

Review

The Art and Science of Solubility Measurements: What Do We Learn?¹

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Solubility and related phenomena constitute one of the oldest fields in physical chemistry, and also one of the most important. Given its wide scope, a short review cannot possibly be comprehensive, and I shall focus on just a few selected topics which reflect my current research interests, such as the solubility of supercritical solutes (gases) in liquids. First, I shall concisely present the thermodynamic formalism relevant for the study of *nonelectrolyte* solutions and indicate the most significant recent experimental results. Selected aspects of solubility data reduction and data correlation will be touched upon, including a critical discussion of some popular approximations. This will be accompanied by a survey of current estimation techniques for indispensable auxiliary quantities, such as virial coefficients and partial molar volumes at infinite dilution. One of the goals here is to clarify issues frequently overlooked and to dispel misconceptions encountered in the literature. Finally, a few experimental results obtained for dilute *aqueous* nonelectrolyte solutions will be discussed, and their relevance in biophysical chemistry indicated. Inevitably, pride of place will be given to the Henry fugacity (also known as Henry's law constant) and to various key caloric quantities which may be derived therefrom through van't Hoff analysis of high-precision solubility data.

Keywords: Solubility, Solution Thermodynamics, Henry Fugacity, Enthalpy Changes on Solution, Heat Capacity Changes on Solution, Partial Molar Volumes at Infinite Dilution

The entire history of chemistry bears witness to the extraordinary importance of the phenomena of solubility.

Joel H. Hildebrand and Robert L. Scott

The Solubility of Nonelectrolytes
3rd edition, Reinhold, New York, 1950



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1. Introduction

For more than a century, the physico-chemical investigation of solubility and related phenomena has belonged to the most important topics in chemistry, a fact concisely summarized in 1950 by the introductory statement of Hildebrand and Scott quoted above.¹⁾ Indeed, the study of the solubility of nonelectrolytes in liquids has contributed decisively to the development of the highly formalized general discipline of solution thermodynamics,²⁻⁶⁾ for instance by providing idealized solution models, such as the one based on the Lewis-Randall (LR) rule, or the one based on Henry's law (HL).⁵⁻⁸⁾ Frequently, the terms *solution* and *mixture* are used synonymously to indicate a homogeneous phase (gaseous or liquid or solid) containing two or more chemically different substances, though the latter term should preferably be restricted to the case where all the components are in the same physical state as the solution.

Most of this review will focus on *liquid binary* nonelectrolyte solutions, though occasionally extensions to multi-component systems will be indicated. A solution will be called *dilute* when one component, called the *solute*, is present in much smaller quantity compared with the other component, called the *solvent*. When considering only interactions with nearest neighbors, a rough estimate of the dilute region is provided by $x_2 < 0.01$, where x_2 denotes the solute mole fraction. Of particular interest are properties in the limit of *infinite dilution*: they will be indicated by a superscript ∞ attached to the property symbol. Finally we note that the term *solubility* at any specified temperature and pressure is usually associated with the limiting composition of the liquid solution phase in the presence of a co-existing phase (*saturation* solubility).

Liquid-phase solubility data⁹⁾ are required in surprisingly diverse areas of the pure and applied sciences, for instance in chemical engineering, geochemistry, environmental science, biophysics and biomedical technology. In particular we note that separation processes based on vapor-liquid equilibria (VLE), liquid-liquid equilibria (LLE) and solid-liquid equilibria (SLE) all involve liquid multicomponent systems, and that the majority of chemical synthesis reactions takes place in the liquid phase. When we focus on *water*^{10,11)} as solvent, the following three aspects are of particular importance:

- Water is the most abundant substance on the surface of the earth. The approximate water supply amounts to roughly 13.4×10^{20} kg, of which the saline ocean waters constitute by far the largest portion: *ca.* 96.5%, *i.e.* about 12.9×10^{20} kg. Only a small fraction

of the earth's freshwater (less than 0.3%), *i.e.* roughly 0.001×10^{20} kg, is found in rivers and lakes, the remainder being stored in the Arctic and Antarctic ice caps, in glaciers and in fresh groundwater.¹²⁾

- Water is the only substance on earth that occurs naturally in all three states of matter, which fact is closely related to the size of the earth and that the earth's orbit is located in the so-called habitable zone of the solar system.¹³⁾ In turn, this is prerequisite for the emergence of life on earth.¹⁴⁻²¹⁾
- Liquid water (and to a lesser extent water vapor and ice), sustains life on earth as we know it. In fact, water is the principal constituent of all living organisms, making up about 70% by weight of the human body. In the biochemistry of the cell, water plays an essential role for the structure, stability, dynamics and function of biomacromolecules²²⁻²⁵⁾ to the extent that it may no longer be regarded as being a mere medium in which bio-processes occur, but, as recently suggested by Ball^{24,26)}, rather as an indispensable *active* matrix, something like a "biomolecule" itself.

Considering the wide scope of solubility-related fields indicated above, it is not surprising that the subject has such a vast literature.

At this juncture, perhaps a few words are in order to indicate the *three main* reasons for the enormous efforts invested into experimental, theoretical and computer-based work on solubility in general, and on liquid-phase nonelectrolyte solubility in particular. First, it is hoped that by studying solution properties we will be able to improve our knowledge of *interactions* between molecules of different species in bulk liquid phases. Second, the appearance of *new* physical phenomena not found in the pure components is scientifically fascinating as well as challenging, and adds a new dimension to research. These two aspects are of great importance in the *real world* of applied chemistry, chemical engineering and, of course, biophysical chemistry, since the majority of technologically important processes and of biophysically significant systems involves liquid solutions, and the practitioner there has to deal with them efficiently (and pragmatically). This covers the third major reason. **Fig.1** illustrates the relative positions of experiment, theory and computer simulation by showing what may be learned from a comparison of respective results under idealized conditions.²⁷⁾

Experiments are the fundament of science, yet the huge number of potentially useful solubility data

connected with binary, ternary, quaternary, *etc.* solutions at different temperatures and pressures effectively precludes the experimental determination of solubilities for all but a few representative *key systems* of physico-chemical/technological interest. This is best illustrated by calculating the number of multicomponent solutions containing r components which can be formed out of, say, $n = 1000$ important chemicals.

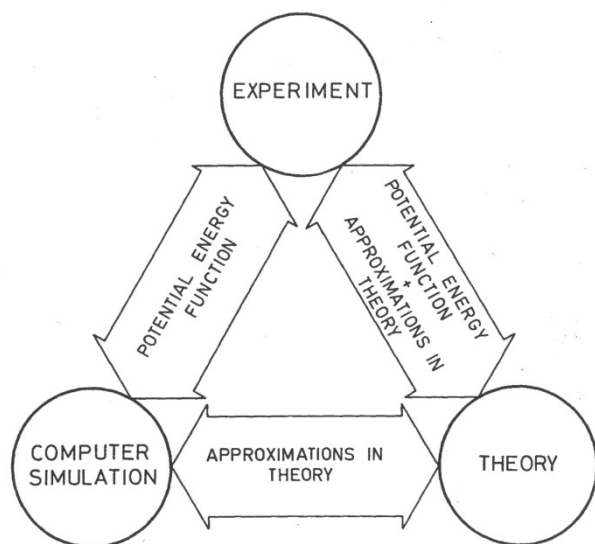


Fig.1 The three *pillars of science*: experiment, theory and computer simulation. The double-headed arrows indicate possible, fundamentally important comparisons (from Wilhelm²⁷).

This r -combination is given by

$$C(n,r) = \binom{n}{r} = \frac{n(n-1)\cdots(n-r+1)}{r!} \quad (1)$$

whence $C(1000,2) = 4.995 \times 10^5$ different binary solutions may be formed, $C(1000,3) = 1.66167 \times 10^8$ different ternary solutions, $C(1000,4) = 4.141712475 \times 10^{10}$ different quaternary solutions, and so forth. Reliable and effective prediction methods are thus an indispensable tool of the trade, which requirement is met, for instance, by group contribution methods (DISQUAC, UNIFAC).²⁸⁻³¹ While they work reasonably well for excess molar Gibbs energies G^E and excess molar enthalpies H^E , however, predicted results for excess molar heat capacities at constant pressure C_P^E are frequently not satisfactory. Similar comments apply to the COSMO-RS and related models.³²⁻³⁹

Evidently, a short review must be selective, and thus I shall focus on just a few areas which reflect my current research interests. For instance, VLE involving a

supercritical solute, that is the solubility of gases in liquids, will be discussed in some detail, including a discussion of the van't Hoff type analysis of high-precision solubility data. Pride of place will be given to the Henry fugacity (this quantity is also known as Henry's law constant) which is certainly one of the most misunderstood quantities in physical chemistry. *Aqueous nonelectrolyte solutions*, a topic to which I have contributed for about 35 years, will receive special attention. In fact, Henry fugacities and some closely related derived quantities may be used advantageously for the discussion of *hydrophobic effects*, which are generally regarded as playing an important role in a wide variety of biological processes, such as protein folding and the self-assembly of amphiphiles into membranes.⁴⁰⁻⁵⁵

The coverage throughout will be necessarily brief, and for details the interested reader should consult the pertinent literature provided. Note that my choices for references are illustrative and not comprehensive. For the omission of many interesting papers I would like to offer my apologies in advance.

2. Thermodynamic Fundamentals

In this section I will present a brief overview of classical thermodynamics applicable to non-electrolyte solutions in general, and to solutions of supercritical substances, *i.e.* gases, in liquids in particular.^{7,8,56-60} When discussing solutions and solubility, say, the solubility of a pure gas in a pure liquid at a given temperature T and pressure P , one is either predominantly interested in quantities which characterize the equilibrium *solubility* itself in the presence of both *coexisting phases*, for instance in the vapor-liquid distribution coefficient or *K-value* of the solute in the solvent, or in *single-phase properties*, such as the partial molar volume or the partial molar heat capacity of the solute in the liquid solution. Note that experimental LLE and SLE determinations are usually performed close to *isobaric* conditions, while VLE experiments are preferably performed *isothermally*.

A general criterion for phase equilibrium in *PVT-systems* (V denotes the molar volume) of *uniform* temperature and pressure is the equality of the chemical potential μ_i of each constituent component i in all coexisting phases $\alpha, \beta, \gamma, \dots$, or equivalently, the equality of the fugacity f_i of each constituent component i in all coexisting phases. For vapor-liquid equilibrium in an N -component system of uniform T and P , where $\alpha = V$ designates vapor, and $\beta = L$ designates liquid, we thus obtain.⁶

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

or, more conveniently for practical application,

$$f_i^V(T, P, \{x_i^V\}) = f_i^L(T, P, \{x_i^L\}), \quad i=1, 2, \dots, N \quad (3)$$

where N is the number of components, $\{x_i^V\}$ is the set of vapor-phase mole fractions and $\{x_i^L\}$ is the set of liquid-phase mole fractions; for any phase π we have $x_i^\pi = n_i^\pi / \sum_i n_i^\pi$, where n_i^π is the amount of substance of component i in this phase, and $\sum_i x_i^\pi = 1$. The link of eq. (3) with measurable VLE-related quantities may be established by two *entirely equivalent* formal approaches.⁵⁻⁸⁾ In the first, the equilibrium condition is rewritten in terms of the *fugacity coefficient* of component i in solution in phase $\pi = \alpha, \beta, \gamma, \dots$, which quantity is defined by

$$\phi_i^\pi(T, P, \{x_i^\pi\}) = f_i^\pi(T, P, \{x_i^\pi\}) / x_i^\pi P \quad (4)$$

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

$$y_i \phi_i^V(T, P, y_i) = x_i \phi_i^L(T, P, x_i), \quad i=1, 2, \dots, N \quad (5)$$

For obvious reasons, this approach is known as the (ϕ, ϕ) method.

The thermodynamic description of liquid-liquid equilibria and solid-liquid equilibria is based on the same general criteria stated above for VLE, eqs. (2) and (3). For instance, indicating the coexisting liquid phases by L_1 and L_2 , respectively, we obtain for LLE at uniform temperature and pressure

$$f_i^{L1}(T, P, \{x_i^{L1}\}) = f_i^{L2}(T, P, \{x_i^{L2}\}), \quad i=1, 2, \dots, N \quad (6)$$

Further treatment of LLE and SLE, however, is predominantly based on the use of activity coefficients, which quantities will be formally introduced below, and corresponding models. Real systems show a rich diversity of LLE and SLE behavior, meriting separate reviews each.^{6,61-65)} In this review, these two topics will not receive any further consideration.

Perfectly general equations, valid for both fluid phases V and L, allow the calculation of the component fugacity coefficients at any desired pressure or amount-of-substance density $\rho = 1/V$ from *PVT* equations-of-state (EOS) for the solution/ mixture, with the proviso, of course, that the EOS is valid over the entire range of integration. In terms of a *volume-explicit* EOS

$$Z = PV/RT = Z(T, P, \{x_i^\pi\}), \quad \text{where } Z \text{ is the}$$

compression factor of the solution in phase $\pi = V$ or L , and R is the gas constant, and dropping the superscript π where unambiguously permissible,

$$\ln \phi_i^\pi = \int_0^P \left[\left(\partial(nZ) / \partial n_i \right)_{T, P, n_{j \neq i}} - 1 \right] \frac{dP}{P}, \quad \text{constant } T, \{x_i^\pi\} \quad (7)$$

with $n = \sum_i n_i$. When a *pressure-explicit* EOS

$$Z = Z(T, V, \{x_i^\pi\}) \text{ is used, we obtain}$$

$$\ln \phi_i^\pi = \int_V^\infty \left[\left(\partial(nZ) / \partial n_i \right)_{T, nV, n_{j \neq i}} - 1 \right] \frac{dV}{V} - \ln Z, \quad \text{constant } T, \{x_i^\pi\} \quad (8)$$

Since the majority of the EOS in use is pressure-explicit rather than volume-explicit, the most important exception being the volume-explicit virial EOS, eq. (8) is more useful in VLE problems than eq. (7).

In the second approach, the component fugacities in the vapor phase are again expressed in terms of fugacity coefficients, but the liquid-phase fugacities of the components are now expressed in terms of appropriately normalized *liquid-phase activity coefficients*. For a *binary* solution at constant T and P , we have the following possibilities:

- When ideal-solution behavior is based on the *Lewis-Randall rule* (LR), see below, that is when we assume the validity of

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

over the entire composition range $0 \leq x_i \leq 1$, the corresponding activity coefficients are given by

$$\begin{aligned}
 \gamma_i^{\text{LR}}(T, P, x_i) &= f_i^{\text{L}}(T, P, x_i) / f_i^{\text{LR}}(T, P, x_i) \\
 &= f_i^{\text{L}}(T, P, x_i) / x_i f_i^{\text{L}*}(T, P),
 \end{aligned}
 \quad i = 1, 2 \quad (10)$$

whence

$$\begin{aligned}
 f_i^{\text{L}}(T, P, x_i) &= \gamma_i^{\text{LR}}(T, P, x_i) x_i f_i^{\text{L}*}(T, P)
 \end{aligned}
 \quad (11)$$

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

$$f_i^{\text{L}*}(T, P) = \phi_i^{\text{L}*}(T, P) P \quad (12)$$

is the fugacity of pure component i in either a real or a hypothetical liquid state at (T, P) of the liquid solution,

and $\phi_i^{\text{L}*}(T, P)$ is its fugacity coefficient. The activity coefficients are said to be normalized *symmetrically* when the definition eq. (10) applies for *all* components, and

$$\gamma_i^{\text{LR}} \rightarrow 1 \text{ as } x_i \rightarrow 1, \text{ constant } T, P \quad (13)$$

This approach is also known, somewhat loosely, as being based on *Raoult's law* (see below).

- Ideal-solution behavior based on *Henry's law* (HL), see below, is characterized by assuming the validity of

$$f_i^{\text{HL}}(T, P, x_i) = x_i h_{i,j}(T, P), \quad (14)$$

over the entire composition range $0 \leq x_i \leq 1$, whence the corresponding activity coefficients are given by

$$\begin{aligned}
 \gamma_i^{\text{HL}}(T, P, x_i) &= f_i^{\text{L}}(T, P, x_i) / f_i^{\text{HL}}(T, P, x_i) \\
 &= f_i^{\text{L}}(T, P, x_i) / x_i h_{i,j}(T, P),
 \end{aligned}
 \quad i = 1, 2; \quad i \neq j \quad (15)$$

and thus

$$f_i^{\text{L}}(T, P, x_i) = \gamma_i^{\text{HL}}(T, P, x_i) x_i h_{i,j}(T, P) \quad (16)$$

Here, $h_{i,j}(T, P)$ denotes the *Henry fugacity* of component i dissolved in liquid j at T and P of the liquid solution. This quantity is also known as Henry's law constant. The value of the Henry fugacity depends not only on T and P but also on the identities of solute i and solvent j (the other component), whence the *double* subscript has been added. The activity coefficients are said to be normalized *unsymmetrically* when for the solvent ($i = 1$) the definition eq. (10) applies, and for the solute ($i = 2$) the definition eq. (15) applies. Their limiting behavior is thus given by

$$\gamma_1^{\text{LR}} \rightarrow 1 \text{ as } x_1 \rightarrow 1, \text{ constant } T, P \quad (17a)$$

$$\gamma_2^{\text{HL}} \rightarrow 1 \text{ as } x_2 \rightarrow 0, \text{ constant } T, P \quad (17b)$$

Since *experiment* indicates that at constant T and P the limiting value of the ratio f_i^{π} / x_i^{π} for $x_i^{\pi} \rightarrow 0$ is *finite*, by de l'Hôpital's rule

$$\lim_{x_i^{\pi} \rightarrow 0} \left(\frac{f_i^{\pi}}{x_i^{\pi}} \right) = \left(\frac{df_i^{\pi}}{dx_i^{\pi}} \right)_{x_i^{\pi} = 0} = h_{i,j}^{\pi}(T, P),$$

constant T, P (18)

is obtained. Equation (18) defines the *Henry fugacity* $h_{i,j}^{\pi}(T, P)$ of i dissolved in j for *any phase* π (L or V).

At $x_i^{\pi} = 0$, f_i^{π} must also become zero, and the limiting slope of the curve f_i^{π} vs. x_i^{π} at constant T and P is identified as the Henry fugacity. *Henry's law is a limiting law, and for real solutions it is approximately valid for small values of x_i^{π}* , with the experimental precision determining the observed apparent validity range.

At constant temperature and pressure, the limiting composition dependence of f_i^{π} / x_i^{π} at the other end of the composition range, *i.e.* for $x_i^{\pi} \rightarrow 1$, is evidently characterized by $f_i^{\pi} \rightarrow f_i^{\pi*}$. Through application of the isothermal-isobaric Gibbs-Duhem equation

$$x_1^{\pi} \frac{d \ln f_1^{\pi}}{dx_1^{\pi}} + x_2^{\pi} \frac{d \ln f_2^{\pi}}{dx_2^{\pi}} = 0 \quad (19)$$

in conjunction with eq. (18) used for the other component $j \neq i$,

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

constant T, P (20)

is obtained, where $f_i^{\pi*}(T, P)$ denotes the fugacity of pure component i at T and P of the solution and in the *same* physical state. Equation 20 is called the *Lewis-Randall rule*. It is valid in *any phase* π (L or V) and shows that in the limit for $x_i^{\pi} \rightarrow 1$ both f_i^{π} and its derivative with respect to x_i^{π} at constant T and P become equal to the fugacity of pure i . *The Lewis-Randall rule is*

a limiting law, and for real solutions it is approximately valid for values of x_i^π near unity, with the experimental precision determining the observed apparent validity range.

For real systems, in general it is found that $h_{i,j}(T, P) \neq f_i^{L*}(T, P)$. We note that as a consequence of the above, by differentiating the defining equation for $\gamma_i^{LR}(T, P, x_i)$, eq. (10), with respect to x_i at constant T and P , we find that the *limiting slope* of the activity coefficient curve for $x_i \rightarrow 1$ is zero:

$$\lim_{x_i \rightarrow 1} \left(\frac{d\gamma_i^{LR}}{dx_i} \right) = 0, \quad \text{constant } T, P \quad (21)$$

The ideal-solution model based on the Lewis-Randall rule, *i.e.* eq. (9), is preferably used when component i can exist as a pure liquid at the temperature of the solution. Whenever a component cannot exist as a pure liquid at the temperature of the solution, a situation encountered with solutions of supercritical solutes (gases) in liquids, the alternative ideal-solution model based on Henry's law, *i.e.* eq. (14), may be advantageously used for that component (the solute). The condition for vapor-liquid phase equilibrium may now be recast either into

$$\phi_i^V(T, P, y_i) y_i P = \gamma_i^{LR}(T, P, x_i) x_i f_i^{L*}(T, P) \quad (22)$$

or, equivalently, into

$$\phi_i^V(T, P, y_i) y_i P = \gamma_i^{HL}(T, P, x_i) x_i h_{i,j}(T, P) \quad (23)$$

These two approaches are known as the (ϕ, γ) methods.

At this juncture, several points should be emphasized (for details see refs. 5-8, 57-60). Since the approaches to the thermodynamic description of VLE introduced above are all equivalent, the various quantities associated with them are, of course, connected with each other by exact relations. For instance, comparison of eq. (11) with eq. (16) shows that ($i = 1$ or 2 , $j = 1$ or 2 ; $i \neq j$)

$$\frac{\gamma_i^{LR}(T, P, x_i)}{\gamma_i^{HL}(T, P, x_i)} = \frac{h_{i,j}(T, P)}{f_i^{L*}(T, P)} \quad (24)$$

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

$$\gamma_i^{LR\infty} = h_{i,j} / f_i^{L*} \quad (25)$$

whence

$$\gamma_i^{HL} = \gamma_i^{LR} / \gamma_i^{LR\infty} \quad (26)$$

and

$$\lim_{x_i \rightarrow 1} \gamma_i^{LR} = 1 \quad (27)$$

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

By definition, eq. (4) applies for every component i in solution in any phase π , whence according to the defining relation for Henry's law, eq. (18), the *important, generally valid* relation

$$\begin{aligned} \phi_i^{\pi\infty}(T, P) &= \lim_{x_i^\pi \rightarrow 0} \phi_i^\pi(T, P, x_i^\pi) \\ &= \frac{1}{P} \lim_{x_i^\pi \rightarrow 0} \left[\frac{f_i^\pi(T, P, x_i^\pi)}{x_i^\pi} \right] \\ &= \frac{h_{i,j}^\pi(T, P)}{P}, \end{aligned} \quad \text{constant } T, P \quad (28)$$

is obtained,^{7,8,57-59,66)} where $\phi_i^{\pi\infty}(T, P)$ is the fugacity coefficient of component i at infinite dilution in phase π . Equation (28) immediately yields the thermodynamically correct limiting value of the Henry fugacity as the *critical point of the solvent* (with critical temperature $T_{c,1}$, critical pressure $P_{c,1}$ and critical molar volume $V_{c,1}$) is approached:^{7,8,57-59,66)}

$$\begin{aligned} \lim_{\substack{T \rightarrow T_{c,1} \\ P_{s,1} \rightarrow P_{c,1}}} h_{2,1}(T, P_{s,1}) \\ = \phi_2^{V\infty}(T_{c,1}, P_{c,1}) P_{c,1} \end{aligned} \quad (29)$$

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

$$\phi_2^{V\infty}(T_{c,1}, P_{c,1}) = \phi_2^{L\infty}(T_{c,1}, P_{c,1}) \quad (30)$$

Here, $h_{2,1}(T, P_{s,1})$ denotes the Henry fugacity determined experimentally at the vapor pressure $P_{s,1}(T)$ of the solvent. Note that the subscript s always denotes *saturation conditions*. A considerably more elaborate derivation was presented by Beutier and Renon⁶⁷⁾. Equation (29) conclusively shows that Hayduk and Buckley's assertion⁶⁸⁾ that the solubilities of

different gases in a given solvent tend to coincide at a temperature near the solvent's critical temperature is untenable.

The following equations provide some rigorous links between a thermodynamic description of a *liquid* solution/mixture based on activity coefficients and one based on fugacity coefficients and hence directly on an equation of state. For instance,

$$\gamma_i^{\text{LR}} = \phi_i^{\text{L}} / \phi_i^{\text{L}*} \quad (31)$$

$$\gamma_i^{\text{HL}} = \phi_i^{\text{L}} / \phi_i^{\text{L}\infty} \quad (32)$$

and

$$\gamma_i^{\text{LR}\infty} = \phi_i^{\text{L}\infty} / \phi_i^{\text{L}*} \quad (33)$$

Finally, I emphasize the close connection with *residual* quantities in (T, P, x) -space.^{7,8)} For instance

$$\begin{aligned} f_i^{\text{L}*}(T, P) / P \\ &= \phi_i^{\text{L}*}(T, P) \\ &= \exp\left(G_i^{\text{R,L}*}(T, P) / RT\right) \end{aligned} \quad (34)$$

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

$$\begin{aligned} h_{i,j}(T, P) / P \\ &= \phi_i^{\text{L}\infty}(T, P) \\ &= \exp\left(\mu_i^{\text{R,L}\infty}(T, P) / RT\right) \end{aligned} \quad (35)$$

where $\mu_i^{\text{R,L}\infty}$ is the residual chemical potential of component i at infinite dilution in solvent j in the liquid phase. Of course, entirely analogous relations are valid for the phase $\pi = \text{V}$, *i.e.* the vapor phase.

Equations (5), (22) and (23) may each serve as a rigorous thermodynamic basis for the treatment of VLE. The decision what approach to adopt is by and large a matter of taste and convenience. VLE involving fairly simple fluids may conveniently be treated in terms of the (ϕ, ϕ) approach, eq. (5), because the use of a single EOS valid for both phases V and L has some computational advantage and a certain aesthetic appeal. However, the emphasis is on "fairly simple", since no generally satisfactory EOS for dense fluids of practical, that is to say, chemical engineering importance has as yet been developed. At low to moderate pressures and for mixtures where the critical temperature $T_{c,i}$ of each component is distinctly larger than the experimental temperature, and when the interest is on the composition dependence of the various thermodynamic quantities over the entire composition range $0 \leq x_i \leq 1$ (or a large part thereof), VLE data reduction, VLE calculations and

VLE predictions are preferably based on the classical Lewis-Randall (ϕ, γ) formalism, eq. (22), implying the symmetric convention for the activity coefficients. This approach is readily extended to multicomponent systems. However, when we consider a binary system for which component 2, designated the *solute*, is *supercritical*, no experimental vapor pressure of the solute exists, and thus its fugacity $f_2^{\text{L}*}(T, P)$ as a *real*, pure liquid at the temperature of interest does not exist. An alternative approach is thus indicated, the most *natural* choice being the use of the Henry's law (ϕ, γ) formalism, eq. (23), for the solute, while for the solvent, component 1, the Lewis-Randall formalism, eq. (22), is maintained. It has the unquestioned advantage that the Henry fugacity $h_{2,1}$,

and hence γ_2^{HL} , are unambiguously accessible according to an *experimental* procedure as indicated by eq. (18) and detailed below. The experimental quantities may be obtained, at least in principle, to any desired degree of accuracy.^{7,57)} Since the Henry's law formulation for the component fugacity of the solute ($i = 2$), see eq. (16), is of central importance in the discussion of *dilute* solutions, it may also be used when $T < T_{c,i}$, *i.e.* for subcritical VLE when the focus is on *high dilution* properties. We note, however, that rigorous extensions to *mixed* solvents are rather complex. The ensuing problems have been discussed in depth by Van Ness and Abbott.⁶⁹⁾

The Henry fugacity of a supercritical solute 2 dissolved in liquid solvent 1 is defined by eq. (18) with $\pi = \text{L}$. For VLE, because of the phase equilibrium criterion eq. (3), and eq. (4),

$$f_2^{\text{L}}(T, P, x_2) = \phi_2^{\text{V}}(T, P, y_2) y_2 P \quad (36)$$

where all quantities refer to the *actual* VLE conditions. In conjunction with the definition eq. (18), eq. (36) provides the classical experimental basis for the determination of $h_{2,1}^{\text{L}}(T, P_{s,1}) = h_{2,1}(T, P_{s,1})$ from *isothermal* VLE measurements (determination of P, x_2, y_2) at decreasing pressure $P \rightarrow P_{s,1}(T)$, and concomitantly decreasing $x_2 \rightarrow 0$ and $y_2 \rightarrow 0$, according to

$$\begin{aligned}
 h_{2,1}(T, P_{s,1}) &= \lim_{x_2 \rightarrow 0} \left(\frac{f_2^L(T, P, x_2)}{x_2} \right) \\
 &= \lim_{\substack{x_2 \rightarrow 0 \\ y_2 P \rightarrow 0 \\ \text{constant } T}} \left(\frac{\phi_2^V(T, P, y_2) y_2 P}{x_2} \right), \quad (37)
 \end{aligned}$$

That is to say, the Henry fugacity referring to the *liquid phase* is obtained as the intercept of a plot, at constant T , of $\phi_2^V(T, P, y_2) y_2 P / x_2$ against x_2 .⁷⁰⁾ Here, $\phi_2^V(T, P, y_2)$ must be calculated with a suitable vapor-phase EOS (see eqs. (7) and (8), and the appropriate section below).

Once $h_{2,1}(T, P_{s,1})$ has been obtained by this extrapolation method, the VLE measurements at $P > P_{s,1}(T)$ allow extraction of the liquid-phase

activity coefficients γ_2^{HL} , though frequently experimental imprecision precludes obtaining reliable results. For isothermal conditions, at *each* experimental composition x_2 eq. (16) applies,

$$f_2^L(T, P, x_2) = \gamma_2^{\text{HL}}(T, P, x_2) x_2 h_{2,1}(T, P) \quad (38)$$

necessarily with a different corresponding experimental total equilibrium pressure. Thus, for each VLE experiment the respective Henry fugacities $h_{2,1}$ as well

as the corresponding activity coefficients γ_2^{HL} at x_2 refer to *different* experimental pressures. For the reduction, correlation and further use of high-precision gas solubility data, it is advantageous to select at each temperature the vapor pressure $P_{s,1}(T)$ of the solvent as *reference pressure*. With this convention and taking into account the pressure dependences of the various quantities involved^{7,57,70)} (see also below), *i.e.*

$$\begin{aligned}
 &h_{2,1}(T, P) \\
 &= h_{2,1}(T, P_{s,1}) \exp \left\{ \int_{P_{s,1}}^P \frac{V_2^{\text{L}\infty}(T, P)}{RT} dP \right\} \quad (39)
 \end{aligned}$$

and

$$\begin{aligned}
 &\gamma_2^{\text{HL}}(T, P, x_2) \\
 &= \gamma_2^{\text{HL}}(T, P_{s,1}, x_2) \\
 &\quad \times \exp \left\{ \int_{P_{s,1}}^P \frac{V_2^{\text{L}}(T, P, x_2) - V_2^{\text{L}\infty}(T, P)}{RT} dP \right\} \quad (40)
 \end{aligned}$$

we obtain the pressure-corrected isothermal-isobaric liquid-phase activity coefficient based on Henry's law at the *reference pressure* $P_{s,1}(T)$ at mole fraction x_2 via

$$\begin{aligned}
 &\gamma_2^{\text{HL}}(T, P_{s,1}, x_2) \\
 &= \frac{\phi_2^V(T, P, y_2) y_2 P}{x_2 h_{2,1}(T, P_{s,1})} \exp \left\{ - \int_{P_{s,1}}^P \frac{V_2^{\text{L}}(T, P, x_2)}{RT} dP \right\} \quad (41)
 \end{aligned}$$

Here, $V_2^{\text{L}}(T, P, x_2)$ is the partial molar volume of the solute at mole fraction x_2 in the liquid phase, and $V_2^{\text{L}\infty}(T, P)$ is the partial molar volume of the solute at infinite dilution. The exponentials in eqs. (39) – (41) are known as *Poynting correction factors*; and the integrals as *Poynting integrals*. The preexponential factor on the right-hand side of eq. (41) is a dimensionless group containing the experimental data, the Henry fugacity already extracted therefrom, and the vapor-phase fugacity coefficient. In order to evaluate the Poynting integral in eq. (41), information is needed on the composition dependence of the partial molar volume of the solute as well as on its pressure dependence. Note that (I) at *high* dilution $V_2^{\text{L}}(T, P, x_2) \cong V_2^{\text{L}\infty}(T, P)$, and (II) for gaseous solutes well below the critical temperature $T_{c,1}$ of the solvent, the pressure dependence of the partial molar volumes is rather small. Thus at low pressures, the Poynting correction factor typically differs from unity by only a few parts per thousand.^{70,71)} The magnitude of the Poynting correction is illustrated in **Fig.2**, for a series of fictitious *pure* liquids, by replacing V_2^{L} in the Poynting integral by $V^{\text{L}*}$, which denotes a pure-liquid molar volume. Here, the pressure dependence of $V^{\text{L}*}$ has been accounted for by the *modified Tait equation* (MTE),^{57,72)} a versatile liquid-phase EOS which is usually satisfactory for pressures up to about 100 MPa:

$$V_S^L(T, P) / V_S^{L*} = \left[1 + m \beta_{T,s}^{L*} (P - P_s) \right]^{-1/m} \quad (42)$$

$V_S^{L*} = V_S^{L*}(T, P_s)$ is the molar volume of the liquid at saturation, P_s is the vapor pressure, $\beta_{T,s}^{L*}$ is the isothermal compressibility of pure saturated liquid, and m is a pressure-independent parameter. For many organic liquids, experimental values cluster around $m = 10$, with only a small temperature dependence.

The composition dependence of the constant-temperature, constant-pressure activity coefficients $\gamma_2^{\text{HL}}(T, P_{s,1}, x_2)$ obtained via eq. (41) may be represented by any appropriate correlating equation compatible with the number and the precision of the experimental results.

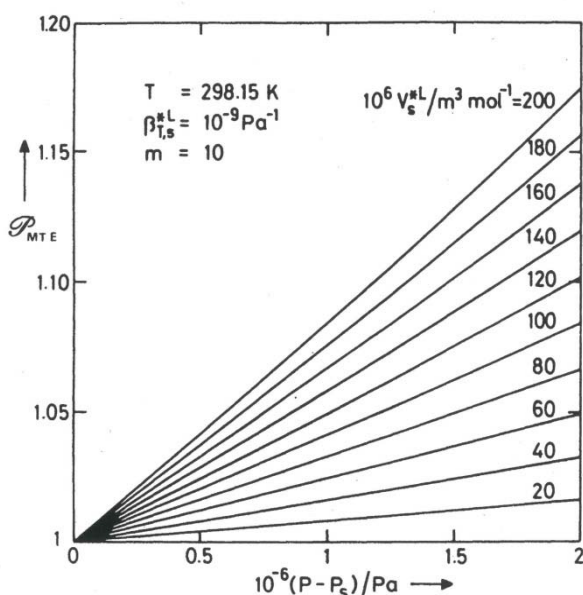


Fig.2 Poynting correction \mathbb{P}_{MTE} as a function of applied pressure $P - P_s$, at $T = 298.15$ K, for a series of fictitious pure liquids, all with isothermal compressibility $\beta_{T,s}^{L*} = 1 \times 10^{-9} \text{ Pa}^{-1}$, and molar volumes at saturation as indicated. Using the modified Tait equation (MTE),^{57,72)} one obtains

$$\mathbb{P}_{\text{MTE}} = \exp \left\{ \frac{V_S^{L*}}{RT} \frac{\left(1 + m \beta_{T,s}^{L*} (P - P_s) \right)^{(m-1)/m} - 1}{(m-1) \beta_{T,s}^{L*}} \right\}$$

Equations (37) and (41) are the *key equations* in the *classical sequential* approach to gas-solubility *data reduction* (supercritical solute) and most frequently adopted. Based on the definition eq. (18), entirely equivalent expressions relating the Henry fugacity to *limiting slopes* may be derived. They simply reflect the focusing of *interest on the solute* in a composition range *very close* to pure solvent, though, of course, “very close” varies from system to system.

The sequential approach to gas solubility measurements makes little use of the information thermodynamics supplies on the VLE equilibrium equation pertaining to the *solvent*, but, of course, for general equilibrium *calculations* it is needed. The resulting expressions are analogous to those used for subcritical, Lewis-Randall-based VLE calculations. For instance, for a binary solution, by combining eq. (22) for $i = 1$ (the solvent) with eq. (23) for $i = 2$ (the solute), and incorporating the appropriate Poynting corrections, the total experimental pressure is obtained as^{7,57)}

$$P = x_1 f_{s,1}^{L*} \gamma_1^{\text{LR}}(T, P_{s,1}, x_1) \frac{1}{\phi_1} \times \exp \left\{ \int_{P_{s,1}}^P \frac{V_1^L}{RT} dP \right\} + x_2 h_{2,1}(T, P_{s,1}) \gamma_2^{\text{HL}}(T, P_{s,1}, x_2) \frac{1}{\phi_2^V} \times \exp \left\{ \int_{P_{s,1}}^P \frac{V_2^L}{RT} dP \right\} \quad (43)$$

Here, $f_{s,1}^{L*} = f_1^{L*}(T, P_{s,1}) = P_{s,1} \phi_{s,1}^{V*}$ is the orthobaric fugacity of the pure solvent, see eq. (12), $\phi_{s,1}^{V*} = \phi_1^{V*}(T, P_{s,1})$ is the fugacity coefficient of pure solvent vapor at saturation, $\phi_i^V = \phi_i^V(T, P, y_i)$ denotes the vapor-phase fugacity coefficient of component i ($= 1$ or 2) in the vapor phase at mole fraction y_i , and $V_1^L = V_1^L(T, P, x_1)$ in the Poynting integral for the solvent is its partial molar volume in the liquid solution.

To summarize: depending on the type of liquid solution, both the LR-based and the HL-based approaches, as outlined above, provide adequate prescriptions for data reduction, correlation and calculation in experimental vapor-liquid phase

equilibrium investigations. The central quantities of interest in a binary system, that is $f_1^{L*}, f_2^{L*}, h_{2,1}, \gamma_1^{LR}, \gamma_2^{LR}, \gamma_2^{HL}$, are thermodynamic properties pertaining to the *liquid phase*. For instance, LR-based activity coefficients lead to excess molar Gibbs energies

$$G^E = RT \sum_i x_i \ln \gamma_i^{LR} \quad (44)$$

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

$$\left(\frac{\partial \ln h_{2,1}(T, P)}{\partial T} \right)_P = - \frac{\Delta H_2^\infty(T, P)}{RT^2} \quad (45)$$

and its pressure dependence by

$$\left(\frac{\partial \ln h_{2,1}(T, P)}{\partial P} \right)_T = \frac{V_2^{L\infty}(T, P)}{RT} \quad (46)$$

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

Equation (45) provides the rigorous basis for obtaining enthalpies of solution through *van't Hoff analysis* of high-precision solubility data of gases in liquids.^{7,8,56,57,70,71,73,74,102} Since

$$\left(\frac{\partial \Delta H_2^\infty(T, P)}{\partial T} \right)_P = \Delta C_{P,2}^\infty(T, P) \quad (47)$$

the partial molar heat capacity change

$$\Delta C_{P,2}^\infty = C_{P,2}^{L\infty} - C_{P,2}^{pg*}$$

on solution may also be

obtained by van't Hoff analysis. Here, $C_{P,2}^{L\infty}$ is the partial molar heat capacity at constant pressure of the solute at infinite dilution in the liquid solvent, and $C_{P,2}^{pg*}$ is the molar heat capacity at constant pressure of the pure solute in the perfect-gas state.

Equation (46) allows the calculation of the Henry fugacity of solute 2 dissolved in liquid solvent 1 for any desired pressure (*Poynting* correction, see eq. (39)), which is one of the main reasons why reliable $V_2^{L\infty}$ data over wide temperature ranges are so much in demand. The analogous equation for the LR activity coefficients ($i = 1$ or 2) is

$$\begin{aligned} & \left(\frac{\partial \ln \gamma_i^{LR}(T, P, x_i)}{\partial P} \right)_{T, x_i} \\ &= \frac{V_i^L(T, P, x_i) - V_i^{L*}(T, P)}{RT} \end{aligned} \quad (48)$$

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

$$\begin{aligned} & \left(\frac{\partial \ln \gamma_2^{HL}(T, P, x_2)}{\partial P} \right)_{T, x_2} \\ &= \frac{V_2^L(T, P, x_2) - V_2^{L\infty}(T, P)}{RT} \end{aligned} \quad (49)$$

The most important application of VLE relations is in the design of separation processes for the chemical industry. A frequently used measure of the tendency of a given component to distribute itself between the coexisting equilibrium phases is the *vapor-liquid distribution coefficient* or *K-value*. For a binary solution at *equilibrium* pressure P , it is defined by

$$K_{2,1}(T, P) = \left(\frac{y_2}{x_2} \right)_{\text{equil}} \quad (50)$$

and thus refers *only* to the actual conditions at *phase equilibrium*. With the help of eq. (5), the general expression

$$K_{2,1}(T, P) = \frac{\phi_2^L(T, P, x_2)}{\phi_2^V(T, P, y_2)} \quad (51)$$

is obtained, which provides the link to EOS-based calculations. Using eqs. (33) and (28), the infinite-dilution limit of the *K-value* may be profitably expressed as^{7,8,59,75}

$$\begin{aligned} K_{2,1}^\infty(T, P_{s,1}) &= \frac{\phi_2^{L\infty}(T, P_{s,1})}{\phi_2^{V\infty}(T, P_{s,1})} \\ &= \frac{\gamma_2^{LR\infty}(T, P_{s,1}) \phi_2^{L*}(T, P_{s,1})}{\phi_2^{V\infty}(T, P_{s,1})} \end{aligned} \quad (52a)$$

$$= \frac{h_{2,1}(T, P_{s,1})}{\phi_2^{V\infty}(T, P_{s,1}) P_{s,1}} \quad (52b)$$

Another practically important and widely used distribution coefficient is the *Ostwald coefficient*

$L_{2,1}(T, P)$,^{7,8,57,75-76} which quantity is the ratio of the amount-of-substance densities (amount-of-substance concentrations) of solute 2 in the *equilibrium* phases at experimental temperature T and corresponding equilibrium pressure P :

$$L_{2,1}(T, P) = \left(\frac{\rho_2^L}{\rho_2^V} \right)_{\text{equil}} \quad (53)$$

where $\rho_2^\pi = x_2^\pi / V^\pi = x_2^\pi \rho^\pi$, $\pi = L$ or V , V^π is the corresponding molar volume, and ρ^π is the total amount-of-substance density.

The infinite-dilution limit of the Ostwald coefficient,

$$\begin{aligned} L_{2,1}^\infty(T, P_{s,1}) &= \lim_{P \rightarrow P_{s,1}} L_{2,1}(T, P) \\ &= \lim_{P \rightarrow P_{s,1}} \left(\frac{\rho_2^L}{\rho_2^V} \right)_{\text{equil}} \end{aligned} \quad (54)$$

is rigorously connected with the Henry fugacity $h_{2,1}(T, P_{s,1})$.^{7,8,57,75-77}

$$\begin{aligned} L_{2,1}^\infty(T, P_{s,1}) &= \frac{RT}{h_{2,1}(T, P_{s,1}) V_{s,1}^L} Z_{s,1}^V \phi_2^{V\infty}(T, P_{s,1}) \end{aligned} \quad (55)$$

and with the K -value:

$$L_{2,1}^\infty(T, P_{s,1}) = \frac{1}{K_{2,1}^\infty(T, P_{s,1})} \frac{V_{s,1}^V}{V_{s,1}^L} \quad (56)$$

Here, $Z_{s,1}^V = P_{s,1} V_{s,1}^V / RT$ is the compression factor of pure saturated solvent vapor, $V_{s,1}^L$ is the molar volume of the pure saturated liquid solvent and $V_{s,1}^V$ is the molar volume of the pure saturated solvent vapor. Both the Ostwald coefficient and the K -value are distribution coefficients pertaining to the solute dissolved in the solvent in the two *coexisting* phases L and V , and therefore refer *only* to the actual *equilibrium pressure* P at the experimental temperature T . In contradistinction to these quantities, I reiterate that the Henry fugacity is a *single phase* property, which fact is most clearly indicated by eq. (35): this equation shows that $\phi_2^{L\infty}(T, P)$ and hence $h_{2,1}(T, P)/P$ are equal to the exponential of the residual chemical potential of solute i

at infinite dilution in liquid solvent j , divided by RT , at temperature T and at *any* pressure $P \geq P_{\text{equilib}}$. As such, for use in vapor-liquid phase *equilibrium* problems, *i.e.* data reduction, data correlation and data prediction, only their values referred to the actual equilibrium pressure are relevant. At infinite dilution, we have for the equilibrium pressure $P = P_{s,1}(T)$, and thus we have $h_{2,1}(T, P_{s,1})$ as the centrally important quantity.

Finally we note that

$$\begin{aligned} \lim_{T \rightarrow T_{c,1}} L_{2,1}^\infty(T, P_{s,1}) &= \lim_{T \rightarrow T_{c,1}} K_{2,1}^\infty(T, P_{s,1}) \\ &= \lim_{T \rightarrow T_{c,1}} (V_{s,1}^V / V_{s,1}^L) = 1 \end{aligned} \quad (57)$$

When $T \rightarrow T_{c,1}$, the limiting values of $L_{2,1}^\infty(T, P_{s,1})$ and of $K_{2,1}^\infty(T, P_{s,1})$ are identically unity, and yield directly the important relation eq. (29).^{75,76} The Ostwald coefficient is widely used in the discussion of hydrophobic effects,^{42-44,70} which topic is, as indicated in the introduction, a vast research area by itself.

3. Tackling Experimental Reality: Subtleties of Approximation

In the preceding section, the formalism relevant for the thermodynamic description of vapor-liquid equilibria has been summarized concisely, with the focus being on *binary* solutions containing a *supercritical* component, that is, on the solubility of gases in liquids. In this section I shall briefly review a few selected popular approximations, dictated by experimental reality, to some of the exact relations obtained so far, as well as selected estimation methods for key properties. For more comprehensive overviews see refs. 6, 7 and 57, and, in particular, the monograph by Poling, Prausnitz and O'Connell.⁷⁸

Since Henry fugacities and related quantities are usually referred to orthobaric conditions, reliable vapor pressure data $P_s = P_s(T)$ are indispensable, as are data on critical temperature, critical pressure and critical volume. For water, the most interesting and important solvent, Poling *et al.*⁷⁸ recommend $T_c = 647.14$ K, $P_c = 22.064$ MPa, and $V_c = 55.95$ cm³·mol⁻¹.

As pointed out above, when using the classical sequential approach for the determination of the Henry fugacity, as exemplified by eqs. (37) and (41), a vapor-phase EOS is required for calculating the fugacity

coefficient $\phi_2^V(T, P, y_2)$. Since the majority of gas-solubility measurements are performed in the low to moderate pressure domain, virial equations are the equations of choice. They are superior to cubic EOS and computationally convenient. Using a two-term volume-explicit virial equation, *i.e.*, $Z^V(T, P, y_2) \equiv PV^V/RT = 1 + B(T, y_2)P/RT$, in eq. (7) leads to the widely used expression for the fugacity coefficient of component i in a binary vapor mixture

$$\ln \phi_i^V = \frac{P}{RT} \left(B_{ii} + y_j^2 \delta_{12} \right), \quad i, j = 1, 2, \quad i \neq j \quad (58)$$

with $\delta_{12} = 2B_{12} - (B_{11} + B_{22})$. Here,

$B = y_1 B_{11} + y_2 B_{22} + y_1 y_2 \delta_{12}$ is the second virial coefficient of the mixture, B_{11} and B_{22} are the second virial coefficients of the pure components, and B_{12} designates a composition-independent interaction virial coefficient (cross-coefficient). The fugacity coefficient of the solute at infinite dilution in the vapor phase is thus given by

$$\ln \phi_2^{V\infty} = \frac{P}{RT} (2B_{12} - B_{11}) \quad (59)$$

and the fugacity coefficient of pure component 2 by

$$\ln \phi_2^{V*} = \frac{P}{RT} B_{22} \quad (60)$$

The quite popular rule-of-thumb $\phi_2^V(T, P, y_2) = \phi_2^{V*}(T, P)$ may frequently be rather unsatisfactory:

e.g. for the evaluation of $\phi_2^{V\infty}$ it only holds if

$$B_{12} = (B_{11} + B_{22})/2.$$

Frequently, experimental results on second virial coefficients, in particular for mixtures,⁷⁹⁾ are not available. Even for pure water vapor the situation below about 400 K is not entirely satisfactory and subject to intensive research.⁸⁰⁾ Thus, for VLE data reduction and VLE calculation one has to depend heavily on semiempirical estimation methods, which are predominantly based on the *extended corresponding states theorem*. One of the most popular and reliable methods is due to Tsonopoulos which, since its inception in 1974, has been revised and extended several times.⁸¹⁾ The reduced pure-substance second virial coefficient at a reduced temperature $T_{r,i} = T/T_{c,i}$ of a substance with an acentric factor ω_i is given by

$$\frac{B_{ii}(T_{r,i})P_{c,i}}{RT_{c,i}} = \sum_{l=0}^3 b_{l,i} B^{(l)}(T_{r,i}) \quad (61)$$

where $b_{0,i} = 1$, and

$$B^{(0)}(T_{r,i}) = 0.1445 - 0.3300 \frac{1}{T_{r,i}} - 0.1385 \frac{1}{T_{r,i}^2} - 0.0121 \frac{1}{T_{r,i}^3} - 0.000607 \frac{1}{T_{r,i}^8} \quad (62)$$

and $b_{1,i} = \omega_i$, and

$$B^{(1)}(T_{r,i}) = 0.0637 + 0.331 \frac{1}{T_{r,i}^2} - 0.423 \frac{1}{T_{r,i}^3} - 0.008 \frac{1}{T_{r,i}^8} \quad (63)$$

The next term must be included for substances with sizeable reduced *dipole moments* $p_{r,i}$.^{7,27)} For several compound classes, such as ketones and alkyl halides, *specific* expressions for $b_{2,i}(p_{r,i})$ are known,⁸¹⁾ and

$$B^{(2)}(T_{r,i}) = \frac{1}{T_{r,i}^6} \quad (64)$$

For the *hydrogen-bonded* normal 1-alkanols, in the *units used in ref. 81*, $b_{2,i} = 0.0878$, and an additional substance-specific parameter $b_{3,i}(p_{r,i})$ is needed ($b_{3,\text{methanol}} = 0.0525$),⁸¹⁾ and

$$B^{(3)}(T_{r,i}) = -\frac{1}{T_{r,i}^8} \quad (65)$$

For water, $b_{2,\text{water}} = -0.0109$, and $b_{3,\text{water}} = 0$. “New”, “experimental” results may lead to revisions, in particular of the Tsonopoulos functions $B^{(2)}$ and $B^{(3)}$, and the coefficients $b_{2,i}$ and $b_{3,i}$.

In order to estimate second virial cross-coefficients B_{ij} , appropriate semiempirical *combining rules* have to be used to obtain the characteristic *interaction* parameters $T_{c,ij}$, $P_{c,ij}$, $V_{c,ij}$, ω_{ij} , $b_{2,ij}$ and $b_{3,ij}$ from the pure-substance quantities. These interaction quantities then replace the corresponding pure-substance quantities in eqs. (61) through (65) to yield cross-coefficients $B_{ij}(T_{r,ij})$ at a reduced temperature

$T_{r,ij} = T/T_{c,ij}$. Nearly always, these combining rules incorporate *one* additional binary interaction parameter k_{ij} (usually distinctly smaller than 1) which is intended to improve on the geometric-mean approximation for $T_{c,ij}$, that is

$$T_{c,ij} = \left(1 - k_{ij}\right) \left(T_{c,i} T_{c,j}\right)^{1/2} \quad (66)$$

However, k_{ij} also contains, implicitly, empirical corrections for the remaining simple combining rules for $P_{c,ij}$, $V_{c,ij}$, ω_{ij} , etc. Equation (66) is definitely the most crucial combining rule for the prediction of B_{ij} . Experiment-based optimized values of k_{ij} for quite a few mixture types have been reported in the literature, together with appropriate correlations. For instance, for binaries where both components belong to either rare gases, or simple molecular gases, or essentially nonpolar hydrocarbons, k_{ij} may be estimated from⁷⁸

$$k_{ij} = 1 - \frac{8 \left(V_{c,i} V_{c,j}\right)^{1/2}}{\left(V_{c,i}^{1/3} + V_{c,j}^{1/3}\right)^3} \quad (67)$$

Other (semi-)empirical estimation methods may be found, for instance, in refs. (6), (78) and (82).

In the key relations eq. (37) and (41) for the classical, sequential approach to gas-solubility data reduction, the influence of composition upon the liquid-phase fugacity of the solute has been separated formally from the influence of pressure (see eqs. (46) and (49)). However, a rigorous evaluation of the Poynting integrals would require a detailed knowledge of the composition dependence as well as the pressure dependence of the *partial molar volume* $V_2^L(T, P, x_2)$ at each temperature of interest. Such comprehensive information will rarely be available, whence for the great majority of solubility measurements approximations at various levels of sophistication must be introduced to allow adequate VLE data reduction. The situation becomes particularly demanding at high pressures and/or when the solvent critical region is approached, where Poynting corrections become significant. With solubility experiments, usually the focus is on properties at *high* dilution, and typical gas-solubility measurements do *not* cover large composition ranges. At pressures reasonably close to $P_{s,1}$, and thus at *very* small mole fractions x_2 and at temperatures well below the critical temperature of the solvent, to an excellent approximation the partial molar volume $V_2^L(T, P, x_2)$ of eq. (41) may be replaced by a

pressure-independent partial molar volume at infinite dilution $V_2^{L\infty}(T, P_{s,1})$. The preferred experimental methods for determining $V_2^{L\infty}$ are either precision dilatometry or precision densimetry or magnetic float methods.⁸³⁻⁹¹⁾ However, compared to the large body of data on gas solubilities,^{9,56,92,93)} experimental results on $V_2^{L\infty}$ (and on V_2^L in general) of gases dissolved in liquids are not plentiful, whence reliable semi-empirical estimation methods are indispensable. Evidently, more experimentally determined partial molar volumes at infinite dilution, covering *large* temperature ranges including the critical region, are highly desirable.

The Handa-Benson correlation^{84,94)} is a versatile method for the prediction of partial molar volumes of gases at infinite dilution in non-aqueous solvents at atmospheric pressure, usually within about $\pm 10\%$ of known experimental values:

$$\frac{P_{c,2} V_2^{L\infty}}{RT_{c,2}} = 0.088 + 2.763 \frac{TP_{c,2}}{T_{c,2} \Pi_{s,1}^{L*}} \quad (68)$$

where

$$\Pi_{s,1}^{L*} = \frac{T \alpha_{P,s,1}^{L*}}{\beta_{T,s,1}^{L*}} - P_{s,1} \quad (69)$$

is the internal pressure,

$\alpha_{P,1}^{L*} = \left(V_1^{L*}\right)^{-1} \left(\partial V_1^{L*} / \partial T\right)_P$ is the isobaric

expansivity, and $\beta_{T,1}^{L*} = -\left(V_1^{L*}\right)^{-1} \left(\partial V_1^{L*} / \partial P\right)_T$ is the isothermal compressibility, respectively, of the pure liquid solvent.

Scaled particle theory (SPT) has also been used successfully by Pierotti,⁹⁵⁾ among others,^{56,96-99)} to calculate Henry fugacities, ΔH_2^∞ , $\Delta C_{P,2}^\infty$ and $V_2^{L\infty}$ of non-polar and polar gases in non-polar and polar solvents, including water. Note, however, that in order to obtain reasonable results, the *experimental* density of the pure solvent as well as its derivatives $\alpha_{P,s,1}^{L*}$ and

$\beta_{T,s,1}^{L*}$ have to be used. If a two-step dissolution process is considered, that is to say (I) creation of a cavity in the solvent large enough to accommodate a solute molecule, and (II) introduction into the cavity of a solute molecule which interacts realistically with the surrounding solvent molecules, such a heuristical application of SPT yields

$$V_2^{L\infty} = V_{\text{cav}} + \beta_{T,s,1}^{L,*} (G_{\text{int}} + RT) \quad (70)$$

Here, $V_{\text{cav}} = (\partial G_{\text{cav}} / \partial P)_T$, G_{cav} is the partial molar Gibbs energy of cavity formation, and G_{int} is the partial molar Gibbs energy of interaction between the solute molecule and the solvent. The SPT expressions for these quantities are well known and may easily be found in the literature. Interestingly, the isothermal compressibility of water at 1.01325×10^5 Pa (= 1 atm) exhibits a *minimum* value at 46.5 °C, *i.e.* $\beta_{T,1}^{L,*} / \text{Pa}^{-1} = 44.149 \times 10^{-11}$, as compared to $\beta_{T,1}^{L,*} / \text{Pa}^{-1} = 50.885 \times 10^{-11}$ at 0 °C and $\beta_{T,1}^{L,*} / \text{Pa}^{-1} = 49.019 \times 10^{-11}$ at 100 °C, respectively.¹⁰⁰⁾ In conjunction with eq. (70), this quite unusual temperature dependence suggests that, at least for some solutes in water, $V_2^{L\infty}$ vs. T may also show a (shallow) minimum, which behavior has indeed been reported for a few solutions.^{91,101,102)} Additional high-precision work in this area would be desirable. For many liquids, a *self-consistent* set of *effective* Lennard-Jones (6,12) interaction parameters has been provided by Wilhelm and Battino.⁹⁷⁾ The correlational and predictive powers of SPT-based methods can be substantially improved by introducing the concept of *temperature-dependent effective size parameters* as suggested by Wilhelm,¹⁰³⁾ and by Schulze and Prausnitz.¹⁰⁴⁾

At the critical point of the solvent, $V_2^{L\infty}$ of a *volatile* solute *diverges* to $+\infty$.^{86,87,105-112)} The source of this divergence is seen by considering the definition of the solute's partial molar volume

$$V_2^L = V^L + (1 - x_2) \left(\frac{\partial V^L}{\partial x_2} \right)_{T,P} \quad (71)$$

and the thermodynamic identity

$$\begin{aligned} \left(\frac{\partial V^L}{\partial x_2} \right)_{T,P} &= - \left(\frac{\partial V^L}{\partial P} \right)_{T,x_2} \left(\frac{\partial P}{\partial x_2} \right)_{T,V^L} \\ &= V^L \beta_{T,x_2}^L \left(\frac{\partial P}{\partial x_2} \right)_{T,V^L} \end{aligned} \quad (72)$$

Here, β_{T,x_2}^L denotes the isothermal compressibility of the dilute solution with mole fraction x_2 . In the limit $x_2 \rightarrow 0$, β_{T,x_2}^L approaches the isothermal compressibility of the pure solvent, which quantity

diverges strongly at the solvent's critical point. Note, however, that the critical exponent characterizing the divergence behavior depends on the path of approach.

The factor $(\partial P / \partial x_2)_{T,V^L}$ in eq. (72) is a slowly varying function remaining finite at the critical point of the solvent where for $x_2 \rightarrow 0$ it becomes the *Krichevsky parameter*.¹¹³⁻¹¹⁵⁾ This important parameter determines the *sign* and the *amplitude* of the critical divergence of $V_2^{L\infty}$ and other partial molar quantities of the solute at infinite dilution, such as the partial molar enthalpy or the partial molar isobaric heat capacity. It may be evaluated from the *initial* slopes of the critical line of a binary solution, *i.e.* at infinite dilution of the solute:

$$\begin{aligned} A_{\text{Kr}} &= \left(\frac{\partial P}{\partial x_2} \right)_{T,V^L}^{\infty,c} \\ &= \left(\frac{dP}{dx_2} \right)_{\text{cr.l.}}^{\infty,c} - \left(\frac{dP_{s,1}}{dT} \right)^c \left(\frac{dT}{dx_2} \right)_{\text{cr.l.}}^{\infty,c} \end{aligned} \quad (73a)$$

$$= \left[\left(\frac{dP}{dT} \right)_{\text{cr.l.}}^{\infty,c} - \left(\frac{dP_{s,1}}{dT} \right)^c \right] \left(\frac{dT}{dx_2} \right)_{\text{cr.l.}}^{\infty,c} \quad (73b)$$

Here, the superscript c indicates evaluation at the critical point of the pure solvent, and the subscript cr.l. indicates that the derivative is taken along the critical line of the solution. In the case of aqueous solutions, the limiting slope of the vapor pressure curve at the critical temperature of pure water¹¹⁶⁾ is

$$\begin{aligned} \left(dP_{s,1} / dT \right)^c &= 2.68 \times 10^5 \text{ Pa} \cdot \text{K}^{-1}; \text{ note that at the critical point this quantity equals the isochoric thermal pressure coefficient } \gamma_{V,1}^* \left(T_{c,1}, V_1^* = V_{c,1} \right) = \\ &= (\partial P / \partial T)_{V_1^*} = V_{c,1} \text{ of fluid component 1. The} \end{aligned}$$

Krichevsky parameter is *positive* for volatile nonelectrolytes, and *negative* for electrolytes, because adding, say, a small amount of salt to liquid water will lower the pressure. For convenience I list values of A_{Kr} for a few selected *aqueous* nonelectrolyte solutions:¹¹⁵⁾

$A_{\text{Kr}} / \text{MPa} = 163$ for Ar, 148 for Xe, 172 for N₂, 166 for O₂, 162 for CO, 163 for CH₄, 163 for C₂H₆, 154 for C₃H₈, 141 for C₂H₄, 203 for CF₄, and 213 for SF₆.

The uncertainties of these values are appreciable, and depending on the evaluation method used, are expected to amount to about ± 20 MPa.

As concerns the limiting value of the finite partial molar volume of the *solvent*, V_1^L , *contrary* to intuition for some paths it does *not* converge to the critical molar volume of the pure solvent,^{110,112)} $V_{c,1}$. For instance, along the critical line

$$\lim_{x_2 \rightarrow 0} V_1^L = V_{c,1} - RT/A_{Kr} \quad (74)$$

Correlating, and *a fortiori* predicting, partial molar volumes at infinite dilution over large temperature and pressure ranges including the critical region has remained a challenge.¹¹⁷⁻¹²⁰⁾ The major recent contribution by Plyasunov, Shock and O'Connell¹²⁰⁾ presents a corresponding-states approach based on the use of the infinite-dilution solute-solvent direct correlation function integral

$$C_{2,1}^\infty = 1 - \frac{V_2^{L\infty}}{\beta_{T,1}^* RT} \quad (75)$$

With precision gas solubility experiments, the focus is usually on the high-dilution region, with the Henry fugacity being the “object of desire”.^{56,70,71,92,96,102,121-128)} However, with rather few exceptions, precision solubility measurements do *not* cover extended composition ranges, though by now it should be clear that this topic has many interesting facets and intriguing problems. Fortunately, the development of new experimental techniques for vapor-liquid equilibrium measurements in general, and as applied to dilute solutions in particular, continues unabated. Those potentially interested in constructing precision equipment are referred to reviews, for instance, by Wilhelm,⁷⁾ Raal and Ramjugernath,^{129,130)} Richon and de Loos,¹³¹⁾ Dohnal,¹³²⁾ and Maurer and Pérez-Salado Kamps.¹³³⁾

As pointed out above (see also refs. (7) and (57)), the composition dependence of the activity coefficients $\gamma_2^{HL}(T, P_{s,1}, x_2)$ obtained *via* eq. (41) may be represented by any adequate correlating equation. For instance, we may use the simple two-suffix *Margules* equation

$$\ln \gamma_2^{HL}(T, P_{s,1}, x_2) = A(x_1^2 - 1) \quad (76)$$

where $A = A(T, P_{s,1})$ is a solution-specific parameter. Focusing now on dilute solutions at not too high pressures, to an excellent approximation $V_2^L(T, P, x_2)$ may be replaced by a pressure-independent partial molar volume at infinite dilution, $V_2^{L\infty}(T, P_{s,1})$, whence the *Krichevsky-Ilinskaya* equation

$$\ln \left(\frac{\phi_2^V(T, P, y_2) y_2 P}{x_2 h_{2,1}(T, P_{s,1})} \right) - \frac{(P - P_{s,1}) V_2^{L\infty}(T, P_{s,1})}{RT} = A(x_1^2 - 1) \quad (77)$$

is obtained. At high dilution, the inevitable experimental scatter often tends to obscure the composition dependence of activity coefficients, and the use of the approximation $\gamma_2^{HL} = 1$, independent of the composition, may be permissible. This yields the *Krichevsky-Kasarnovsky* equation

$$\ln \left(\frac{\phi_2^V(T, P, y_2) y_2 P}{x_2} \right) = \ln h_{2,1}(T, P_{s,1}) + \frac{(P - P_{s,1}) V_2^{L\infty}(T, P_{s,1})}{RT} \quad (78)$$

Quite often, this equation has been used for the determination of $V_2^{L\infty}$ from gas-solubility measurements at *elevated* pressures: plotting the left-hand side of eq. (78) against the applied pressure $P - P_{s,1}$, the intercept gives the Henry fugacity, and the slope gives $V_2^{L\infty}$. However, at high pressures, the solubility may already be appreciable and hence the underlying assumptions too severe. Partial molar volumes of gases in liquids at infinite dilution obtained this way should always be regarded with caution and may be unreliable.

Using less sophisticated instruments for measurements on dilute solutions at fairly low pressures well below the critical temperature $T_{c,1}$, the Poynting correction may be small compared to the experimental imprecision. When neglected, we obtain

$$\phi_2^V(T, P, y_2) y_2 P = x_2 h_{2,1}(T, P_{s,1}) \quad (79)$$

And finally, assuming $\phi_2^V = 1$ (*i.e.* the vapor phase behaves as an ideal-gas mixture) leads to the *simplest* and *most familiar* equation

$$P_2 \equiv y_2 P = x_2 h_{2,1} \quad (80)$$

which is *Henry's law* as known from many introductory text books and thermodynamics courses.

As already pointed out in connection with the definition eq. (18), Henry's law is a *limiting law*. The composition range over which it is *approximately* valid is known as the “Henry's law region”. Its extent is bounded by the experimental imprecision, which in turn depends on the method and apparatus selected for the

measurements and on the data reduction method used. It is expected, of course, to vary with the chemical nature of the solute and the solvent.^{134,135)}

Starting from the general equilibrium criterion for the solvent (*cf.* also the first term on the right-hand side of eq. (43)), at the *reference pressure* $P_{s,1}(T)$ at mole fraction x_1 in the liquid phase and y_1 in the coexisting vapor phase, the pressure-corrected isothermal-isobaric liquid-phase activity coefficient for the solvent, which is based on the Lewis-Randall rule, is given by

$$\gamma_1^{\text{LR}}(T, P_{s,1}, x_1) = \frac{\phi_1^{\text{V}}(T, P, y_1) y_1 P}{x_1 P_{s,1} \phi_{s,1}^{\text{V}*}} \exp \left\{ - \int_{P_{s,1}}^P \frac{V_1^{\text{L}}(T, P, x_1)}{RT} dP \right\} \quad (81)$$

A series of approximations may now be applied, quite analogous to those applied above to eq. (41). Again, when the focus is on solutions at not too high pressures, to an excellent approximation $V_1^{\text{L}}(T, P, x_1)$ may be replaced by its value at $P_{s,1}$ and assumed to be independent of pressure. Thus,

$$\ln \left(\frac{\phi_1^{\text{V}}(T, P, y_1) y_1 P}{x_1 P_{s,1} \phi_{s,1}^{\text{V}*}} \right) - \frac{(P - P_{s,1}) V_1^{\text{L}}(T, P_{s,1}, x_1)}{RT} = \ln \gamma_1^{\text{LR}}(T, P_{s,1}, x_1) \quad (82)$$

For dilute solutions, that is at mole fractions x_1 *very* close to 1, the approximation $V_1^{\text{L}}(T, P_{s,1}, x_1) \cong V_{1,s}^{\text{L}*}$ may be used. Note that the two-suffix Margules equation for the solvent reads

$$\ln \gamma_1^{\text{LR}}(T, P_{s,1}, x_1) = A x_2^2 \quad (83)$$

For conventional VLE data reduction at low to moderate pressures and comprising the *entire* composition range, usually more complex correlating equations for the LR-based activity coefficients are needed.⁶⁾ Two-parameter equations of practical importance are, for instance, the two-parameter (three-suffix) Margules equation, the van Laar equation and the Wilson equation. Frequently the Poynting correction terms are insignificant compared to the experimental imprecision, and may thus be neglected; and at low pressures, the fugacity coefficients are usually of order unity, whence with the additional assumption that the vapor phase behaves ideally, eq. (82) becomes

$$y_1 P = \gamma_1^{\text{LR}} x_1 P_{s,1} \quad (84)$$

The activity coefficient γ_1^{LR} in eq. (84) characterizes non-ideal behavior in the liquid solution and depends only on composition and temperature. For an ideal solution $\gamma_1^{\text{LR}} = 1$, and eq. (84) reduces to *Raoult's law*

$$P_1 = y_1 P = x_1 P_{s,1} \quad (85)$$

Once experimental Henry fugacities for a specific binary solution have been determined over a reasonably large temperature range (but not too close to the critical temperature of the solvent, see below), the question arises as to their most satisfactory mathematical representation as a function of temperature. Depending on the choice of variables, that is T or $1/T$, for expanding the enthalpy of solution, either the *Clarke-Glew* equation¹³⁶⁾

$$\ln \left[h_{2,1}(T, P_{s,1}) / \text{Pa} \right] = A_0 + A_1 (T/\text{K})^{-1} + A_2 \ln(T/\text{K}) + \sum_{i=3}^n A_i (T/\text{K})^{i-2} \quad (86)$$

or the *Benson-Krause* (BK) equation¹³⁷⁾

$$\ln \left[h_{2,1}(T, P_{s,1}) / \text{Pa} \right] = \sum_{i=0}^m a_i (T/\text{K})^{-i} \quad (87)$$

is obtained. On the basis of the ability to fit high-precision Henry fugacity data over fairly large temperature ranges, and of simplicity, the BK power series in $1/T$ appears to be superior.^{7,70,71,102,126,137)}

At this juncture I would like to emphasize that the frequently found sweeping statement “the solubility of a gas in a liquid decreases with increasing temperature” is misleading/incorrect when the entire liquid range between the triple point and the critical point of the solvent is considered. For quite a few systems, the following behavior is *well documented*:^{6,7,57,123,138)} at low temperatures starting at the solvent triple point,

$h_{2,1}(T, P_{s,1})$ typically *increases* with increasing temperature, passes through a *maximum*, and then *decreases* towards its limiting value at the solvent's critical point as indicated by eq. (29), that is towards $\phi_2^{\text{V}\infty}(T_{c,1}, P_{c,1}) P_{c,1}$. An example is provided by

Fig.3, where $\ln \left[h_{2,1}(T, P_{s,1}) / \text{GPa} \right]$ for methane dissolved in liquid water is plotted against temperature.^{70,123)} This system plays an important role in discussions of hydrophobicity. While the Henry fugacity remains *finite* at $T_{c,1}$, see eq. (29), for *volatile* solutes the

limiting value of the temperature derivative of $\ln h_{2,1}(T, P_{s,1})$ diverges to $-\infty$.^{139,140)}

$$\lim_{\substack{T \rightarrow T_{c,1} \\ P \rightarrow P_{c,1}}} \frac{d \ln [h_{2,1}(T, P_{s,1}) / \text{Pa}]}{dT} = -\infty \quad (88)$$

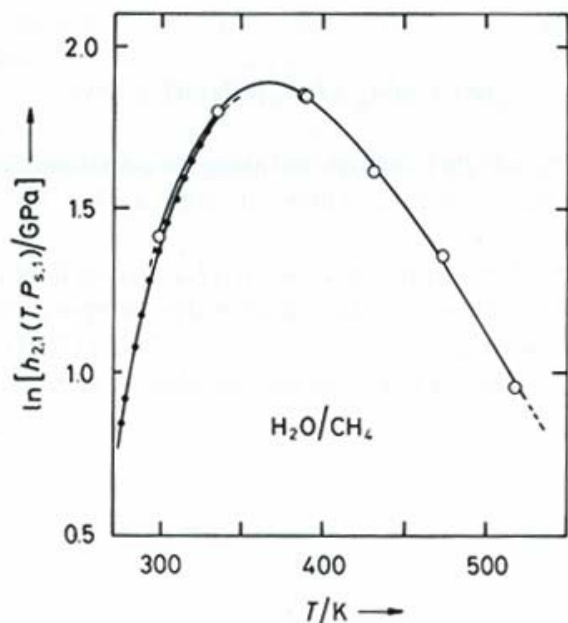


Fig.3 Plot of $\ln [h_{2,1}(T, P_{s,1}) / \text{GPa}]$ against temperature T for methane dissolved in liquid water. $h_{2,1}(T, P_{s,1})$ is the Henry fugacity (Henry's constant) at temperature T and pressure $P_{s,1}(T)$:

•, experimental results of Rettich *et al.*⁷⁰⁾: the average percentage deviation of $h_{2,1}$ from the value calculated via the correlating BK function, eq. (87), is *ca.* $\pm 0.05\%$; \circ , experimental results of Crovetto *et al.*¹²³⁾: the average percentage deviation of $h_{2,1}$ from the value calculated via the correlating BK function, eq. (87), is *ca.* $\pm 2\%$. The limiting value of $h_{2,1}$ as $T \rightarrow T_{c,1}$ is finite and given by eq. (29), the limiting slope of the curve is $-\infty$, see eq. (88).

During the last 20 years or so, several equations for presenting the temperature dependence of the Henry fugacity between the *triple point* temperature and the *critical* temperature of the solvent were developed, the main objective being the incorporation of the thermodynamically correct limiting behavior indicated by eqs. (29) and (88). The solubility-data base predominantly comprises aqueous solutions. Here, just a

few contributions will be presented, and for details I refer to ref. (7) and the original literature. Krause and Benson¹²⁶⁾ suggest

$$\begin{aligned} T_{r,1}^2 \ln [h_{2,1}(T, P_{s,1}) / \text{Pa}] \\ = b_0 T_{r,1}^2 + b_1 (1 - T_{r,1})^{1/3} + b_2 (1 - T_{r,1})^{2/3} \end{aligned} \quad (89)$$

where $T_{r,1} = T/T_{c,1}$. This correlation shows a divergence with a critical exponent close to the expected value.^{112,140-142)} Incorporating theoretical results on the temperature dependence of $h_{2,1}(T, P_{s,1})$ near the critical point of the solvent, the new correlation of Harvey¹³⁸⁾

$$\begin{aligned} \ln [h_{2,1}(T, P_{s,1}) / P_{s,1}] \\ = A / T_{r,1} + B (1 - T_{r,1})^{0.355} / T_{r,1} + C \exp(1 - T_{r,1}) T_{r,1}^{-0.41} \end{aligned} \quad (90)$$

covers the temperature range from 0 °C to near the critical point of water quite satisfactorily, though partial molar volumes at infinite dilution derived therefrom are overestimated in the critical region.^{86,87,118,143,144)} It is, however, *not* restricted to a specific solvent, and has been tested with aqueous solutions as well as with several solutions involving hexadecane as solvent. Note that the exponent 0.355 represents an “effective” critical exponent, as compared to the theoretical value $\beta = 0.326 \pm 0.002$.¹¹²⁾

Until the mid-eighties, high-precision measurements of Henry fugacities over temperature ranges large enough to permit reliable *van't Hoff-type* data analysis constituted the only source of information on *partial molar enthalpy changes on solution* $\Delta H_2^\infty(T, P_{s,1})$, see eq. (45), and *a fortiori* on *partial molar heat capacity changes on solution* $\Delta C_{P,2}^\infty(T, P_{s,1})$, see eq. (47). Since the experimental Henry fugacities at different temperatures refer to different saturation pressures $P_{s,1} = P_{s,1}(T)$, eqs. (45) and (47) have to be augmented accordingly, as detailed by Wilhelm^{7,8,57,70,71,73,76,102,145)} and in other references. For instance, selecting a conventional BK-type fitting equation, eq. (87), to represent the temperature dependence of the $h_{2,1}(T, P_{s,1})$ data, we obtain

$$\frac{\Delta H_2^\infty(T, P_{s,1})}{RT} = \sum_{i=1}^m i a_i (T/K)^{-i} + \frac{V_2^{L\infty}}{R} \frac{dP_{s,1}}{dT} \quad (91)$$

$$\begin{aligned} \frac{\Delta C_{P,2}^\infty(T, P_{s,1})}{R} &= - \sum_{i=2}^m i(i-1) a_i (T/K)^{-i} + 2 \frac{T}{R} \frac{dV_2^{L\infty}}{dT} \frac{dP_{s,1}}{dT} \\ &\quad - \frac{T}{R} \left(\frac{\partial V_2^{L\infty}}{\partial P} \right)_T \left(\frac{dP_{s,1}}{dT} \right)^2 + \frac{TV_2^{L\infty}}{R} \frac{d^2 P_{s,1}}{dT^2} \end{aligned} \quad (92)$$

The additional terms on the right side of the summation terms in eqs. (91) and (92), containing $V_2^{L\infty}$ and its derivatives with respect to T and P and so forth, are referred to in the literature^{126,146)} as *Wilhelm terms*. For aqueous solutions, say, of the rare gases below 100 °C, their contributions are small,¹²⁶⁾ usually smaller than the experimental error associated with current precision measurements.

As discussed above, see eqs. (71) and (72), the partial molar volume of a volatile solute at infinite dilution in a liquid solvent *diverges* to $+\infty$ at the critical point of the solvent, and so will the partial molar enthalpy at infinite dilution, $H_2^{L\infty}$. Its limiting behavior near the solvent's critical point is given by^{110,112,113)}

$$\begin{aligned} H_2^{L\infty} &\approx TV^{L\infty} \beta_{T,x_2}^L \gamma_{V,x_2}^L A_{Kr} \\ &= TV^{L\infty} \alpha_{P,x_2}^L A_{Kr}, \quad \text{as } x_2 \rightarrow 0, \end{aligned} \quad (93)$$

where γ_{V,x_2}^L is the isochoric thermal pressure coefficient of the dilute solution with mole fraction x_2 , and α_{P,x_2}^L is its isobaric expansivity. The isochoric thermal pressure coefficient $\gamma_V = \alpha_P / \beta_T$ remains *finite* at the critical point. Again, the Krichevsky parameter, in conjunction with the indicated solvent properties (molar volume, compressibility or expansivity), governs the near-critical divergence behavior of the partial molar enthalpy at infinite dilution. The partial molar isobaric heat capacity at infinite dilution, $C_{P,2}^{L\infty} = \left(\partial H_2^{L\infty} / \partial T \right)_P$, diverges in a more complex manner and much stronger^{110,112,148-150)} than

either $V_2^{L\infty}$ or $H_2^{L\infty}$. In fact, the experimental results on the *apparent* molar heat capacities of aqueous argon, xenon, methane and eth

ene obtained by Wood's group¹⁴⁸⁻¹⁵⁰⁾ all show a quite similar, remarkable behavior: for pressures of about 28 MPa, the *apparent* molar heat capacity $C_{P,2,app} / \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ of, say, methane¹⁵⁰⁾ initially *decreases* with increasing temperature from *ca.* 245 at 298.15 K to a *minimum* value of 194 at *ca.* 450 K, then *increases* to a *very sharp maximum* value of more than +20 000 at about 663 K, then *decreases* to a *very sharp minimum* value below -20 000 at about 670 K, to reach -1035 at 703.8 K, the upper limit of the experimental temperature range. In a binary solution, the *apparent* molar quantity $M_{2,app}$ of solute 2 dissolved in solvent 1 is defined by

$$M_{2,app} = \frac{nM - n_1 M_1^*}{n_2} \quad (94)$$

where the molar quantity referring to the solution is M , M_1^* is the molar quantity referring to the pure solvent, and n_1 and n_2 are the amounts of substance of solvent and solute, respectively. Evidently, with M_2 denoting a *partial* molar quantity of the solute,

$$M_2 = M_{2,app} + n_2 \left(\frac{\partial M_{2,app}}{\partial n_2} \right)_{T,P} \quad (95)$$

and for $n_2 \rightarrow 0$, *i.e.* at infinite dilution,

$$M_{2,app} = M_2^\infty.$$

The maximum and the minimum of $C_{P,2}^\infty$ vs. T in the critical region can be predicted from Wheeler's lattice gas model.¹⁰⁷⁾ The partial molar isobaric heat capacity $C_{P,2}^\infty$ at the critical pressure $P_{c,1}$ will exhibit a discontinuity at $T_{c,1}$, that is to say $C_{P,2}^\infty$ will go to *positive* infinity if $T_{c,1}$ is approached from lower temperatures $T < T_{c,1}$, and to *negative* infinity if $T_{c,1}$ is approached from higher temperatures $T > T_{c,1}$. At $P > P_{c,1}$, the curve $C_{P,2}^\infty$ vs. T is continuous. For the *nonvolatile* solute boric acid,¹⁵¹⁾ $C_{P,2,app} / \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ of $\text{H}_3\text{BO}_3(\text{aq})$ shows, as expected, an *opposite* temperature dependence: in the critical region, a sharp minimum comes first (below $T_{c,1}$), which is then followed by a sharp maximum (above $T_{c,1}$).

Note that in contrast to the gaseous solutes, in the neighborhood of the critical point of water, the apparent molar volume of $\text{H}_3\text{BO}_3(\text{aq})$ exhibits a *sharp minimum*: at $P = 28 \text{ MPa}$ and *ca.* 666 K , the concentration-corrected $V_2^{\text{L}\infty}$ amounts to $-800 \text{ cm}^3 \cdot \text{mol}^{-1}$.

Undoubtedly, heat capacities are highly important thermophysical quantities from both a practical and a theoretical point of view.^{27,152-154} Since the heat capacity at constant pressure is related to the second derivative of the Gibbs energy with respect to temperature,

$$C_P = -T \left(\partial^2 G / \partial T^2 \right)_P \quad (96)$$

it is a particularly sensitive property to be used (I) for comparing different methods of data treatment, and (II) for model evaluation and improvement by comparing experimental data with theoretical results.

Direct calorimetric determinations of the high-dilution partial molar enthalpy change on solution of a gas in a liquid, $\Delta H_2^\infty(T, P_{\text{s},1})$, have been carried out

by only a very limited number of researchers,¹⁵⁵⁻¹⁶⁵ essentially because of the experimental difficulties associated with accurately measuring very small heat effects in very dilute solutions (typically, mole fraction solubilities at ambient temperatures and 0.1 MPa gas pressure are about 10^{-4} to 10^{-5}). The micro-calorimeters used were developed^{155,156} in the Thermochemistry Laboratory of the University of Lund, Sweden, and in the Chemistry Department of the University of Colorado in Boulder, CO, USA, respectively. *A fortiori*, because of the formidable experimental difficulties encountered in the case of *direct* measurements of heat capacities of gases dissolved in water at very low concentration, there exist only *seven sets* of such data, all originating from the laboratory of R. H. Wood at the University of Delaware in Newark, DE, USA. Wood and collaborators determined the *apparent* molar heat capacities at low concentrations of four inert solutes in water: of aqueous argon,^{148,149} xenon,¹⁴⁹ methane¹⁵⁰ and ethene,¹⁴⁹ and of aqueous CO_2 , H_2S and NH_3 .¹⁵⁰ The sophisticatedly constructed flow calorimeters may be used over very large temperature ranges well into the supercritical region up to $T \approx 720 \text{ K}$. Although these calorimetric measurements were all performed at elevated pressures between, roughly, 17 MPa and 32 MPa , the mole fractions of the dissolved gases are small enough to make the apparent molar heat capacities to a good approximation *equal* to the partial molar heat capacities at infinite dilution, $C_{P,2}^\infty(T, P)$, within experimental error (at temperatures below *ca.* 500 K). At temperatures

well below $T_{\text{c},1}$, $C_{P,2}^{\text{L}\infty}(T, P) \approx C_{P,2}^{\text{L}\infty}(T, P_{\text{s},1})$ is a reasonable approximation, and subtraction of the molar isobaric heat capacity of the pure solute in the perfect gas state¹⁶⁶ yields the partial molar heat capacity change on solution (see above):

$$\begin{aligned} C_{P,2}^{\text{L}\infty}(T, P_{\text{s},1}) - C_{P,2}^{\text{pg}*}(T) \\ = \Delta C_{P,2}^\infty(T, P_{\text{s},1}) \end{aligned} \quad (97)$$

This quantity may be compared to results obtained by van't Hoff analysis of high-precision solubility data, for instance *via* eq. (92). Clearly, much more experimental calorimetric work on simple aqueous solutions at high dilution would be desirable.

When measured over a sufficiently large temperature range, calorimetry-based results on $\Delta H_2^\infty(T, P_{\text{s},1})$ may in turn be used to obtain

$$\begin{aligned} \Delta C_{P,2}^\infty(T, P_{\text{s},1}) = \frac{d\Delta H_2^\infty(T, P_{\text{s},1})}{dT} \\ - \left[V_2^{\text{L}\infty} - T \left(\frac{\partial V_2^{\text{L}\infty}}{\partial T} \right)_P \right] \frac{dP_{\text{s},1}}{dT} \end{aligned} \quad (98)$$

In the temperature regions investigated so far, the second term on the right-hand side of eq. (98) is *much* smaller than the experimental imprecision, whence the approximate relation

$$\Delta C_{P,2}^\infty(T, P_{\text{s},1}) \approx \frac{d\Delta H_2^\infty(T, P_{\text{s},1})}{dT} \quad (99)$$

is entirely satisfactory. It was used by the group in Boulder as well as by the group in Lund.

The large partial molar heat capacity changes $\Delta C_{P,2}^\infty(T, P_{\text{s},1})$ observed when nonpolar molecules are dissolved in *water at ambient* temperature are widely regarded as *the signature of hydrophobicity*, and have frequently been connected with some unspecified ordering of the water molecules around the solute (exemplified by the famous “iceberg model” of Frank and Evans¹⁶⁷). The picture that emerges from structural studies, using the method of neutron diffraction and isotopic substitution, on aqueous solutions of methane¹⁶⁸ is the following: the solute is surrounded by a relatively strong first coordination shell containing about 19 water molecules which are oriented tangentially to the CH_4 molecule, with no evidence of a second coordination shell. There is reasonably good agreement between these observations and those deduced from theoretical model

calculations and computer simulations,¹⁶⁹⁾ though the interaction between the apolar molecules and water appears to be much shorter-ranged than suggested by the model calculations. Neutron diffraction experiments have also been reported for the prototypical hydrophobe argon dissolved in water¹⁷⁰⁻¹⁷²⁾, including measurements at elevated pressures and supercritical conditions. A thorough investigation of the hydrophobic hydration of krypton in liquid water *via* EXAFS (extended X-ray absorption fine structure) spectroscopy over extended temperature and pressure ranges (up to 70 MPa), including a comparison with the *solid clathrate*¹⁷³⁾ structure, is due to Bowron *et al.*¹⁷⁴⁻¹⁷⁷⁾ The coordination number of krypton in water is *significantly different* from that in the solid Kr/H₂O clathrate phase, a result which is critically discussed and compared to *ab initio* molecular dynamics results by Ashbaugh *et al.*¹⁷⁸⁾ and by LaViolette *et al.*¹⁷⁹⁾ In particular, they point out that the revised scaled particle model^{180,181)} is the most successful theory of hydrophobicity for spherical solutes because it incorporates *experimental* information without postulating a clathrate structure. The simpler SPT version of Pierotti,^{95,182)} as applied by Wilhelm and Battino in 1972,⁹⁸⁾ already indicates clearly that the partial molar entropy of cavity formation in water, $S_{\text{cav},2}$, places water apart from all the other solvents studied: at ambient temperatures, (I) $S_{\text{cav},2}$ is *much more negative* in water for all solute hard sphere diameters σ_2 considered⁹⁷⁾ (2.63×10^{-8} cm (He) to 5.51×10^{-8} cm (SF₆)), and (II) $dS_{\text{cav},2}/d\sigma_2$ is *much more negative* in water than in other solvents. The view, that the loss of entropy associated with the accommodation of a small hydrophobe in liquid water is a consequence of creating an appropriate cavity rather than the result of creating ordered clathrate-like structures, is strongly supported by a recent neutron diffraction study of a methane-water solution,¹⁸³⁾ and by molecular dynamics simulations of aqueous solutions of various hydrophobes over a wide concentration range.¹⁸⁴⁾ At small solute concentrations, in the vicinity of the solute, only a moderate water reorientational slowdown (compared to bulk water) is found: the factor is below 2, in accord with NMR experiments,^{185,186)} and no dynamic “icebergs” are formed. Nevertheless, despite substantial progress in this field, many issues remain unresolved and/or controversial, and, of course, new viewpoints emerge. Some are related to the pure solvent itself, while some are related to the ways solutes (small and large, hydrophobes and hydrophiles, proteins, *etc.*) interact with liquid water.^{24,53,187-201)}

Comparing high-precision calorimetric results for $\Delta H_2^\infty(T, P_{s,1})$ and $\Delta C_{P,2}^\infty(T, P_{s,1})$ with van't Hoff-derived enthalpy changes on solution and heat capacity changes on solution, which are obtained by differentiating $\ln h_{2,1}$ *once* or *twice*, respectively, with respect to temperature, constitutes a severe quality test of solubility data. Recently, Wilhelm^{7,73)} and Wilhelm and Battino¹⁴⁵⁾ presented comprehensive compilations as well as such comparisons, at $T = 298.15$ K and $P_{s,1}(298.15 \text{ K}) = 3.1691$ kPa, for many gases dissolved in liquid water (in a few instances the solutes were, in fact, subcritical vapors). In nearly all cases, agreement between these two approaches was entirely satisfactory, *i.e.* it was usually within the combined experimental errors. What a credit to experimental ingenuity and to the skills of solution thermodynamicists!

Concluding Remarks and Outlook

Chemical thermodynamics of solutions in general, and of aqueous solutions in particular, continue to be exciting, developing fields which, combined with advances in the statistical-mechanical treatment of solutions and increasingly sophisticated computer simulations, provide new insights and stimulating connections at the microscopic, mesoscopic and macroscopic level. The major driving forces for progress in instrumentation^{7,57,202,203)} are the desire to increase the applicability area (larger temperature and pressure ranges, ever smaller concentrations, *etc.*), to increase precision and accuracy, to improve on the speed of measurements, and to facilitate application and data transfer. In this review, I have tried first to concisely present the thermodynamic formalism relevant for the study of dilute liquid solutions of nonelectrolytes, and second, to cover the most important aspects of its practical implementation, indicating areas where more and/or more detailed experimental work would be desirable. Throughout, the emphasis was on *aqueous* solutions of supercritical solutes. In particular, three closely related areas have been dealt with prominently:

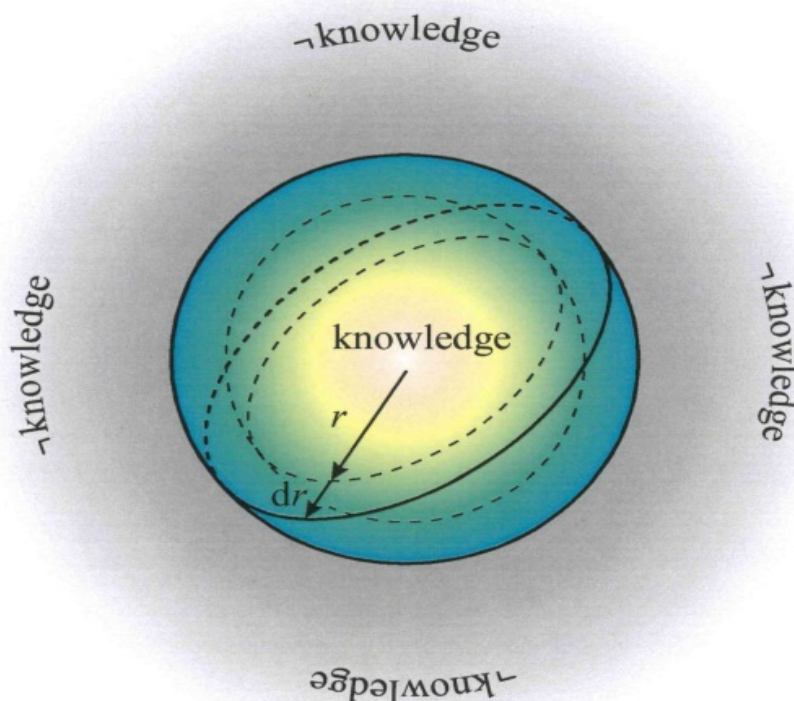
- discussion of solution behavior in terms of the *Henry fugacity* $h_{2,1}(T, P)$ (also known as Henry's law constant) and related quantities, such as *activity coefficients* and *fugacity coefficients*, and exposing some frequently encountered misconceptions;
- reporting on the equivalency of results for caloric quantities (*e.g.* ΔH_2^∞ and $\Delta C_{P,2}^\infty$) derived from solubility measurements *via van't Hoff analysis* with those measured directly with *calorimeters*;

- indication of the most important ramifications of solubility-related topics into neighboring fields of science, in particular into biophysical chemistry.

The first two essentially present the state of the art to the (potential) experimentalist, pointing out unresolved questions and missing experimental data useful for further progress. The third area simply reflects

my conviction that crossdisciplinary fundamental research has always been a potent stimulus for advances in science as well as in technological innovation. This is particularly true for research on the solubility of gases in liquid water, which topic has greatly contributed to our understanding and appreciation of hydrophobic effects, which are thought to play an important role in biology.

With every scientific problem solved, new problems are perceived to exist!



Optimistic interpretation

***Increase of knowledge* $dV = 4\pi r^2 dr$**

***Increase of ¬knowledge* $dA = 8\pi r dr$**

→ Research produces knowledge at a greater rate than ¬knowledge!

Fig.4 The sphere of knowledge suspended in the universe of non-knowledge (symbolized here by ¬knowledge), according to J. Mittelstraß,²⁰⁵⁾ who was stimulated by ideas expressed by Blaise Pascal (1623, Clermont – 1662, Paris).

Note, however, that in biochemical processes, such as protein folding and protein-protein interaction, *hydrophilic effects* may be more important than hydrophobic effects.¹⁹⁹⁻²⁰¹⁾ A rich research field lies ahead, and the increasing number of investigations with a strong biophysical and/or biomedical flavor is thus not surprising.

Studies on solubility in general, and on solubility in water, have come a long way. The field has grown too big to be covered in a modest review article, but for the subsections treated above I hope to have succeeded in providing a feeling for their scope and potential. Related to this practical aspect is a *fundamental philosophical* question: *Is there an end to the age of scientific discovery?* Russell Stannard²⁰⁴⁾ answers in the affirmative (essentially based on practical considerations). A somewhat *different* position is advocated by Jürgen Mittelstraß. One of the recent *Austrian Science Discussions* (Österreichische Wissenschaftstage), organized by the Österreichische Forschungsgemeinschaft, was devoted to the quite general topic of *Image and Reality in Science* (Virtualität und Realität. Bild und Wirklichkeit in den Naturwissenschaften). Of particular relevance for the question raised above is the seminal contribution of Jürgen Mittelstraß, *Thinking the Unthinkable*, where he discussed the so-called *sphere of knowledge* suspended in a universe of *non-knowledge*, see **Fig.4**. This concept is based on the fact that with every scientific problem solved, new problems emerge. Though scientific research continuously exposes us to more and more *non-knowledge*, which is proportional to the sphere's surface, the research-generated knowledge, *optimistically* represented by the sphere's volume, grows faster. According to Mittelstraß, independent of the interpretation selected, there are *no* limits to scientific discovery.

Whatever the arguments, I find the statement by Gilbert Newton Lewis (1875–1946) on the *practical* philosophy of science most appropriate:

The scientist is a practical man and his are practical aims. He does not seek the ultimate but the proximate. He does not speak of the last analysis but rather of the next approximation....On the whole, he is satisfied with his work, for while science may never be wholly right it certainly is never wholly wrong; and it seems to be improving from decade to decade.

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