted almost universally and reflects simply the focusing of interest upon the solute in a composition range very close to pure subcritical component 1. In this classical method of gas-solubility data reduction, very little use is made of the information thermodynamics supplies on the solvent. Since gas solubility is a subdiscipline of VLE, the appropriate general thermodynamic formalism may as well be used and we obtain from Equations 33 and 34 for the total pressure:

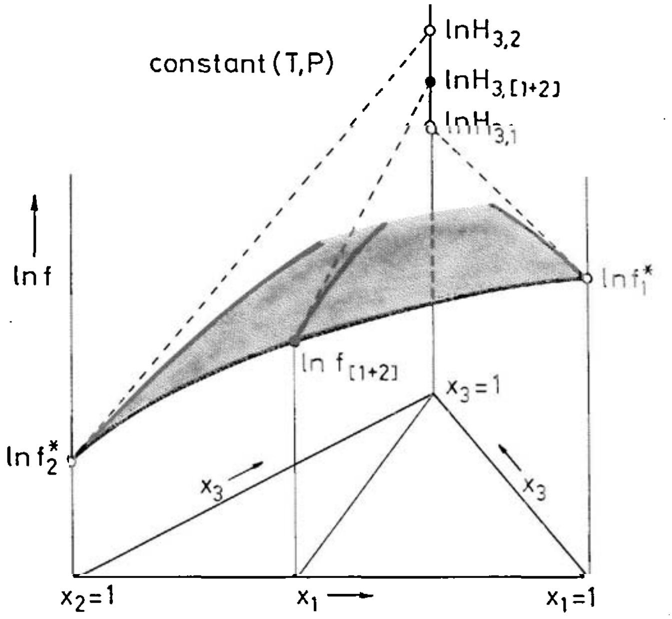


FIGURE 4. Schematic representation of the ln f surface for a ternary solution of a gas, 3, in the mixed solvent [1 + 2]: the Henry coefficient in the pure solvent i (= 1 or 2) is $H_{3,i}$, and in the mixed solvent it is $H_{3[1+2]}$. (From Wilhelm, E., *Pure Applied Chem.*, 57, 303, 1985. With permission.)

$$P = x_1 P_{s,1} \gamma_1(T, P_{s,1}, x_2) \frac{\phi^{*V}_{s,1}}{\phi^V_1} \exp\left\{ \int_{P_{s,1}}^{P} \frac{V^L_1}{RT} dP \right\}$$

$$+ \; x_2 H_{2,1}(T, P_{s,1}) \gamma'_2(T, P_{s,1}, x_2) \frac{1}{\phi^V_2} \exp\left\{ \int_{P_{s,1}}^{P} \frac{V^L_2}{RT} dP \right\} \qquad (39)$$

Isothermal VLE data which give the variation of P with liquid composition may be reduced advantageously by Barker's method,[101] whereby the functional form for the composition dependence of the activity coefficients is assumed in advance. It may be applied also to Equation 39.

A final caveat concerns the extension of the methods just described to multisolute/multisolvent systems. The activity coefficient of any super-critical 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;[32] see also Reference 45. Let it suffice here 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 Figure 4 schematically shows the surface:

$$\ln f = \sum_{i=1}^{3} x_i \ln(f_i/x_i) \qquad (40)$$

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 $x_3 \rightarrow 0$, 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 lnf 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 $x_3 \rightarrow 0$:

$$\ln H_{3,[1+2]} \equiv \lim_{x_3 \rightarrow 0} \left(\ln \frac{f_3}{x_3} \right) = \ln f_{[1+2]} + \lim_{x_3 \rightarrow 0} \left(\frac{\partial \ln f}{\partial x_3} \right)_{T,P,x_1/x_2} \tag{41}$$

where $f_{[1+2]}$ 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 $x_2 = 1$.

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[11,28,40] 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.

B. Thermodynamics of Vapor-Liquid Equilibrium: Practical Implementation

In Section II.A we have reviewed concisely the thermodynamic formalism as applied to mixtures containing supercritical components. Section II.B is devoted entirely to a critical discussion of various approximations to the exact relations obtained so far. These approximations are indispensable when application to experimental reality is desired. Some additional details will be given together with the discussion of experimental techniques.

1.The Vapor Phase

Whatever method for determining $H_{2,1}(T,P_{s,1})$ is selected, say for instance one of the recipes of Equation 36 or Equation 37, evaluation from an experimental isothermal data set requires a vapor-phase EOS for calculating the fugacity coefficient ϕ_2^V (or ϕ_2^{*V}). This quantity is again needed when the key equation is used, i.e., when extraction and subsequent correlation of activity coefficients γ_2' are intended.

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 pressure-explicit virial equation of state[49,104,105,134,135]

$$Z(T,\rho,\{y\}) \equiv P/\rho RT = 1 + \sum_{n=2}^{\infty} B_n(T,\{y\})\rho^{n-1} \tag{42}$$

$$B_n(T,\{y\}) = \frac{1}{(n-1)!} \left(\frac{\partial^{n-1} Z}{\partial \rho^{n-1}} \right)_{T,\{y\};\rho=0} \tag{43}$$

is convenient for the description of real-gas behavior,* and often yields entirely satisfactory results even when truncated after the term which is linear in molar density $\rho \equiv V^{-1}$. The coefficients $B_2 \equiv B$, $B_3 \equiv C$, etc. are known as the second virial coefficient, the third virial coefficient, and so forth, and are functions of temperature and composition only. The general manner of the variation of B and C with temperature is indicated in Figure 5 for a Lennard-Jones (6,12) fluid.[138]

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* We exclude strongly associating fluids, such as alkanoic acids (dimerization). For such substances appropriate "chemical" theories have been developed.[11,40,136,137]

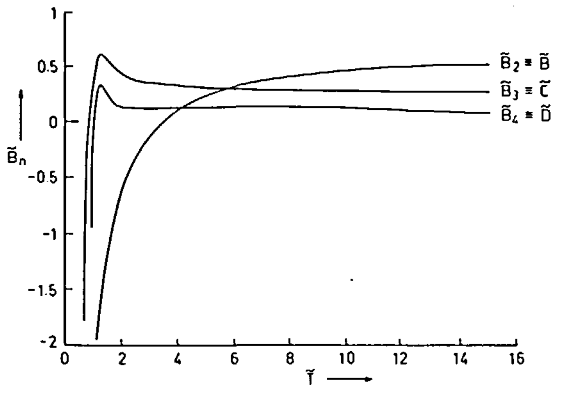

FIGURE 5. Reduced virial coefficients $\tilde{B}_n = B_n/b_0^{n-1}$ as function of reduced temperature $\tilde{T} = kT/\epsilon$ from the Lennard-Jones (6, 12) potential; $b_0 = (2/3)\pi\sigma^3 N_A$. They were computed[138] with the pairwise addivitiy assumption. $\tilde{B}_2 \equiv \tilde{B}$ has a maximum at about $\tilde{T} = 25$. (From Wilhelm, E., *Thermochim. Acta*, 69, 1, 1983. With permission.)

Alternatively, the compressibility factor may be written as a power series in pressure:

$$Z(T,P,\{y\}) = 1 + \sum_{n=2}^{\infty} B_n'(T,\{y\})P^{n-1} \tag{44}$$

$$B_n'(T,\{y\}) = \frac{1}{(n-1)!}\left(\frac{\partial^{n-1}Z}{\partial P^{n-1}}\right)_{T,\{y\};P=0} \tag{45}$$

where the virial coefficients $B_2' \equiv B'$, $B_3' \equiv C'$, etc. of the density (or volume)-explicit EOS, Equation 44, are again functions of temperature and composition only. The coefficients of these two infinite series are closely related, i.e.,

$$B' = B/RT \tag{46}$$

$$C' = (C - B^2)/(RT)^2 \tag{47}$$

$$D' = (D - 3BC + 2B^3)/(RT)^3, \text{ etc.} \tag{48}$$

For a mixture of K components, each with mole fraction y_i ($i = 1,2, \ldots k$)

$$B(T,\{y\}) = \sum_i^K \sum_j^K y_i y_j B_{ij}(T) \tag{49}$$

$$C(T,\{y\}) = \sum_i^K \sum_j^K \sum_k^K y_i y_j y_k C_{ijk}(T), \quad \text{etc.} \tag{50}$$

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. As indicated they are functions of temperature only. For the cross-coefficients certain symmetry relations apply. For example,

$$B_{ij} = B_{ji} \tag{51a}$$

$$C_{ijk} = C_{ikj} = C_{jik} = C_{jki} = C_{kij} = C_{kji}, \quad \text{etc.} \tag{51b}$$

Insertion of Equations 49 and 50 into Equation 29 yields:

$$\ln \phi_i^V = 2\rho^V \sum_j^K y_j B_{ij} + \frac{3}{2}(\rho^V)^2 \sum_j^K \sum_k^K y_j y_k C_{ijk} - \ln Z^V \tag{52}$$

where the summations are overall components. For the gas (i = 2) in a *binary* vapor mixture, Equation 52 reduces to

$$\ln \phi_2^V = 2\rho^V(y_2B_{22} + y_1B_{12}) + \frac{3}{2}(\rho^V)^2(y_2^2C_{222} + 2y_1y_2C_{122} + y_1^2C_{112}) - \ln Z^V \tag{53}$$

where Z^V is given by Equation 42. The fugacity coefficient at infinite dilution is then

$$\ln \phi_2^{\infty V} = 2\rho_1^{*V}B_{12} + \frac{3}{2}(\rho_1^{*V})^2C_{112} - \ln Z_1^{*V} \tag{54}$$

with the asterisked quantities referring to pure solvent vapor.

Unfortunately, experimental results on second interaction virial coefficients are frequently not available, and information on third virial coefficients is even more severely limited.[105] As a result, one has to rely rather heavily on semiempirical correlation methods, the reliability of which may not always be high. This may impede satisfactory reduction of data obtained at high reduced temperatures $T_{r,1}$, where $P_{s,1}$ is already substantial, and/or elevated gas pressures.[139-141]

Cross-coefficients B_{ij} may usually be estimated with reasonable confidence by several well-established correlations, such as the Hayden-O'Connell method[137] of the Pitzer-Curl-Tsonopoulos method.[142,143] The latter is based on the extended corresponding states theorem (CST); in this case, the reduced pure-substance virial coefficient at a reduced temperature $T_r = T/T_c$ is given by

$$\frac{BP_c}{RT_c} = B^{(0)}(T_r) + \omega\, B^{(1)}(T_r) \tag{55}$$

$$\begin{aligned} B^{(0)}(T_r) = {} & 0.1445 - 0.3300\, T_r^{-1} - 0.1385\, T_r^{-2} \\ & - 0.0121\, T_r^{-3} - 0.000607\, T_r^{-8} \end{aligned} \tag{56}$$

$$B^{(1)}(T_r) = 0.0637 + 0.331\, T_r^{-2} - 0.423\, T_r^{-3} - 0.008\, T_r^{-8} \tag{57}$$

where ω is the acentric factor.[30] It is assumed that the same relations hold for the cross-coefficient B_{ij}, but with characteristic parameters (interaction parameters) $T_{c,ij}$, $P_{c,ij}$, and ω_{ij} 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 $T_{r,ij} \equiv T/T_{c,ij}$, and

$$T_{c,ij} = (1 - k_{ij})(T_{c,i}T_{c,j})^{1/2} \tag{58}$$

$$P_{c,ij} = Z_{c,ij}RT_{c,ij}/V_{c,ij} \tag{59}$$

$$V_{c,ij} = \frac{1}{8}(V_{c,i}^{1/3} + V_{c,j}^{1/3})^3 \tag{60}$$

$$Z_{c,ij} = \frac{1}{2}(Z_{c,i} + Z_{c,j}) \tag{61}$$

$$\omega_{ij} = \frac{1}{2}(\omega_i + \omega_j) \tag{62}$$

The quantity k_{ij} is yet another binary interaction parameter (usually much smaller than unity), and may be estimated by various semiempirical correlations.[143] It is similar to the binary interaction parameters used in the more fundamental combining rules for unlike energy parameters of two-parameter pair potentials.[49,144,145]

As a *rough* rule, the virial EOS truncated after the B term should yield reasonable results for[146]

$$P < \frac{T}{2}\sum_{i=1}^{K} y_i P_{c,i} \Big/ \sum_{i=1}^{K} y_i T_{c,i} \tag{63}$$

At higher pressures, or when a higher accuracy in the fugacity coefficient is desired, third virial coefficients are indispensable. Extended CST correlations for C have been presented by Chueh and Prausnitz,[147] Pope et al.[148] (this method is limited, however, to substances with small ω), De Santis and Grande,[149] and most recently by Orbey and Vera.[150]

For pure substances the empirical equation suggested by De Santis and Grande is of the form:

$$C/V_c^2 = C^{(0)}(T_r) + dC^{(1)}(T_r) + d^2C^{(2)}(T_r) \tag{64}$$

The parameter d may be evaluated to a first approximation according to

$$d = \omega\alpha N_A\hat{b}^{-1} \tag{65}$$

Here, α is the mean polarizability, N_A is Avogadro's constant, and $\hat{b}$ is a measure of molecular volume (Bondi[151]); d accounts empirically for the influence of molecular shape and size, and for the influence of nonadditivity effects upon the deviations from the two-parameter CST. Extension to mixtures follows closely Reference 147, that is to say

$$C_{ijk} = (C_{ij}C_{ik}C_{jk})^{1/3} \tag{66}$$

and the C_{ij}, etc. are evaluated via Equation 64 with T_c being replaced by $T_{c,ij}$ (see Equation 58), V_c by $V_{c,ij}$ (see Equation 60), and

$$d_{ij} = \frac{1}{2}(d_i + d_j) \tag{67}$$

With this correlation the virial EOS may be used up to about three fourths of the critical density.

The correlation of Orbey and Vera is of the form:

$$CP_c^2/(RT_c)^2 = C^{(0)}(T_r) + \omega C^{(1)}(T_r) \tag{68}$$

where $C^{(0)}(T_r)$ and $C^{(1)}(T_r)$ are polynomials in T_r^{-1}. For the cross-coefficients the authors again use Equation 66. The Orbey-Vera method performs about as well as the De Santis-Grande method.

As an alternative to the virial EOS, one may use any appropriate analytical EOS to obtain the vapor-phase fugacity coefficient. Examples for calculations of this kind, concerning gaseous mixtures of strongly polar molecules (such as water) with nonpolar or slightly polar molecules (such as methane or carbon monoxide), have been presented in References 152 and 153. In the former, a perturbed-hard-sphere EOS similar to that introduced by Carnahan and Starling[154,155] is used, while the latter utilizes a modified Redlich-Kwong (RK) equation. Comprehensive reviews of advances in this field may be found in References 27, 37, and 48.

For convenience we give here the fugacity coefficient expression for what is perhaps the most popular two-parameter EOS, formulated by Redlich and Kwong[156] in 1949. In the original form (pure fluid):

$$Z = \frac{V}{V-b} - \frac{a}{RT^{1.5}(V+b)} \tag{69}$$

The size parameter b and the attraction parameter a may be obtained from the critical properties by

$$a = \Omega_a R^2 T_c^{2.5}/P_c \tag{70}$$

and

$$b = \Omega_b RT_c/P_c \tag{71}$$

with $\Omega_a = 0.427480$ and $\Omega_b = 0.086640$. Extension to mixtures is straightforward by introducing conventional combining rules.[157] When relinquishing the universal values for Ω_a and Ω_b we obtain for instance

$$b = \sum_i y_i b_i \tag{72}$$

$$a = \sum_i \sum_j y_i y_j a_{ij} \tag{73}$$

$$a_{ij} = \frac{(\Omega_{a,i} + \Omega_{a,j})R^2 T_{c,ij}^{2.5}}{2P_{c,ij}} \tag{74}$$

$$Z_{c,ij} = 0.291 - 0.04(\omega_i + \omega_j) \tag{75}$$

plus the recipes of Equations 58 to 60. Insertion into Equation 29 yields:

$$\ln \phi_i = \ln \frac{V}{V-b} + \frac{b_i}{V-b} - \frac{2\sum_j y_j a_{ij}}{bRT^{1.5}} \ln \frac{V+b}{V} + \frac{ab_i}{b^2RT^{1.5}}\left(\ln \frac{V+b}{V} - \frac{b}{V+b}\right) - \ln Z \tag{76}$$

Here, V is the molar volume calculated from Equation 69 with mixture parameters a and b from Equations 72 and 73, and parameters $\Omega_{a,i}$ and $\Omega_{b,i}$ are permitted to vary somewhat from one substance to another; optimized values have been reported by Chueh and Prausnitz,[157] together with estimates for binary interaction parameters k_{ij} of Equation 58.

The computational convenience associated with a volume-explicit rather than a pressure-explicit EOS leads to the widely used approximation for *low pressures*:

$$Z^V = 1 + BP/RT \tag{77}$$

where B of the mixture is again given by Equation 49. The corresponding expression for the fugacity coefficients is now obtained through insertion of Equation 77 into Equation 30, whence for a binary vapor mixture:

$$\ln \phi_i^V = \frac{P}{RT}(B_{ii} + y_j^2\Delta_{12}) \qquad i = 1 \text{ or } 2 \tag{78}$$

with $\Delta_{12} \equiv 2B_{12} - (B_{11} + B_{22})$. The fugacity coefficient of gas at infinite dilution in the vapor phase is now

$$\ln \phi_2^{\infty V} = \frac{P}{RT}(2B_{12} - B_{11}) \tag{79}$$

To conclude this topic we emphasize that the quite popular rule of thumb:

$$\phi_2^V(T,P,y_2) = \phi_2^{*V}(T,P) \tag{80}$$

may frequently be a rather unsatisfactory assumption and is in general inapplicable for the evaluation of $\phi_2^{\infty V}$. Equation 80 can be justified only if the vapor phase is an ideal solution. It is, however, always a useful approximation when $y_2 \gg y_1$ (it becomes exact for $y_2 \rightarrow 1$). Figure 6 shows component fugacity coefficients for $[(1 - y_2)H_2O + y_2N_2]$ at 423.15 K and two different pressures. They were calculated via Equation 78. Although P′ and P″ are not large, 100 and 475 kPa, respectively, deviations from Equation 80 are significant and amount up to about 4%.

Unless the pressure is *very* low, the assumption $\phi_i^V = 1$ is rarely satisfactory, and should be avoided altogether in experimental work of even moderate precision. In the pressure range 100 to 1000 kPa, ϕ_i^V often differs significantly from unity, in particular for polar substances.

2. *The Liquid Phase*

Consider, for instance, the key relation Equation 38. 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[43,54,56]

1. 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

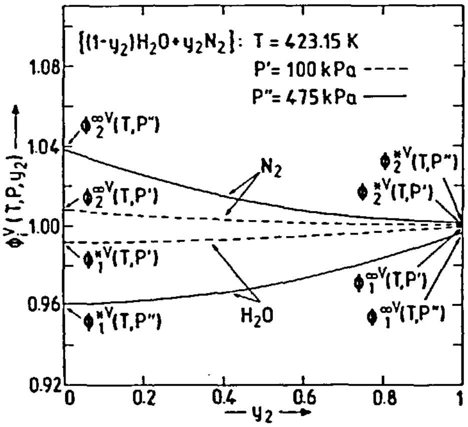

FIGURE 6. Component fugacity coefficients $\phi_i^V(T,Py_2)$ as a function of composition for $\{(1 - y_2)H_2O + y_2N_2\}$ at T = 423.15 K and P' = 100 kPa, and P" = 475 kPa.

be available only in very few cases; for the great majority of solutions, however, approximations at various levels of sophistication must be introduced to make the problem tractable. Similar comments apply, of course, to Equations 23, 25, 27, 28 etc. The situation becomes particularly unsatisfactory at high pressures and when approaching the critical region where the Poynting corrections become significant.

2. 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 few adjustable parameters, that is to say rarely more than two.

Against this background several popular approximations to the key relation Equation 38 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 gas solubilities) and ignoring the Poynting term (which may be acceptable for pressures $P \approx P_{s,1}$ well below the critical region), leads to the simplest and most *familiar* relation:

$$P_2 \equiv y_2P = x_2H_{2,1} \qquad (81)$$

which is often called *Henry's law*. A series of similar approximations to Equation 34 results in *Raoult's law* for the solvent:

$$P_1 \equiv y_1P = x_1P_{s,1} \qquad (82)$$

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

$$y_2\phi_2^V(T,P,y_2)P = x_2H_{2,1} \qquad (83)$$

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:

$$\ln\left(\frac{y_2\phi_2^V(T,P,y_2)P}{x_2H_{2,1}(T,P_{s,1})}\right) = \frac{(P-P_{s,1})V_2^{\infty L}(T,P_{s,1})}{RT} \qquad (84)$$

This expression is known as the *Krichevsky-Kasarnovsky equation.*[158] 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 $V_2^{\infty L}$ 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.[159,160] The preferred experimental method for determining $V_2^{\infty L}$ (and V_2^L) is either precision dilatometry[5,161-164] or precision densimetry[165-170] at very small mole fractions. For a review of the literature on $V_2^{\infty L}$, see Battino and Clever[9,22] and Handa and Benson.[171]

As concerns the modeling of the composition dependence of $\gamma_2{}'$, 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, Equation 17 to 19, the selection of such correlations usually follows rather closely the well-established recipes for the symmetrically normalized activity coefficients. A rigorous connection between $\ln\gamma_2{}'$ and G^E/RT (symmetric convention) is easily established for binary systems.[45] At constant T and P:

$$\ln \gamma_2' = \frac{G^E}{RT} + x_1 \frac{d(G^E/RT)}{dx_2} - \lim_{x_2 \to 0} \frac{d(G^E/RT)}{dx_2} \tag{85}$$

Take, for instance, the simplest nontrivial expression for G^E/RT, that is to say the one-parameter equation:

$$G^E/RT = Ax_1x_2 \tag{86}$$

From Equation 85 and with $\ln \gamma_1 = G^E/RT + x_2[d(G^E/RT)/dx_1]$ we obtain:

$$\ln \gamma_1 = Ax_2^2 \tag{87a}$$

$$\ln \gamma_2' = A(x_1^2 - 1) \tag{87b}$$

Equations 87a and 87b are often called the two-suffix Margules equations. When applied to isothermal, pressure-corrected activity coefficients as discussed above, clearly $A = A(T,P_{s,1})$. Inserting into Equation 38 and maintaining the same level of approximation with respect to V_2^L gives:

$$\ln \left(\frac{y_2\phi_2^V(T,P,y_2)P}{x_2H_{2,1}(T,P_{s,1})}\right) - \frac{(P - P_{s,1})V_2^{\infty L}(T,P_{s,1})}{RT} = A(x_1^2 - 1) \tag{88}$$

which is known as the *Krichevsky-Ilinskaya equation.*[172,173] There can be little doubt that even Equation 88 is not particularly realistic at high pressure 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.*

An example of a two-parameter equation is the one suggested by Prausnitz[11] and Chueh et al.[174] It is analogous to the classical Wohl equation[175] in that the unsymmetric excess Gibbs energy is expanded as a power series in an effective volume fraction Φ_2:

$$\frac{G^{E'}}{RT(x_1q_1 + x_2q_2)} = -\,\hat{\alpha}_{22,1}\Phi_2^2 - \hat{\alpha}_{222,1}\Phi_2^3 - \ldots \tag{89}$$

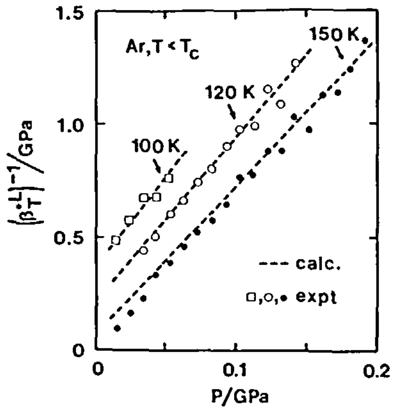

FIGURE 7. Reciprocal isothermal compressiblity $(\beta_T^{*L})^{-1}$ of liquid argon as a function of pressure P at T/K = 100, 120, 150. (□, ○, ●) Experimental points. (---) Calculated (generalized van der Waals approach, see Wilhelm[177]).

$$\Phi_2 = \frac{x_2q_2}{x_1q_1+x_2q_2} \tag{90}$$

$$q_i = V_{c,i}(1 + \hat{\eta}_{2,1}\Phi_2^2) \qquad i = 1 \text{ or } 2 \tag{91}$$

q_i is an effective size parameter for molecule i and $\hat{\eta}_{2,1}$ is called the dilation constant. $\hat{\alpha}_{22,1}$ is a self-interaction coefficient characteristic of the *pairwise* interaction of *solute* molecules in solvent 1; $\hat{\alpha}_{222,1}$ is a self-interaction coefficient characteristic of the interaction between *three solute* molecules in an environment of molecules 1; and so forth. Since the ideal-solution model to which $G^{E'}$ refers (HL) is infinitely dilute in component 2, it is not the unlike-species interaction but rather the self-interaction of solute 2 which causes the initial deviations from ideality. If Equation 89 is truncated after the quadratic term, the two-parameter constant-pressure activity coefficients are[11,174]

$$\ln \gamma_1 = \hat{A}\,\Phi_2^2 + \hat{B}\,\Phi_2^4 \tag{92}$$

$$\ln \gamma_2' = \hat{A}(V_{c,2}/V_{c,1})(\Phi_2^2 - 2\Phi_2) + \hat{B}(V_{c,2}/V_{c,1})(\Phi_2^4 - \frac{4}{3}\Phi_2^3) \tag{93}$$

where $\hat{A} \equiv \hat{\alpha}_{22,1}V_{c,1}$ and $\hat{B} \equiv 3\hat{\eta}_{2,1}\hat{A}$. These equations provide accurate representation of activity coefficients over large composition ranges of nonpolar systems, such as carbon dioxide (1) + oxygen (2) or carbon dioxide (1) + nitrogen (2). For these solutions, partial molar volumes have been obtained experimentally, in addition to VLE data, over a significant composition range.[176]

The magnitude of the Poynting correction, evaluated with a quite generally applicable high-density (liquid-phase) EOS, is indicated by the following specific example. Let the pressure dependence of V^{*L} be accounted for by the *modified Tait equation* (MTE):[43,49,54,177]

$$V^{*L}(T,P)/V_s^{*L} = (1 + m\beta_{T,s}^{*L}\Delta P)^{-1/m} \tag{94}$$

which is usually satisfactory for pressures up to about 100 MPa (see Figure 7). Here $\Delta P \equiv P - P_s$, and m is a pressure-independent parameter. For many organic liquids, experimental values cluster around m = 10, with very small temperature dependence.[177,178] Upon insertion into Equation 24 and integration:

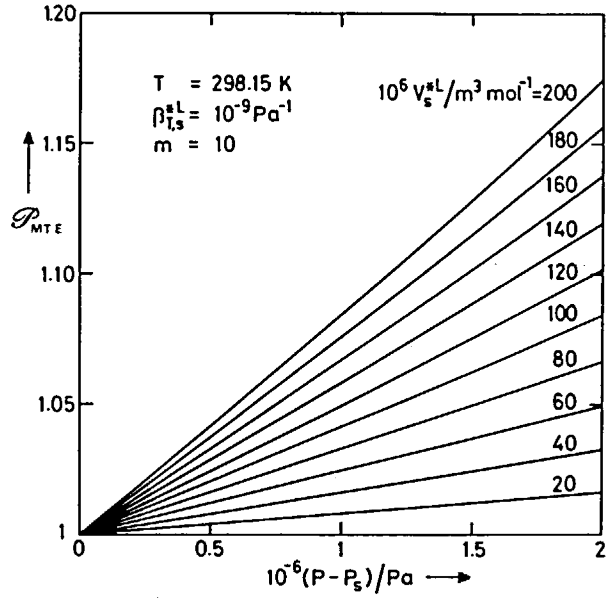

FIGURE 8. Poynting correction $\mathcal{P}_{MTE} \equiv \exp\{\int_{P_s}^{P} V_s^{*L}(T,P)(RT)^{-1}dP\}$ for a series of fictitious fluids, as a function of applied pressure ($P - P_s$). Calculated with the modified Tait equation (MTE) according to Equation 95.

$$\mathcal{P}_{MTE} = \exp\left\{\frac{V_s^{*L}}{RT}\,\frac{(1 + m\beta_{T,s}^{*L}\Delta P)^{\frac{m-1}{m}} - 1}{(m - 1)\beta_{T,s}^{*L}}\right\} \tag{95}$$

is obtained. Figure 8 shows $\mathcal{P}_{MTE}$ for a series of fictitious pure liquids at 298.15 K as a function of pressure. Molar volumes V_s^{*L} range from 20 to 200 cm^3mol^{-1}; all "*substances*" have the same isothermal compressibility $\beta_{T,s}^{*L} = 10^{-9}Pa^{-1}$; and $m = 10$. Consider a typical liquid with molar volume $V_s^{*L} = 120\ cm^3mol^{-1}$. For this liquid the simplification $\mathcal{P} = 1$, even at such a low applied pressure as $\Delta P = 0.2$ MPa, will result in a systematic error of 1% in f^{*L}. For $\Delta P = 2$ MPa we calculate $\mathcal{P}_{MTE} = 1.10$, which is quite a sizeable correction. Qualitatively similar comments apply for the solute.

By now it should be evident that the partial molar volume of the gas in solution is a quantity of importance in the reduction and correlation of precise gas-solubility measurements. Poynting-type corrections are rather ubiquitous in this area: whenever VLE data are discussed at "constant T and P", it is always tacitly assumed that the pressure corrections have been performed properly (see Van Ness[133]). Fortunately, for small pressure ranges $\Delta P = P - P_{s,1}$ and at temperatures well below critical, the uncertainties associated with the commonly used approximations (see above) are frequently small, perhaps even negligible as compared to other uncertainties. However, the scarcity of data on $V_2^{\infty L}$ (or V_2^L in general) of gases in liquids, as compared to the large body of data on gas solubilities, comes as a surprise. Hence, the revived interest in the experimental determination[164,169] of $V_2^{\infty L}$ on the one hand, and in its semiempirical estimation on the other.[171] For instance, recent measurements[169] with a vibrating-tube densimeter[179-181] yielded partial molar volumes at essentially infinite dilution for 20 fluids (about half of them supercritical) dissolved in water. A dilatometric technique (Figure 9) was used in Reference 164 to obtain $V_2^{\infty L}$ for several gases (CH_4, C_2H_6, etc.) in n-alkanes and 1-alkanols. As shown in Figure 10, $V_2^{\infty L}$ in liquid

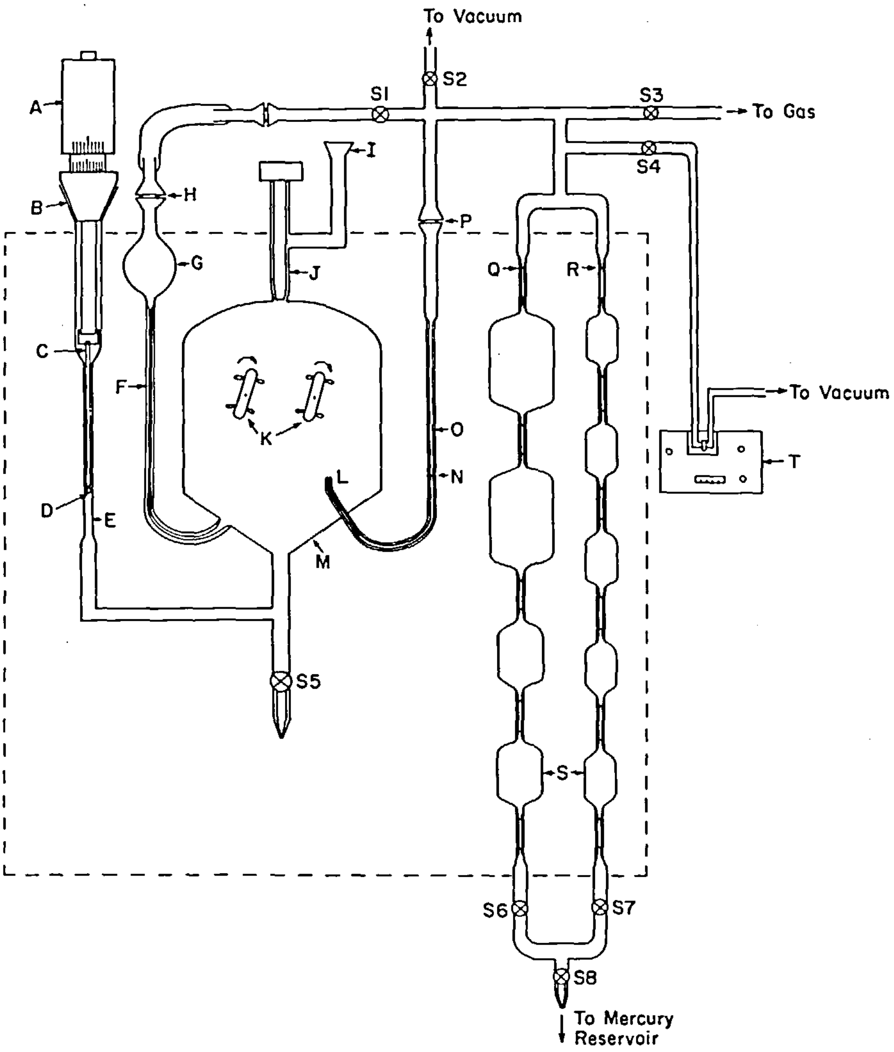

FIGURE 9. Schematic diagram of the dilatometer and burette for determining infinite-dilution partial molar volumes of gases dissolved in liquids:[164] (A) micrometer; (B) ground-glass socket, 14/20 standard taper; (E) Trubore tube, 3 mm i.d.; (F) Trubore capillary, 1 mm i.d.; (G) buffer bulb for mercury; (H and P) O-ring joints for connection to vacuum line; (I) O-ring joint for connection to liquid-degassing apparatus; (J) right-angled stopcock (Fischer and Porter) with 4-mm-bore teflon® plug; (K) twin magnetic stirrers; (L) tip of gas delivery tube; (M) mixing cell, volume ~150cm³, (N, Q, and R) reference marks; (O) Trubore capillary, 1.5 mm i.d.; (S) gas burette; (S1, S2, ..., S8) valves; (T) quartz-spiral pressure gauge (Texas Instruments). For details concerning operation of the instrument see Reference 164. (From Handa, Y. P., D'Arcy, P. J., and Benson, G. C., *Fluid Phase Equil.*, 8, 181, 1982. With permission.)

water is well correlated with $V_{c,2}$. At 298.15 K our results[169] are represented to within approximately ± 10% by the empirical linear relation:

$$V_2^{\infty L}/(\text{cm}^3\text{mol}^{-1}) = 10.74 + 0.2683V_{c,2}/(\text{cm}^3\text{mol}^{-1}) \qquad (96)$$

The broken line in Figure 10 was calculated with the aid of the Brelvi-O'Connell correlation,[182] which should *not* be used at temperature substantially below the critical temperature of the solute $T_{c,2}$, that is to say it should not be used to describe the partial molar volumes of liquids dissolved in liquids. This restriction is clearly shown by the figure. Specifically, Brelvi and O'Connell obtain $V_2^{\infty L}$ from the following expressions:

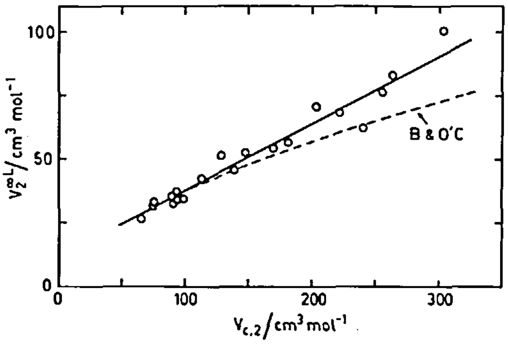

FIGURE 10. Partial molar volumes $V_2^{\infty L}(T,P_{s,1})$ at infinite dilution of 20 gases dissolved in water at 298. 15 K as a function of the critical molar volume of the solute $V_{c,2}$. (——) Linear least squares representation. (---) Calculated according to Brelvi and O'Connell.[182] (O) Experimental results.[169]

$$V_2^{\infty L}/(RT\beta_{T,s,1}^{*L}) = 1 - C_{12}^{\infty L} \qquad (97)$$

$$\ln\,[-C_{12}^{\infty L}(\nu_1/\nu_2)^{0.62}]$$

$$= -2.4467 + 2.12074\tilde{\rho}_1 \qquad \text{for } 2.0 \leq \tilde{\rho}_1 \leq 2.785 \qquad (98a)$$

$$= 3.02214 - 1.87085\tilde{\rho}_1 + 0.71955\tilde{\rho}_1^2 \qquad \text{for } 2.785 \leq \tilde{\rho}_1 \leq 3.2 \qquad (98b)$$

Here $\tilde{\rho}_1 = \nu_1\rho_{s,1}^{*L} = \nu_1/V_{s,1}^{*L}$ is the reduced molar density of the solvent; the ν_i are characteristic molar reducing volumes: and $C_{12}^{\infty L}$ is the reduced volume integral of the molecular direct correlation function between molecules of species 1 and 2.[183]

Other fairly recent semiempirical correlations for $V_2^{\infty L}$ are those presented by Smith and Walkley,[184] Lyckmann et al.,[185] and Handa et al.[164] The latter authors combine their experimental results with critically selected literature data and suggest:

$$V_2^{\infty L}P_{c,2}/RT_{c,2} = 0.088 + 2.763(TP_{c,2}/T_{c,2}\Pi_{s,1}^{*L}) \qquad (99)$$

where $\Pi_{s,1}^{*L}$ is the internal pressure of the pure solvent.[186] Available data indicate that Equation 99 will predict $V_2^{\infty L}(T,P_{s,1})$ of any gas in any solvent to within 10%, provided the temperature is well below $T_{c,1}$.

Scaled particle theory (SPT) has been used by Pierotti[8,26] and Wilhelm et al.[28] among others, to calculate $V_2^{\infty L}$ for nonpolar and polar gases in both nonpolar and polar solvents according to

$$V_2^{\infty L} = V_{CAV} + \beta_{T,s,1}^{*L}(G_{INT} + RT) \qquad (100)$$

Here $V_{CAV} = (\partial G_{CAV}/\partial P)_T$, and the partial molar Gibbs energy of cavity formation is expressed as[8,187]

$$\begin{aligned} G_{CAV}/RT &= -\ln(1 - \eta_1) + 3r\eta_1/(1 - \eta_1) \\ &+ r^2[3\eta_1/(1 - \eta_1) + \frac{9}{2}\eta_1^2/(1 - \eta_1)^2] \\ &+ r^3\pi\sigma_1^3P_{s,1}/(6k_BT) \end{aligned} \qquad (101)$$

and the partial molar Gibbs energy of interaction is approximated by[8,14,26,28]

$$G_{INT}/RT = -\frac{32}{9}\pi N_A \epsilon_{12}\sigma_{12}^3/(k_B T V_{s,1}^{*L}) - \frac{4}{3}\pi N_A(\vec{p}_1^{\,2}\alpha_2$$

$$+ \vec{p}_2^{\,2}\alpha_1)/(k_B T V_{s,1}^{*L}\sigma_{12}^3) - \frac{8}{9}\pi N_A \vec{p}_1^{\,2}\vec{p}_2^{\,2}/(k_B^2 T^2 V_{s,1}^{*L}\sigma_{12}^3) \qquad (102)$$

$\eta_1 = \pi N_A \sigma_1{}^3/(6V_{s,1}^{*L})$ is a dimensionless parameter characterizing the compactness of the solvent, σ_1 and σ_2 are effective size parameters of solvent and solute,[15] respectively; $r = \sigma_2/\sigma_1$, $\sigma_{12} = (\sigma_1 + \sigma_2)/2$; ϵ_1 and ϵ_2 are the effective energy parameters of the assumed Lennard-Jones (6,12) potential;[15] and $\epsilon_{12} = (\epsilon_1\epsilon_2)^{1/2}$. The permanent dipole moments of the components are denoted by $\vec{p}_1$ and $\vec{p}_2$; α_1 and α_2 are the mean polarizabilities; and $k_B = R/N_A$ is Boltzmann's constant.

III. EXPERIMENT

A. Recent Designs of Apparatus

During the last decade major advances in experimental techniques in general, and as applied to dilute solutions in particular, have been reported in the literature. To a significant extent, these efforts have been stimulated by a growing awareness of the practical value of highly accurate thermodynamic data (see Section I). Innovation in experimental techniques may be classified as follows:

1. Novel designs of apparatus which significantly improve experimental precision and accuracy
2. Designs which increase the accessible pressure and temperature ranges of already existing instruments
3. Designs for application to unusual problems
4. Efforts towards simplifying and accelerating data acquisition

It is far beyond the scope of this review to even attempt to catalog, let alone to discuss available experimental methods exhaustively. For those potentially interested in building precision equipment for measuring the solubility of gases in liquids, this section is intended to be a guide to the recent literature; more specifically, the focus will be on a few, selected contributions to listing 1 and, to a much lesser extent, listings 2 to 4. Most of the older, popular designs of apparatus have been reviewed in detail by Battino and Clever[9,22] in 1966 and again in 1975. Additional brief surveys are scattered in general reviews on the thermodynamics of fluid mixtures, such as References 19, 20, 27, 37, 41, and 48.

The most significant recent advance belonging to listing 1 above is undoubtedly due to Benson and Krause (BK).[33,188] 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.[189,190] A schematic representation of the experimental situation[33,42,54,56,191,192] is provided by Figure 11. 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 reliability of the method has been impressively demonstrated by the reported interlab accord on oxygen solubility in water: between 275 and 328 K, the average difference between the Henry coefficients reported by Benson et al.[33] and those reported by Rettich et al.[42,191,192] amounted to about 0.1%.

As shown in Figure 11, the apparatus consists of a degassing device,[193] an equilibrator,[33,42]

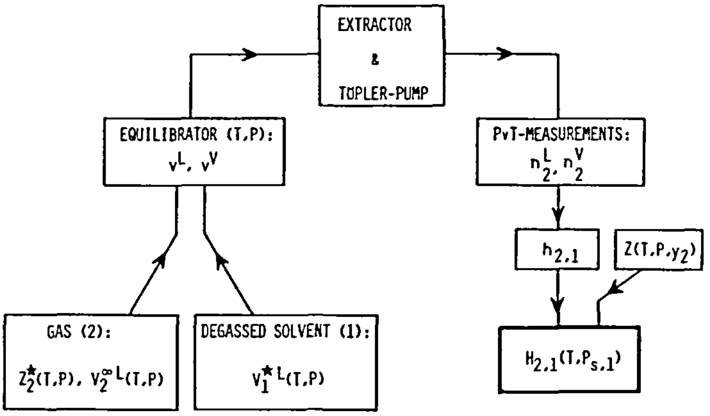

FIGURE 11. Determination (schematic) of Henry coefficients $H_{2,1}(T,P_{s,1})$ with a BK-type apparatus. Also shown are auxiliary quantities, needed for rigorous data reduction. (From Wilhelm, E., *Pure Applied Chem.*, 57, 303, 1985. With permission.)

an extractor (same design as for degassing), the Töpler pump[194] for transferring the dry gas to the manometric system, the high-precision manometric system itself (PvT measurements), and, of course, powerful thermostats (temperature drift < ±0.003 K during 24 hr) and platinum resistance thermometers. These components will be discussed individually below.

Adequate degassing of the solvent is indispensable for all gas-solubility determinations. The wide divergence of reported values of Henry coefficients for some systems is to a significant extent due to failure to completely degas the solvent. Various designs of degassing apparatus have been presented in the literature.[193,195-200] Perhaps the easiest one to fabricate and to operate is described in Reference 193. Essentially it is a 3-ℓ suction flask equipped with all-teflon® stopcocks, one O-ring joint for introducing the solvent, a magnetic stirring bar (8 cm), and a condenser to minimize solvent loss. The liquid is degassed by vigorous stirring and periodically pumping on the flask through a cold trap. For instance, with this technique, the residual air content of water after degassing is easily pushed below 0.001% of the saturation value at room temperature and atmospheric pressure. The time requirement is of the order of 1 hr. We note that this degassing apparatus can be readily scaled up or down.

Failure to attain true vapor-liquid equilibrium is probably the most important single source of error in gas-solubility measurements. The problem of putting a gas and a liquid in equilibrium in a closed vessel is conceptually simple, yet difficult and demanding in practice; frequently it takes a long time to reach equilibrium, say 24 hr or more. The BK equilibrator[33,42,201] (see Figure 12) appears to be the best design for this purpose. All the results obtained so far on aqueous systems have shown this equilibration system to be extremely reliable; see the detailed discussion in Reference 33.

After attaining equilibrium in an adequately controlled thermostat (3-hr drift < ±0.002 K), say after 24 hr, an accurately known volume v^V of the vapor phase is isolated in the vapor-phase sample (VPS) bulb, and a corresponding equally well-known volume v^L of the liquid solution is closed off in the liquid-phase sample (LPS) bulb. First, the gas contained in v^V is dried and then Töpler-pumped into the manometric system to determine the amount of gas n_2^V. Then the gas dissolved in the LPS bulb is extracted, dried, and transferred to the manometric system, where n_2^L is measured.

The amounts of dry gas, n_2^V and n_2^L, are determined by measuring the pressure, temperature, and volume $v_2^* = n_2 V_2^*$ of the pure gas contained in the manometric system (MS):

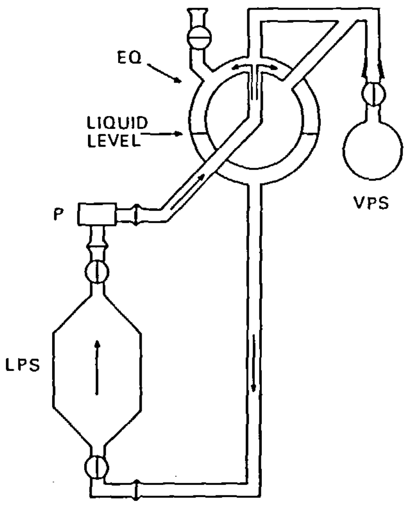

FIGURE 12. BK-type glass apparatus[33,42] for the equilibration of gases with liquids: EQ, spherical equilibrator, P, centrifugal pump; VPS, vapor-phase sample bulb, LPS, liquid-phase sample bulb. Arrows indicate the direction of liquid flow.

$$n_2 = (RZ_2^*)^{-1}[Pv_2^*T^{-1}]_{MS} \tag{103}$$

with appropriate superscripts V or L attached to n_2. The compressibility factor Z_2^* of the pure gas is easily computed from a two-term (or three-term) virial equation. For instance at low pressures:

$$Z_2^* = 1 + (B_{22}/R)[PT^{-1}]_{MS} \tag{104}$$

Preferably, pressures are measured with a quartz Bourdon tube manometer,[42,191,192] which should be periodically checked against a gas-lubricated piston pressure gauge or similar devices. Benson and Krause use a precision mercury manometer. Temperatures are determined with platinum resistance thermometers.[202] They should be checked regularly with triple-point-of-water cells and benzoic acid cells[42,191,192] or other suitable temperature standards on the IPTS-68 scale. The imprecision associated with these PvT measurements is usually below ±0.02%.

As was shown in Reference 42, Henry coefficients of sparingly soluble gases may be obtained according to

$$H_{2,1}(T,P_{s,1}) = \lim_{x_2 \to 0} [h_{2,1}Z^V(T,P,y_2)\phi_2^V(T,P,y_2)] \tag{105}$$

where the "uncorrected Henry coefficient" $h_{2,1}$ is given by

$$h_{2,1} = (n_2^V/n_2^L)(\hat{v}^L/v^V)RT/V_1^{*L} \tag{106}$$

When dealing with solutions at mole fractions of dissolved gas of the order of 10^{-5}

$$\hat{v}^L \simeq v^L - n_2^L(V_2^{\infty L} - V_1^{*L}) \tag{107}$$

Note that the total equilibrium pressure P does not appear explicitly in Equation 105. 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 Reference 42.

The average combined random error (imprecision) associated with $H_{2,1}(T,P_{s,1})$ obtained in the manner outlined above, reflects mainly the uncertainty of the measurements of n_2^V, n_2^L, and of T; it is estimated to be less than ±0.05%. The combination of the experimentally determined quantities contained in the "uncorrected Henry coefficient" $h_{2,1}$ minimizes the impact of almost all systematic analytical errors. For the systems investigated so far,[33,42,191,192] the maximum systematic error, associated with uncertainties of the virial coefficients, $V_2^{\infty L}$, T, P, R, etc. should not exceed ±0.05%. These error estimates are corroborated by the goodness of fit of appropriate correlating equations (see below), and by the highly satisfactory agreement[42,191,192] with the results obtained by Benson and Krause[33] for oxygen dissolved in water.

The development of new approaches and of new equipment continues unabated, and in recent years important contributions to listings 2 to 4 of the classification scheme given above have been communicated. None of them, however, yields data with a precision comparable to that obtained with a BK-type apparatus, the difference being usually one order of magnitude or more.

For instance, an instrument similar to that described by Ben-Naim and Baer[203] has been used extensively by Wen et al.[204-206] The imprecision of their solubility data for perfluorocarbon gases dissolved in water is of the order of 1% (temperature range: $278 < T/K < 303$, $P \approx 0.1$ MPa). A microgasometric apparatus has been used for fluorine-containing gases dissolved in water by Park et al.[64] The solubility of hydrogen in diols and their ethers for pressures up to 10 MPa and temperatures between 298 and 373 K were measured by Brunner[207] and discussed in terms of the Krichevsky-Kasarnovsky equation. The error of measurement is estimated to be less than $0.02x_2$, where x_2 is the mole fraction of dissolved gas (see also References 75 and 208) and less than 0.002P, where the pressure has been measured with a strain-gauge pressure transducer. The transducer is calibrated with the aid of a pressure balance before and after each series of experiments.

An interesting new method has been developed by Pollack and Himm,[209,210] and was used to measure the solubility of xenon in liquid n-alkanes (n-C_5H_{10} through n-$C_{20}H_{42}$, $283 < T/K < 323$). It is based on the determination of the distribution of the radioactive isotope ^{133}Xe between the vapor phase and the liquid phase, respectively, by measuring quantitatively the intensity of the gamma radiation emitted (see also Reference 4). The quantity so determined is the so-called Ostwald coefficient (see below).

A method which requires only small amounts of gas and liquid (usually 1 to 5 cm^3), and which allows the rapid study of gas solubilities, has been described by Brass et al.[211] It depends on observing the pressure at which a measured amount of gas is just completely dissolved in a known amount of liquid and is thus reminiscent of the "indirect solubility measurement" approach of Potter et al.[139,212] (see below) and the bubble point method for VLE as suggested by Dixon and McGlashan.[213] Brass et al. designed their apparatus for convenience rather than accuracy: the imprecision is about ±2%, the inaccuracy about ±5% within the pressure range 0.1 to 3 MPa and between 273.15 and 363.15 K.

Most of the gas-solubility measurements reported in the literature have been performed at or close to 298.15 K, and data extending to temperatures near the critical temperature of the solvent are rather scarce; this is even the case for gases dissolved in the most important liquid of all, water.[139,140,214-216] The instrument designed by Potter et al.[139,212] is shown schematically in Figure 13. After the gold-lined autoclave is loaded with a known amount of gas and brought to the desired temperature, the gas pressure is recorded. Known amounts of pure water are then injected in increments into the autoclave using the screw pump. After each incremental injection and reattainment of thermal equilibrium (usually 15 to 30 min), the pressure is again recorded. As long as a vapor phase remains in the autoclave in equilibrium with the liquid solution, additions of water raise the pressure only moderately.

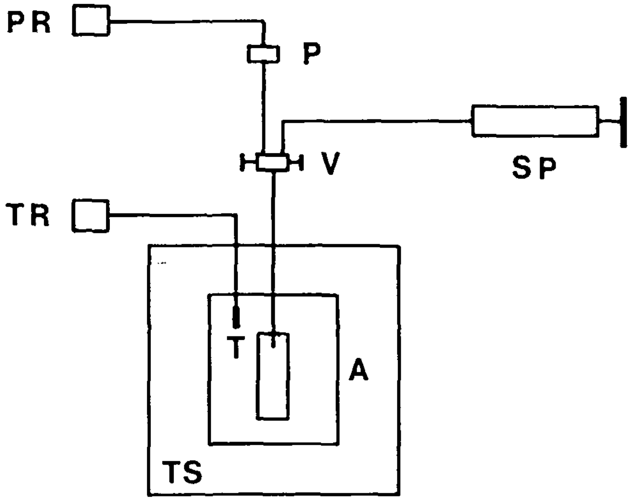

FIGURE 13. Gas-solubility apparatus designed by Potter and Clynne[139] (schematic): A, gold-lined autoclave; TS, thermostat; T, Pt resistance thermometer; TR, temperature readout; P, pressure transducer; PR, pressure readout; SP, screw pump; V, valve.

After the last bubble of vapor has vanished, addition of more water causes a relatively large increase in pressure: that is to say, when plotting P vs. n_{H_2O} two essentially straight lines with significantly different slopes are observed. Since the amounts of gas and water present at the intersection point are known, Henry coefficients may be obtained therefrom. Despite the apparently good reproducibility (approximately 1 to 2%), their results on the rare gases in water deviate as much as 20% from the values reported by Crovetto et al.[140] Even at low temperatures, significant differences to reliable literature values are observed.[28,140]

Other recent contributions to the measuring technique at elevated temperatures are due to Crovetto et al. who introduced an analytical method[140] as well as one[141] similar to the Potter-Brass approach (see above). The overall imprecision of the derived Henry coefficients is found to be roughly between 1 and 2%. Systems investigated so far are Ne, Ar, Kr, Xe, and CH_4 in H_20 and D_20, and C_2H_6 in H_20. Within experimental error, their results agree with critically selected literature data[28] and recent high-precision values[42] (see also Figure 14).

For measuring the solubility of helium in water and in aqueous solutions of CsCl, NaCl, and $MgCl_2$ up to 40 MPa, that is to say for determining the Setschenow coefficients for helium in these solutions, Gerth[217] has used an analytical method[218] similar to those used by other workers.[219-222] However, much smaller liquid volumes are required, and the estimated inaccuracy of the measured solubilities is given as ±0.8% at pressures below 15 MPa and ±0.5% at higher pressures.

As an example for a conventional design which can rapidly yield reasonably accurate gas solubilities in *liquid mixtures* across the full composition range, we present the design of Armitage et al.[223] Measuring burettes are utilized to add the degassed liquids to a calibrated vessel containing the gas. The rate of attaining the equilibrium is enhanced by circulating the liquid mixture through the gas using a magnetically operated glass pump, similar to that of Dymond and Hildebrand[224] and of Cukor and Prausnitz.[225] This continuous-dilution apparatus is simple to use, considerably more convenient than batch methods, and yields solubilities accurate to within 1%.

Gas chromatography (GC)[34] has been applied increasingly in solubility measurements.

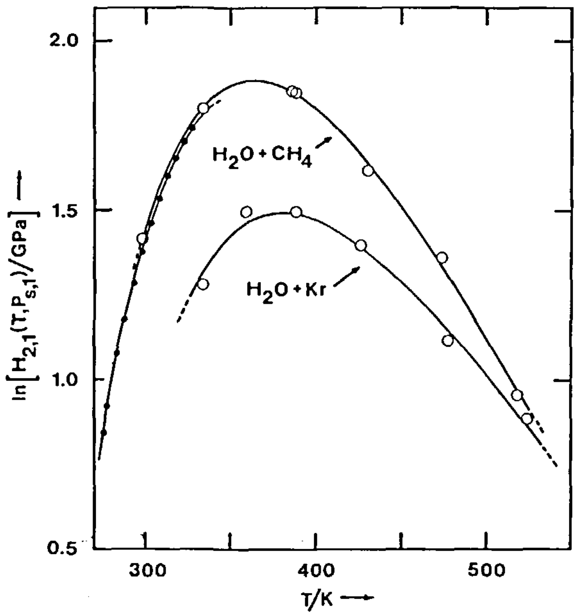

FIGURE 14. Plot of ln $[H_{2,1}(T,P_{s,1})/\text{GPa}]$ against temperature T for krypton and methane dissolved in water. (○) Crovetto et al.[140] (●) Rettich et al.[42]

First of all, it has been used as an analytical tool to obtain the amount of gas dissolved in a liquid sample. Second, since the basic process in gas-liquid chromatography (GLC) is the equilibration of a volatile solute between a liquid stationary phase of sufficiently low vapor pressure and a carrier gas, which is nearly insoluble in the stationary phase (mostly helium is used), the chromatographic technique may be used to determine Henry coefficients or activity coefficients at infinite dilution. For the determination of $H_{2,1}$ of vapors and very soluble gases, say with $H_{2,1} < 5$ MPa, GLC has been shown to be a fast and reasonably accurate technique.[226,227] On the other hand, for light gases which are not very soluble in most solvents (and hence elute rapidly), accurate data cannot be obtained by conventional elution GLC because of the limitations in the evaluation of the retention time of a hypothetical unretained solute or the mathematical dead time.[228-232] An important contribution to this topic is due to Lin and Parcher,[233] who have extended the range of applicability of elution GLC up to $H_{2,1} \leq 80$ MPa by using a mass spectrometer as the detection system: Henry coefficients of 11 light gases, such as Ar, Kr, N_2, O_2 etc., dissolved in *n*-hexadecane, *n*-octacosane (n-$C_{28}H_{58}$), and *n*-hexatriacontane (n-$C_{36}H_{74}$) were measured at several temperatures between 298.15 and 413.15 K.

As concerns the use of GC as an analytical tool, we present here the careful study of Cosgrove and Walkley[234] on the solubility of Ar, Kr, N_2, O_2, CH_4, C_2H_6, SF_6, and CF_4 in H_2O and D_2O over the temperature range 278.15 to 313.15 K. Good agreement with reliable literature data was obtained throughout. An interesting new design for the determination of $H_{2,1}$ (or γ_2^∞) has been reported in several variants by Renon et al.[235-238] It is based on the elution of the solute from the liquid solution by a constant inert gas flow, and the application of GLC for studying the variation of gas-phase composition with time. Systems investigated with this inert gas stripping method include a wide range of normal and branched alkanes in *n*-hexadecane,[236] *n*-octadecane,[237] etc. The reproducibility is usually in the 1 to 2% region. Recently, the method has been extended to cover VLE in multicomponent systems,[238] such as methane + *n*-butane + *n*-decane, up to 20 MPa and 423 K. This fast and reliable method should prove valuable in a variety of industrial applications involving systems composed of light and heavy hydrocarbons, for instance in pipeline design or tertiary oil recovery.

Albeit somewhat outside the scope of this review, one other recently developed technique concerning gas transport through polymer membranes should be mentioned. Gas permeability is an important property of polymer films used for packaging. The transport process can be divided into three steps: solution of the gas molecule on one face of the membrane, diffusion through the polymer, and evaporation from the other face. Soles et al.[239] measured transport rates for argon diffusing through polyethylene by monitoring the pressure decay $\Delta P(t)$, where t is the time, between two reservoirs connected by a polyethylene membrane. By analyzing the $\Delta P(t)$ data, both the Henry coefficients of the gas dissolved in the polymer and the diffusivity can be evaluated from a single run. The inaccuracy of this method should not exceed 5% for both quantities.

We conclude this section by reiterating that the coverage of recent experimental developments is not exhaustive. There exist quite a number of additional valuable contributions to this field, sometimes tailored to meet specialized demands in industry. Some of these, which have been published during the last 5 years or so, are listed summarily in References 240 to 255; see also Section I.

B. Presentation of Results

Once one has accumulated experimental Henry coefficients $H_{2,1}(T,P_{s,1})$ for a given gas-solvent system over a certain temperature range, the question arises as to their most satisfactory mathematical representation. Since as yet no theoretically well-founded model of any general validity has been devised, one has to rely upon more or less empirical (and thus, to some extent, arbitrary) representations. Data of the quality obtained through use of BK-type equipment are well suited for examining how various functions fit the temperature dependence of the Henry coefficients.

To date, the most frequently used approaches are those advocated by Clarke and Glew (CG)[256,257] or by Benson and Krause.[33,188] These authors assume that $\ln(H_{2,1}/\mathrm{Pa})$ and its derivatives are well-behaved functions of either the thermodynamic temperature T, or the inverse temperature T^{-1}. Subsequently, the enthalpy of solution (see below) is expanded in a Taylor series about either a suitably chosen reference temperature, or about an inverse reference temperature. When adopting the former procedure (CG), the temperature dependence of $H_{2,1}(T,P_{s,1})$ is represented by

$$\ln[H_{2,1}(T,P_{s,1})/\mathrm{Pa}] = A_0 + A_1(T/K)^{-1} + A_2\ln(T/K) + A_3(T/K) + A_4(T/K)^2 + \ldots \qquad (108)$$

We note that the 3-term version of Equation 108 is the well-known Valentiner equation.[258] Frequently, for computational convenience, the temperature variable is chosen as 10^{-2} T/K instead of T/K. When the method of Benson and Krause is used, the results are fitted by a power series in T^{-1}:

$$\ln[H_{2,1}(T,P_{s,1})/\mathrm{Pa}] = \sum_{i=0}^{n} a_i(T/K)^{-i} \qquad (109)$$

It is, of course, essential that some appropriate statistical criterion of goodness of fit be applied. For instance, the number of terms in either series should be based upon the F_x test,[259] in conjunction with experience as to the precision attainable with a particular experimental method.

From the high-precision work of Benson et al.[33,188] and Rettich et al.[42,191,192] on the solubility of various gases in water, the following picture emerges. When applied over the same range of temperature (say 273.15 to 333.15 K), the *three-term* version of the power series in T^{-1} is evidently superior to the three-term CG equation: the percent standard deviation, or the average percent deviation, is always considerably smaller. Additional terms often provide no, or comparatively little, improvement over the three-term BK fit. To fit the data adequately with a CG-type series at least *four terms* are required. On the basis of ability to fit accurate data over reasonably large temperature ranges, and of simplicity, the BK power series in T^{-1} appears to be the best empirical function proposed to date for representing the variation of $H_{2,1}(T,P_{s,1})$ with T.

Whatever representation, BK or CG, is selected, the following point should be kept in mind. While numerical differences between values for Henry coefficients generated from either the BK or CG equation are usually exceedingly small within the temperature range covered by experiment, care must be exercised when extrapolation to significantly higher or lower temperatures is desired because of increasing divergence of the smoothing functions. Closely related to this problem are Beutier and Renon's[260] and Wilhelm's[43,56] recently published results on the limiting behavior of $H_{2,1}(T,P_{s,1})$ as $T \rightarrow T_{c,1}$ and $P_{s,1} \rightarrow P_{c,1}$ (see below).

Henry coefficients $H_{2,1}(T,P_{s,1})$ obtained at different temperatures T refer, of course, to different pressures $P_{s,1}(T)$. The pressure variation is coupled with the temperature variation through the rigorous Clapeyron equation:

$$\frac{dP_{s,1}}{dT} = \frac{P_{s,1}\Delta H_1^{vap}}{RT^2\Delta Z^*_{s,1}} \tag{110}$$

where ΔH_1^{vap} is the enthalpy of vaporization of pure solvent, and $\Delta Z^*_{s,1} \equiv Z^{*V}_{s,1} - Z^{*L}_{s,1}$ is the difference of the compressibility factors of pure coexisting solvent vapor and liquid.

Until very recently, precision measurements of $H_{2,1}(T,P_{s,1})$ over sufficiently large ranges of temperature constituted the only reliable source of information on enthalpy changes upon solution, ΔH_2°, and *a fortiori* on heat capacity changes upon solution, $\Delta C^\circ_{P,2} = (\partial \Delta H_2^\circ/\partial T)_P$, of sparingly soluble gases in liquids. Specifically,[42,43]

$$\begin{aligned}\Delta H_2^\circ(T,P_{s,1})/RT &\equiv (H_2^{\infty L} - H_2^{\circ V})/RT \\ &= -T\,\frac{d\ln[H_{2,1}(T,P_{s,1})/Pa]}{dT} + \frac{V_2^{\infty L}}{R}\,\frac{dP_{s,1}}{dT}\end{aligned} \tag{111}$$

where $H_2^{\infty L}$ is the partial molar enthalpy of the solute at infinite dilution in the liquid solvent, and $H_2^{\circ V}$ is the molar enthalpy of pure solute in the perfect-gas reference state. The first term on the rhs of Equation 111 is obtained from one of the selected fitting equations. Usually, the *second term is not included*, despite the fact that its value increases rapidly with increasing temperature (see Figure 15). Its evaluation requires information on the partial molar volume at infinite dilution (at T and $P_{s,1}$) and on the temperature dependence of the vapor pressure of the pure solvent. Unfortunately, in the temperature region where this term is significant, $V_2^{\infty L}$ data are often not available and one has to rely upon correlation methods, such as the ones discussed in Section II.B.2. As concerns $dP_{s,1}/dT$, this quantity may be calculated from any suitable vapor pressure correlation, for instance from the Antoine equation, the Lee-Kesler equation[261] (for nonpolar liquids), the Scott-Osborne equation,[262] or from a Chebyshev polynomial representation as suggested by Ambrose and Lawrenson.[263] At temperatures far below $T_{c,1}$, the magnitude of the second term will frequently, but not necessarily, be rather small as compared to that of the first term. Take, e.g., methane dissolved in water. The temperature of minimum solubility, i.e, where $H_{2,1}(T,P_{s,1})$ vs. T shows a maximum (see Figure 14), is about $T_{max} = 363$ K. Evidently, the first term of Equation 111 is here exactly zero, and ΔH_2° $(T = T_{max}, P_{s,1})$ is entirely due to the second term. This point has to be kept in mind when comparison with direct calorimetric results is desired (see below).

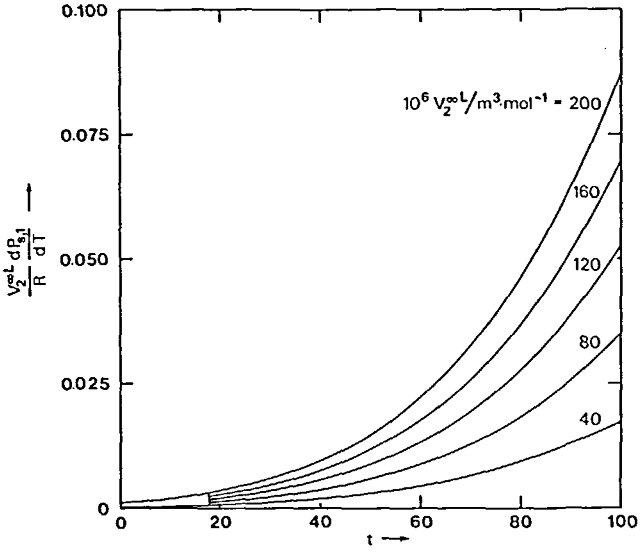

FIGURE 15. $V_2^{\infty L} R^{-1} (dP_{s,1}/dT)$ as a function of t = T/K - 273.15 for several fictitious solutes dissolved in water: $40 \leq V_2^{\infty L}/(cm^3 \cdot mol^{-1}) \leq 200$.

An argument analogous to that used above has to be applied to obtain a rigorous value of the heat capacity change upon solution:

$$\Delta C^{\circ}_{P,2}(T,P_{s,1})/R \equiv (C^{\infty L}_{P,2} - C^{\circ V}_{P,2})/R$$

$$= \frac{d\Delta H^{\circ}_2(T,P_{s,1})}{RdT} - \frac{1}{R}\left[V_2^{\infty L} - T\left(\frac{\partial V_2^{\infty L}}{\partial T}\right)_P\right]\frac{dP_{s,1}}{dT} \qquad (112)$$

Here $C^{\infty L}_{P,2}$ is the partial molar heat capacity of the solute at infinite dilution in the liquid solvent, and $C^{\circ V}_{P,2}$ is the molar heat capacity at constant pressure of the pure solute in the perfect-gas reference state.

Thermodynamic data pertaining to the dissolution of a rare gas or a simple hydrocarbon in water are fundamental for any discussion of hydrophobic effects[38,39] (or when other solvents are concerned, of solvophobic effects[15]). However, due to the low solubilities of these substances in water at temperatures around 298 K and ordinary pressures ($\approx$0.1 MPa), direct precise calorimetric measurements have not been possible until recently, and all values for the enthalpy changes upon solution ΔH°_2, and of course for $\Delta C^{\circ}_{P,2}$, had to be derived from solubility measurements. The disadvantage inherent in this procedure is that it requires a first and second differentiation of $\ln[H_{2,1}(T,P_{s,1})/Pa]$ to yield the desired quantities. No matter how this is done, each differentiation step increases the inaccuracy by, roughly, one order of magnitude. It is only from very accurate solubility studies over a reasonably large temperature range that one can expect to obtain reliable values for ΔH°_2 and, *a fortiori*, for $\Delta C^{\circ}_{P,2}$. Hence, the interest in developing precision calorimetry to the point where it can cope with these systems and provide independent direct information on enthalpy and heat capacity changes upon solution.[264-268]

Direct calorimetric determination of the enthalpy change accompanying the dissolution of a sparingly soluble gas in water has been pioneered by Wadsö (Sweden) and Gill (U.S.) and resulted in the design of two somewhat different flow calorimetric techniques.[264,266-268] In general, values for ΔH°_2 obtained from these two methods agree within the limits of experimental error. As shown in Table 1, accord with the results obtained from the high-

Table 1

PARTIAL MOLAR ENTHALPY CHANGES $\Delta H_2^\infty(T,P_{s,1})$ UPON SOLUTION OF SEVERAL GASES IN WATER AT 298.15 K. A COMPARISON BETWEEN VALUES OBTAINED FROM GAS SOLUBILITY AND CALORIMETRIC MEASUREMENTS

	$10^{-3}\Delta H_2^\infty(T,P_{s,1})/(J \cdot mol^{-1})$		
		Calorimetry	
Gas	Gas solubility	Dec and Gill[266,267]	Olofsson et al.[268]
O_2	- 12.02[33]	- 12.03	- 12.00
CH_4	- 13.19[42]	- 13.18	- 13.06
C_2H_6	- 19.50[42]	- 19.52	- 19.30
C_3H_8	- 23.14[269]	- 23.27	- 22.90
C_2H_4	- 16.29[269]	- 16.46	—

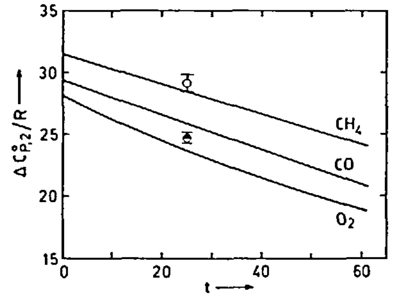

FIGURE 16. Temperature dependence of the partial molar heat capacity change upon solution, $\Delta C_{P,2}^\circ/R \equiv (C_{P,2}^{*L} - C_{P,2}^{\circ V})/R$ for (water + oxygen),[33] (water + carbon monoxide),[191] and (water + methane).[42] Circles denote results obtained from calorimetric measurements of ΔH_2^∞ at several temperatures[268] according to $\Delta C_{P,2}^\circ = (\partial \Delta H_2^\infty/\partial T)_P$: (○) CH_4 dissolved in H_2O. (◓) O_2 dissolved in H_2O. $t = T/K - 273.15$.

precision solubility studies of Benson and Krause[33] and Rettich et al.[42,269] is equally satisfactory. As concerns novel calorimetric designs to measure ΔH_2^∞ of gases in organic liquids, such as benzene or tetrachloromethane, see References 270 to 272.

When ΔH_2^∞ is measured at several temperatures, heat capacity changes upon solution may be obtained. The very recent calorimetric results for oxygen and methane dissolved in water at 298.15 K (Olofsson et al.[268]) have been incorporated in Figure 16 which shows the dependence of $\Delta C_{P,2}^\circ$ on T as obtained from high-precision solubility measurements.[33,42,191] Again, agreement is excellent and highlights the progress made in the past few years (see Wilhelm[49,56]).

We now will establish a thermodynamically rigorous relation between the Henry coefficient and the Ostwald coefficient,[273] another widely used practical measure of gas solubility. This quantity is also of central importance in the theory of hydrophobic effects as advanced by Ben-Naim.[38]

Let the Ostwald coefficient be defined by

$$L_{2,1}(T,P) \equiv (\rho_2^L/\rho_2^V)_{equil} \tag{113}$$

where $\rho_2 \equiv n_2/v = x_2\rho = x_2/V$, 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), and $V = v/(n_1 + n_2)$ is the corresponding molar volume. The limiting value of $L_{2,1}$ for vanishingly small concentration ρ_2 is denoted by

$$L_{2,1}^{\infty} \equiv \lim_{\substack{\rho_2^L \to 0 \\ P \to P_{s,1}}} L_{2,1}(T,P) = \lim_{\substack{\rho_2^L \to 0 \\ P \to P_{s,1}}} (\rho_2^L/\rho_2^V)_{equil} \tag{114}$$

Equation 113 in conjunction with the equilibrium condition formulated on the basis of Henry's law yields,[43,56] after some algebraic manipulation, the rigorous relations:

$$L_{2,1}(T,P) = \frac{RT}{\gamma_2'(T,P,x_2)H_{2,1}(T,P)V^L(T,P,x_2)} Z^V(T,P,y_2)\phi_2^V(T,P,y_2) \tag{115}$$

$$= \frac{RTZ^V(T,P,y_2)\phi_2^V(T,P,y_2)}{\gamma_2'(T,P_{s,1},x_2)H_{2,1}(T,P_{s,1})V^L(T,P,x_2)} \exp\left\{-\int_{P_{s,1}}^{P} \frac{V_2^L(T,P,x_2)}{RT}\,dP\right\} \tag{116}$$

where $V^L(T,P,x_2)$ is the molar volume of the liquid solution. Hence, in the limit of $\rho_2^L \to 0$ we obtain with $V^L(T,P,x_2) \to V_1^{*L}(T,P_{s,1})$:

$$L_{2,1}^{\infty} = \frac{RT}{H_{2,1}(T,P_{s,1})V_{s,1}^{*L}} Z_{s,1}^{*V}\phi_2^{\infty V}(T,P_{s,1}) \tag{117}$$

At low to moderate pressures, Equation 54 may be applied, whereby

$$Z_{s,1}^{*V}\phi_2^{\infty V}(T,P_{s,1}) = \exp\left\{2\rho_{s,1}^{*V}B_{12} + \frac{3}{2}(\rho_{s,1}^{*V})^2C_{112}\right\} \tag{118}$$

Note that the orthobaric molar density $\rho_{s,1}^{*V} \equiv 1/V_{s,1}^{*V}$ of pure solvent vapor has to be determined by an iterative procedure through use of the virial equation of state Equation 42.

Alternatively, for low pressures, one may use the virial equation in its volume-explicit form, whence after series expansion:

$$Z_{s,1}^{*V}\phi_2^{\infty V}(T,P_{s,1}) = 1 + 2\left(\frac{P_{s,1}}{RT}\right)B_{12} + \left(\frac{P_{s,1}}{RT}\right)^2 B_{11}(2B_{12} - B_{11}) \tag{119}$$

The above conversion formulas are exact to the order of approximation implied by the use of the virial equation. For vapor pressures up to a few tenths of a megapascal, differences between results obtained from either Equation 118 or Equation 119 will usually be negligibly small. For correlation purposes, the variation of $L_{2,1}^{\infty}$ with temperature is often accounted for by either a BK or a CG-type smoothing equation.

As reported recently,[43] Equation 117 provides a rigorous expression for the limiting value of the Henry coefficient as $T \to T_{c,1}$ and $P_{s,1} \to P_{c,1}$:

$$\lim_{T \to T_{c,1}} H_{2,1}(T,P_{s,1}) = P_{c,1}\phi_2^{\infty V}(T_{c,1}P_{c,1}) \tag{120}$$

which equation was also given by Beutier and Renon.[260] 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[274] is in variance with Equation 120. Considering the relative ease of obtaining the limiting value of the Henry coefficient as $T \rightarrow T_{c,1}$, it is rather surprising that it was not reported earlier.

We conclude this section by briefly remarking on the presentation, as function of temperature, of the quantity $A(T,P_{s,1})$, which appeared in Equation 88 as the simplest means to correlate isothermal, isobaric activity coefficients $\gamma_2'(T,P_{s,1},x_2)$. For each temperature and reference pressure $P_{s,1}(T)$, $A(T,P_{s,1})$ is obtained as the slope of the linear plot:

$$\left[\ln\left(\frac{y_2\phi_2^V(T,P,y_2)P}{x_2H_{2,1}(T,P_{s,1})}\right) - \frac{(P-P_{s,1})V_2^{\infty L}(T,P_{s,1})}{RT}\right] \text{ vs. } x_2(x_2 - 2)$$

The resulting set of data $\{A[T,P_{s,1}(T)],T\}$ may then be correlated by either a BK or a CG-type equation, or by any other suitable expression.

IV. ESTIMATION OF HENRY COEFFICIENTS

The thermodynamic properties of dilute solutions can be exhaustively described by means of the formal treatment(s) introduced in Section II. Until now, this point of view has been predominant. It is the purpose of this last section to review very briefly some recent molecular-thermodynamic advances of relevance to dilute solutions. In other words, work will be discussed where the emphasis is on linking our knowledge about intermolecular forces to macroscopic, measurable quantities, such as Henry coefficients. By necessity, this link is the more problematic, that is to say it will be the more empirical, the more complex the solution. Selection of the material will be strongly biased in favor of application oriented contributions.

The regular solution theory (RST) of Hildebrand and collaborators[12] has been used extensively in the development of semiquantitative prediction schemes for the solubility of gases in (nonpolar) liquids. The central quantity here is the solubility parameter δ, which is defined as the square root of the cohesive energy density of the liquid; it is usually calculated from the energy of vaporization:

$$\delta = \left(\frac{\Delta U^{vap}}{V^{*L}}\right)^{1/2} \tag{121}$$

Specifically, Prausnitz and Shair[275] (see also Yen and McKetta[276]), by using the RST equation for the symmetric activity coefficient (see also Equation 17), suggested the following expression:

$$H_{2,1} = f_2^*(\text{hyp. liq.}) \exp\left\{\frac{V_2^*(\text{hyp. liq.})[\delta_1 - \delta_2(\text{hyp. liq.})]^2}{RT}\right\} \tag{122}$$

As indicated, Equation 122 involves three parameters for the supercritical component in a pure hypothetical liquid state: in Reference 275 values of $V_2^*(\text{hyp. liq.})$ and $\delta_2(\text{hyp. liq.})$ were tabulated for several gases, and a graphical corresponding-states correlation was given for $f_2^*(\text{hyp. liq.})$ at a reference pressure $P_{ref} = 1$ atm (= 101325 Pa). At any other pressure, the Poynting correction in the following form is applied:[11,12]

$$f_2^*(\text{hyp. liq. at } P) = f_2^*(\text{hyp. liq. at } P = P_{ref}) \exp\left(\frac{V_2^*(\text{hyp. liq.})(P-P_{ref})}{RT}\right) \tag{123}$$

More recent work based on solubility parameters is due to Sagara et al.,[277] Linford and Thornhill,[86,278] Brelvi,[279] and Sebastian et al.[76] The latter authors develop a correlation for the solubility of hydrogen in hydrocarbon solvents at temperatures from 310 to 700 K and pressures up to 30 MPa. This kind of information is required for engineering design and analysis of reaction kinetics of hydrofining processes. Comparison of predicted results with experimental solubility data for hydrogen in 22 binary and ternary solutions shows an overall absolute deviation of about 6%, which is distinctly better than the Chao-Seader or Grayson-Streed correlations.

During the last decade, group contribution methods[107-111,280] have been increasingly used to predict VLE for liquid mixtures of nonelectrolytes. This approach has recently been extended to include systems with supercritical components, that is to say to the estimation of Henry coefficients. In Reference 281, the ASOG method for the symmetric activity coefficient in conjunction with the Prausnitz-Shair correlation for f_2^{*L}(hyp. liq.) is used to predict the solubility of nonpolar gases (O_2, N_2, CH_4, etc.) in water, in normal alcohols (CH_3OH through n-$C_8H_{17}OH$), and in mixed solvents (H_2O + CH_3OH, H_2O + C_2H_5OH, etc.). The average deviation between the observed and the predicted values is 6% in the pure and 10% in the mixed solvents. A modified version of the UNIFAC method is presented in Reference 132. It includes a so-called free-volume term, which has been suggested for polymer solutions by Oishi and Prausnitz[282] and a new method for the evaluation of f_2^{*L}(hyp. liq.). Along similar lines is the recent work of Antunes and Tassios,[283] though these authors used the original Prausnitz-Shair correlation (by fitting it to a polynomial in $T_{r,2}$). Note, however, that Sander et al.[284] have recently applied the UNIFAC method to the solubility of gases in pure liquids and liquid mixtures *without* introducing a free-volume contribution.

Extended corresponding states theory (CST) has also been used to develop estimation methods for $H_{2,1}$ (see for instance Gunn et al.[285] and Yorizane and Miyano[286]). The latter correlation rather successfully includes the solubility behavior of the quantum gases.

One of the most successful methods to estimate $H_{2,1}$ is based on a semiempirical use[8,14-16,28,287,288] of the scaled particle theory (SPT).[121,187,289-293] The dissolution process is thought to consist of two steps: (1) creation of a cavity in the solvent which is large enough to accommodate a solute molecule, and (2) insertion into the cavity of a solute molecule which then interacts with the solvent in some specified manner. Associated with step (1) is the partial molar Gibbs energy of cavity formation, G_{CAV}, which is given by Equation 101, and with step (2) the partial molar Gibbs energy of interaction, G_{INT}, which is given by Equation 102 (if moments higher than the dipole moment are neglected). The Henry coefficient is thus expressed as

$$\ln\left[\frac{H_{2,1}(T,P_{s,1})V_{s,1}^{*L}}{RT}\right] = \frac{G_{CAV}}{RT} + \frac{G_{INT}}{RT} \tag{124}$$

The SPT formalism is readily extended to include mixed solvents and electrolyte solutions (salt effects).[26,294,295]

Figure 17 shows experimental Henry coefficients for CO and N_2 dissolved in water[191,192] as a function of temperature, the correlations provided by the appropriate smoothing equations (BK or CG), and results obtained by application of SPT in its simplest version.[8,14,15,26,28] The agreement between measured and calculated $H_{2,1}(T,P_{s,1})$ is quite satisfactory over the whole temperature range covered by experiment, though it is evident that this approach will yield rapidly deteriorating results at elevated temperatures. However, the correlational and predictive powers of this method can be substantially improved by introducing the concept of temperature-dependent effective size parameters into the formalism, as suggested by Wilhelm,[296] and more recently by Montfort and Perez,[297] Schaffer and Prausnitz,[77] and Schulze and Prausnitz.[298] For instance, reasonably accurate prediction of the observed maxima of the curves $H_{2,1}(T,P_{s,1})$ vs. T for gases dissolved in water becomes feasible[298] by introducing

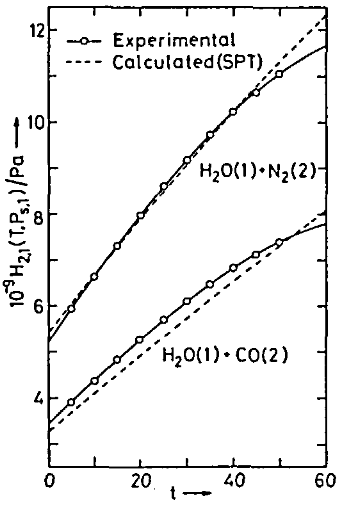

FIGURE 17. Henry coefficients $H_{2,1}(T,P_{s,1})$ for (water + nitrogen) and (water + carbon monoxide) as functions of temperature: t = T/K − 273.15.[191,192] (○) Experimental results. (—) Either CG or BK smoothing equations. (---) Obtained via scaled particle theory (SPT). (From Wilhelm, E., *Pure Applied Chem.*, 57, 303, 1985. With permission.)

$$\sigma_{12} = \frac{1}{2}(\sigma_1 + \sigma_2)\cdot\mathcal{F}(T) \qquad (125a)$$

$$\mathcal{F}(T) = 1.2978 - 141.75\,(T/K)^{-1} + 16280\,(T/K)^{-2} \qquad (125b)$$

Various versions of perturbation theory have been applied in predicting Henry coefficients and related quantities. The Tiepel and Gubbins[84] method is essentially based on the first-order perturbation theory of Leonard, Henderson, and Barker (LHB);[299] it yields reasonable results for the Henry coefficients in mixed solvent systems. When using the Weeks-Chandler-Anderson (WCA) reference system,[300,301] Tiepel and Gubbins satisfactorily predict the thermodynamic properties of gases dissolved in electrolyte solutions, provided they are salting-out systems.[302] For salting-in systems, only the qualitative features are reproduced. Neff and McQuarrie[18] were able to show that Pierotti's relations[8,26] may be obtained as special cases of their more rigorous perturbation treatment. In particular, their expression for the chemical potential includes an extra term which considers the change in the hard-sphere radial distribution function of the solvent upon adding a solute molecule; it had not been included in previous work.

In a series of papers, Goldman applies a variety of statistical-mechanical methods to gas solubility,[303] i.e., LHB theory, variational or Mansoori-Canfield (MC) theory,[304,305] WCA theory, etc. while focusing on contributions originating from nonclassical translational behavior. Several simple systems are investigated, for instance, H_2 in CH_4 and He in N_2, and for most the WCA predictions for $H_{2,1}$ are closer to experimental values than either the LHB or the MC results. This is in agreement with the fact that the first-order WCA theory provides a more accurate estimate of the Helmholtz energy of dense fluids than either one of the other two first-order theories. First-order perturbation theory of convex-molecule systems was applied by Boublik and Lu[306] to predict $H_{2,1}$, $V_2^{\infty L}$ and ΔH_2° of Ar, CH_4, N_2, O_2, and CO_2 in benzene and CCl_4 at 298.15 K. The Kihara acentric pair potential was used to characterize the intermolecular interactions. While calculated values of $H_{2,1}$ and $V_2^{\infty L}$ agree rather well with experimental results, the accord for ΔH_2° is only qualitative.

Perturbed hard chain theory is extended to asymmetric mixtures through a modified one-fluid theory approximation in Reference 307. A liquid-phase partition function of the Flory-Prigogine type in conjunction with the local composition concept and a two-fluid theory of mixtures is used by Brandani and Prausnitz[89] to correlate Henry coefficients for gases dissolved in pure liquids and liquid mixtures.

A method for the prediction of $H_{2,1}$ in pure and mixed solvents via CST modeling of the direct correlation function integrals in terms of reduced density and temperature is presented by Mathias and O'Connell[88] (see also Reference 87).

Many aspects of molecular-thermodynamic methods for predicting Henry coefficients and related quantities from a set of more or less readily available pure component parameters (or binary gas-liquid data in the case of gas solubility in mixed solvents) have been reviewed in the literature (see for instance References 11, 12, 19, 22, 26 to 28, 35, 37, 40, 46 to 48, 115 to 130, and 187). This set of articles, in conjunction with the original work cited here, should provide a reasonably broad basis for anyone planning to enter this field.

V. CONCLUDING REMARKS

The assortment of modern instrumentation accessible to today's experimentalist has made possible the study of highly dilute solutions of gases in liquids with unparalleled precision, accuracy, and speed over wide ranges of temperature and pressure. The best method at hand for the determination of Henry coefficients, the BK method, is characterized by a typical average percent deviation from the selected smoothing function of less than 0.05%. The absolute accuracy is most probably of the same order.[33,42,191,192,269]

Cross-fertilization with other disciplines, in particular with precision calorimetry, has recently become very important.[264,266-268] For the first time we are in the position to directly measure enthalpy changes upon solution (and therefrom derive heat capacity changes) of sparingly soluble gases in liquids. "Sparingly soluble" means here, for instance, a mole fraction solubility of CH_4 in H_2O at 298.15 K and $P = 0.1$ MPa of, roughly, $x_2 = 2.5 \times 10^{-5}$. In fact, one of the objectives of this review was to indicate new, active, and exciting interdisciplinary topics (see Section I). The increasing number of investigations with a strong biophysical and/or biomedical flavor is particularly noteworthy. 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 in binary mixtures containing a supercritical component, 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 phase and the vapor phase. There can be little doubt that this method will become more prominent for relatively simple solutions. Yet, as long as the interest is focused on solutions of gases in liquids consisting of significantly anisotropic molecules which, perhaps, possess a permanent dipole moment (or quadrupole moment, etc.) and exhibit molecular flexibility and/or association, the Henry's law approach appears to be much more convenient and hence superior to the others, and it is hard to imagine its replacement. This is particularly true for the most important class of solutions — aqueous solutions.

Quite some space was devoted to recent developments in measurement techniques and/or estimation methods for such auxiliary quantities as partial molar volumes and virial coefficients. Though advances have been quite impressive, many rather surprising gaps still exist.

As concerns methods for the very precise determination of the solubility of gases in liquids, that is to say for Henry coefficients $H_{2,1}(T,P_{s,1})$, special attention was given to

Benson-Krause type equipment.[33,42,191,192] Besides, several other designs have been briefly discussed, which either increase the accessible temperature and pressure ranges significantly or help to accelerate data collection. Their precision (and accuracy) were judged so that a potential user may select the technique most compatible with his needs.

This review was written in the first place to present the state of the art for the experimentalist. However, a brief survey of recent molecular thermodynamic contributions to this field has been included, mainly for the following two reasons. First, to provide a guide to rational estimation techniques for Henry coefficients in the absence of experimental data. This aspect will be particularly important for application-oriented work on gas solubility. And second, to allow, perhaps, a more detailed discussion of experimental results, which may in turn influence further research activities.

VI. GLOSSARY OF SYMBOLS

Note: a few symbols, which occur only at one or two places in the text, have been omitted. Some of the symbols listed below may be modified further, with obvious meaning, by adding appropriate superscripts and/or subscripts.

a	attraction parameter (Redlich-Kwong EOS)
a_i	coefficient in BK-type fitting equation
A	parameter in the two-suffix Margules equation
$\hat{A}$	Chueh-Muirbrook-Prausnitz parameter
A_i	coefficient in CG-type fitting equation
b	size parameter (Redlich-Kwong EOS)
$\hat{b}$	molecular volume (Bondi)
B	second virial coefficient of a mixture
$\hat{B}$	Chueh-Muirbrook-Prausnitz parameter
B_{ii}	second virial coefficient of pure i
B_{ij}	second virial cross-coefficient
C	third virial coefficient of a mixture
C_{iii}	third virial coefficient of pure i
C_{ijk}	third virial cross-coefficient
$C_{P,2}^{oV}$	molar heat capacity of pure 2 in the perfect-gas state
$C_{P,2}^{\infty L}$	partial molar heat capacity of 2 at infinite dilution (liquid phase)
$\Delta C_{P,2}^{o}$	$\equiv C_{P,2}^{\infty L} - C_{P,2}^{oV}$, heat capacity change upon solution of 2 in 1
$C_{12}^{\infty L}$	reduced volume integral of the molecular direct correlation function (infinite dilution)
d	DeSantis-Grande parameter
f	fugacity
f_i	component fugacity of substance i in a solution
G^E	excess molar Gibbs energy
G_{CAV}	partial molar Gibbs energy of cavity formation
G_{INT}	partial molar Gibbs energy of interaction
$h_{2,1}$	"uncorrected Henry coefficient" of solute 2 dissolved in solvent 1
$H_{2,1}$	Henry coefficient of solute 2 dissolved in solvent 1
$H_{3,[1+2]}$	Henry coefficient of solute 3 dissolved in the mixed solvent [1 + 2]
H_2^{oV}	molar enthalpy of pure 2 in the perfect-gas state

$H_2^{\infty L}$	partial molar enthalpy of 2 at infinite dilution (liquid phase)
ΔH_2°	$\equiv H_2^{\infty L} - H_2^{\circ V}$, enthalpy change upon solution of 2 in 1
ΔH^{vap}	molar enthalpy of vaporization
k_B	Boltzmann's constant
k_{ij}	binary interaction parameter
K	number of components
$L_{2,1}$	Ostwald coefficient of solute 2 dissolved in solvent 1
m	parameter in the modified Tait equation
n	total amount of substance; $n = \Sigma n_i$
n_i	amount of substance i
N_A	Avogadro's constant
P_i	permanent dipole moment of i
P	pressure
P_i	$\equiv y_iP$, partial pressure of i
$P_{s,i}$	vapor pressure of i
$\mathcal{P}$	Poynting correction
r	$\equiv \sigma_1/\sigma_2$, ratio of effective hard-sphere diameters
R	$= 8.31441\ J{\cdot}K^{-1}{\cdot}mol^{-1}$, gas constant
t	$\equiv T/K - 273.15$
T	thermodynamic temperature
ΔU^{vap}	molar energy of vaporization
v	(experimentally determined) volume
$\hat{v}^L$	$\simeq v^L - n_2^L(V_2^{\infty L} - V_1^{*L})$
V	molar volume (of a mixture)
V_i	partial molar volume of i
V_i^*	molar volume of pure i
$V_i^{\infty L}$	partial molar volume of i at infinite dilution (liquid phase)
V_{CAV}	$= (\partial G_{CAV}/\partial P)_T$
x_i	liquid-phase mole fraction of i
y_i	vapor-phase mole fraction of i
Z	$\equiv PV/RT$, compressibility factor

Greek Letters

α	mean polarizability
$\widehat{\alpha}_{22,1}$	self-interaction coefficient (between two solute molecules 2 dissolved in solvent 1)
β_T	$\equiv -V^{-1}(\partial V/\partial P)_T$, isothermal compressibility
γ_i	liquid-phase activity coefficient of i
δ_i	solubility parameter of i
Δ_{12}	$\equiv 2B_{12} - (B_{11} + B_{22})$
ϵ_i	dispersion energy parameter of i
ϵ_{ij}	interaction energy parameter
η_1	$\equiv \pi N_A\sigma_1^3/(6V_{s,1}^{*L})$, reduced density ("compactness") of solvent 1
$\widehat{\eta}_{2,1}$	dilation constant
μ_i	chemical potential of i
ν_i	characteristic molar volume of i (Brelvi-O'Connell)
π	number of phases
$\Pi_{s,1}^{*L}$	internal pressure of pure solvent 1 (saturation condition)

ρ	$\equiv V^{-1}$, total molar density; $\rho = \Sigma \rho_i$
ρ_i	$\equiv n_i/v$, concentration (molar density) of i
$\tilde{\rho}_1$	$\equiv \nu_1 \rho^{*L}_{s,1}$, reduced molar density of solvent 1 (Brelvi-O'Connell)
σ_i	effective hard sphere diameter of i
σ_{12}	$= (\sigma_1 + \sigma_2)/2$
ϕ_i	fugacity coefficient of component i in a solution
$\phi_i^{\infty V}$	fugacity coefficient of component i at infinite dilution (vapor phase)
Φ_2	effective volume fraction of solute 2 (Wohl-type equation)
ω	acentric factor
Ω_a, Ω_b	Redlich-Kwong parameters

Superscripts

*	pure substance
o	perfect-gas state or standard state
∞	infinite dilution
L	liquid phase
V	vapor phase
′	unsymmetric convention

Subscripts

i or j or k	general indexes; in most cases, i = 1 denotes the solvent, and i = 2 denotes the solute
ij	"binary" or "interaction" quantity
c	critical (or pseudocritical) quantity
r	reduced quantity
s	saturation (orthobaric) condition

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