

Chemical Thermodynamics: A Journey of Many Vistas

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Abstract Chemical thermodynamics is of central importance in chemistry, physics, the biosciences and engineering. It is a highly formalized scientific discipline of enormous generality, providing a mathematical framework of equations (and a few inequalities), which yields exact relations between macroscopically observable thermodynamic equilibrium properties of matter and restricts the course of any natural process. While these aspects alone are already of the greatest value for practical applications, in conjunction with judiciously selected molecular-based models of material behavior, that is to say by using concepts from statistical mechanics, experimentally determined thermodynamic quantities contribute decisively towards a better understanding of molecular interactions and hence of real macroscopic systems. A plenary lecture affords the lecturer an opportunity to survey a *few* reasonably large sub-areas of the fields he works/worked in and to reflect on them from the perspective of many years of research. The general subject I selected for this review, i.e. *chemical thermodynamics* of liquid nonelectrolytes (pure or mixed), is vast. Over the last decades, the field's impressive growth has been stimulated by the continuously increasing need for thermophysical property data and phase equilibrium data in the applied sciences, and it has greatly profited by advances in experimental techniques, by advances in the theory of liquids in general, and by advances in computer simulations of reasonably realistic model systems in particular. Specifically, I shall focus on just three topics of increasing complexity: (1) *heat capacities* and related quantities of fairly simple molecular liquids, predominantly at or near orthobaric conditions; (2) chemical thermodynamics of binary liquid mixtures containing one *strongly dipolar* aprotic component; (3) caloric properties of dilute solutions of nonelectrolytes, with emphasis on properties of *aqueous solutions at infinite dilution* (which are of importance in biophysical chemistry).

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Every novel is a debtor to Homer. Every carpenter who shaves with a fore-plane borrows the genius of a forgotten inventor.

Ralph Waldo Emerson in: *Representative Men. Seven Lectures: I. Uses of Great Men*, pp. 7–38, The Riverside Press, Cambridge, Mass., U.S.A. (1893)

1 Introduction

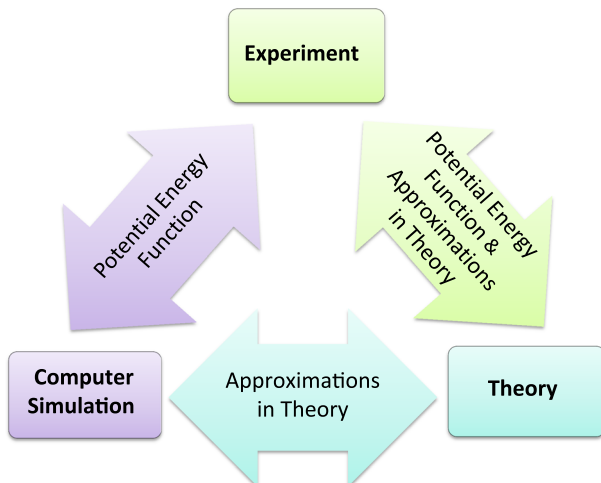
Taking advantage of being a plenary lecturer at the 20th Ulm-Freiberger Calorimetry Conference in Freiberg, Saxony, the German analogue to the Calorimetry Conference Series in the USA, I will present some areas of chemical thermodynamics of liquid non-electrolyte systems (either pure or mixed) which are representative of my long-time research interests in liquid state physical chemistry. In fact, “*back to the roots!*” and “*forwards to new frontiers!*” will be the leading mottos. While the title of this lecture is intentionally quite general, the focus will be on just *three* topics:

- Heat capacities and related properties of fairly simple molecular liquids, predominantly at, or near, saturation conditions [1–9].
- Caloric properties of binary liquid mixtures containing one strongly polar aprotic component [10–17].
- Caloric properties of dilute solutions of nonelectrolytes, with emphasis on high-dilution properties of aqueous solutions [18–34].

All three topics are more complex and less understood than might be supposed. In order to keep the review to a reasonable size, the coverage throughout is necessarily brief. For the omission of many interesting papers I would like to offer my apologies in advance: my choices for references are illustrative and not comprehensive.

Thermodynamics rests on an experiment-based axiomatic fundament. Experiments, together with theory and computer simulation, are the pillars of science, and Fig. 1 (the “knowledge triangle” [35]) indicates what may be learned from a comparison of respective results under idealized conditions. It may be used to illustrate the process of *inductive* reasoning in science, also known informally as *bottom-up* reasoning, which amplifies and generalizes our experimental observations, eventually leading to theories and new knowledge. In contradistinction, *deduction*, informally known as *top-down* reasoning, orders and explicates already existing knowledge, thereby leading to predictions which may be corroborated by experiment, or falsified (see Popper [36]). As pointed out by Dyson [37], “*Science is not a collection of truths. It is a continuing exploration of mysteries...an unending argument between a great multitude of voices.*” The most popular heuristic principle to guide our hypothesis testing in these arguments is known as *Occam’s Razor*, named after the Franciscan friar William of Ockham (England, ca. 1285–1349). Also called the principle of parsimony or the principle of the economy of thought, it states that the number of assumptions to be incorporated into an adequate model should be kept minimal. While this is the preferred approach, the model with the fewest assumptions may

Fig. 1 The three pillars of science: experiment, theory and computer simulation. The double-headed arrows indicate possible, fundamentally important comparisons that will contribute to a deeper understanding of the role of approximations concerning interaction energies and theoretical models [6, 27]



turn out to be wrong. More elaborate versions of Occam's razor have been introduced by modern scientists, and for in-depth philosophical discussions see, for instance, Mach [38], Popper [36], Swinburne [39], Katz [40], and Sober [41].

In the three topics I shall present in this review, the formal framework of chemical thermodynamics has been augmented by simple ideas from molecular theory, effectively anchoring them in the field of *molecular thermodynamics*. This term was coined by Prausnitz [42, 43] more than four decades ago. It is a field of great academic fascination, an indispensable part of physical chemistry as well as of chemical engineering. The impressive growth of molecular thermodynamics has been stimulated by the continuously increasing need for thermodynamic property data and phase equilibrium data [44–62] in the applied sciences, and has greatly profited by unprecedented advances in experimental techniques [63–71], by advances in the theory of liquids in general [72–91], and by advances in computer simulations of reasonably realistic model systems [92–102].

2 Heat Capacities and Related Properties of Pure Liquids

Heat capacities belong to the most important thermodynamic/thermophysical properties, this fact has been amply documented [6, 7, 9, 71, 103, 104]. For PVT systems, where P denotes the pressure, V the molar volume, and T the thermodynamic temperature, there are three liquid-state heat capacities in common use (in the following, for the sake of brevity and whenever unambiguously possible, the descriptive superscript L for liquid, the superscript V for vapor, and the superscript asterisk (*) indicating a pure-substance property will be omitted). The molar heat capacity at *constant volume* C_V , also known as the molar isochoric heat capacity, is defined by

$$C_V \equiv (\partial U / \partial T)_V = T(\partial S / \partial T)_V = -T(\partial^2 F / \partial T^2)_V, \quad (1)$$

the molar heat capacity at *constant pressure* C_P , also known as the molar isobaric heat capacity, is defined by

$$C_P \equiv (\partial H / \partial T)_P = T(\partial S / \partial T)_P = -T(\partial^2 G / \partial T^2)_P, \quad (2)$$

and the molar heat capacity at *saturation* C_σ of a liquid maintained at all temperatures in *equilibrium* with an infinitesimally small amount of vapor at the corresponding *vapor pressure* $P_\sigma(T)$ is defined by [76]

$$C_\sigma \equiv T(\partial S/\partial T)_\sigma. \quad (3)$$

This heat capacity is more closely related to conventional adiabatic calorimetry, where measurements are performed on samples consisting of saturated liquid in equilibrium with a small amount of its vapor enclosed in a *constant-volume* vessel [76, 103, 105]. Here, all the symbols have their usual significance, i.e. U is the molar internal energy, H is the molar enthalpy, S is the molar entropy, F is the molar Helmholtz energy, and G is the molar Gibbs energy. The corresponding extensive quantities are obtained through multiplication with the total amount of substance $n = m/M_m$, where m is the mass of the liquid, and M_m is its molar mass [106, 107]. Note that henceforward derivatives along the *saturation* (or *orthobaric*) curve will be indicated by the subscript σ .

C_p and C_σ are related as follows [9, 76, 103, 104]:

$$C_\sigma = C_p - TV\alpha_p\gamma_\sigma, \quad (4)$$

$$= C_p - TV(\alpha_p - \alpha_\sigma)\gamma_V, \quad (5)$$

$$= C_p - V\alpha_p\Delta_{\text{vap}}H/\Delta_{\text{vap}}V. \quad (6)$$

Here, $V = V^L(T, P_\sigma(T))$ is the molar volume of the liquid at saturation, $\gamma_\sigma \equiv (\partial P/\partial T)_\sigma$ denotes the slope of the vapor–pressure curve, i.e. dP_σ/dT , and

$$\alpha_p \equiv V^{-1}(\partial V/\partial T)_p = -\rho^{-1}(\partial \rho/\partial T)_p. \quad (7)$$

is the *isobaric expansivity* of the liquid, with $\rho \equiv M_m/V$ being the mass density. For the expansivity α_σ of a liquid remaining in contact with its vapor equilibrium phase we obtain

$$\alpha_\sigma \equiv V^{-1}(\partial V/\partial T)_\sigma = \alpha_p - \beta_T\gamma_\sigma, \quad (8)$$

$$= \alpha_p(1 - \gamma_\sigma/\gamma_V), \quad (9)$$

where

$$\beta_T \equiv -V^{-1}(\partial V/\partial P)_T = \rho^{-1}(\partial \rho/\partial P)_T \quad (10)$$

denotes the *isothermal compressibility*, and

$$\gamma_V \equiv (\partial P/\partial T)_V = \alpha_p/\beta_T \quad (11)$$

is the *isochoric thermal pressure coefficient*. Below the normal boiling point the difference $\alpha_p^L - \alpha_\sigma^L$ is usually very small.

$$\gamma_V^L - \gamma_\sigma = \alpha_\sigma^L/\beta_T^L, \quad (12)$$

and at the critical point, which is characterized by the critical temperature T_c , the critical pressure P_c , and the critical molar volume V_c

$$\gamma_V^L(T_c, P_c) = \gamma_V^V(T_c, P_c) = \gamma_\sigma(T_c) \quad (13)$$

remain *finite*. Here, the superscript V indicates the vapor phase. Equation 6 is obtained with the help of the exact Clapeyron equation

$$\gamma_\sigma = \frac{\Delta_{\text{vap}}H}{T\Delta_{\text{vap}}V} \tag{14}$$

where $\Delta_{\text{vap}}H$ is the molar enthalpy of vaporization, and $\Delta_{\text{vap}}V \equiv V^V(T, P_\sigma(T)) - V^L(T, P_\sigma(T))$ is the volume change on vaporization, with $V^V(T, P_\sigma(T))$ denoting the molar volume of the vapor at saturation.

Neither C_P nor C_σ is equal to the change of the enthalpy of the liquid with temperature along the saturation curve, which quantity is given by [9, 76, 103, 104]

$$\left(\frac{\partial H}{\partial T}\right)_\sigma = C_P + V(1 - T\alpha_P)\gamma_\sigma, \tag{15}$$

$$= C_\sigma + V\gamma_\sigma. \tag{16}$$

Since $U = H - PV$,

$$\left(\frac{\partial U}{\partial T}\right)_\sigma = C_\sigma - P_\sigma V\alpha_\sigma, \tag{17}$$

$$= C_V + V\alpha_P(T\gamma_V - T\gamma_\sigma - P_\sigma). \tag{18}$$

Thus, for the saturated liquid at temperatures well below the critical temperature, where usually $0 < T\alpha_P^L < 1$, the following sequence is obtained:

$$\left(\frac{\partial H^L}{\partial T}\right)_\sigma > C_P^L > C_\sigma^L > \left(\frac{\partial U^L}{\partial T}\right)_\sigma > C_V^L. \tag{19}$$

The differences between the first four quantities are generally *much* smaller than the difference between $(\partial U^L/\partial T)_\sigma$ and C_V^L . At low vapor pressures, the difference between C_σ^L and C_P^L is frequently negligible (see above), but at higher vapor pressures corrections in the spirit of Eq. 4 have to be applied. The *general* form of the equations derived above may also be applied to the *saturated vapor* [76, 103], where, however, the difference $C_\sigma^V - C_P^V$ is *always* significant since $\alpha_P^V V^V$ is always large. In fact, for vapors of substances consisting of *small* molecules, such as argon, carbon dioxide, ammonia and water (steam), $\alpha_P^V V^V$ may be large enough to make C_σ^V even *negative*. Finally we note that the difference between the isobaric heat capacities in the vapor phase and the liquid phase at equilibrium may be expressed as

$$C_P^V - C_P^L = \left(\frac{\partial \Delta_{\text{vap}}H}{\partial T}\right)_\sigma - \gamma_\sigma \left[\Delta_{\text{vap}}V - T \left(\frac{\partial \Delta_{\text{vap}}V}{\partial T}\right)_P \right], \tag{20}$$

$$= \left(\frac{\partial \Delta_{\text{vap}}H}{\partial T}\right)_\sigma - \frac{\Delta_{\text{vap}}H}{T} \left[1 - \left(\frac{\partial \ln(\Delta_{\text{vap}}V)}{\partial \ln T}\right)_P \right]. \tag{21}$$

Equation 21 is known as the *Planck* equation. At temperatures well below the critical temperature, where γ_σ is small, the frequently used approximate relation

$$C_P^V - C_P^L \approx \left(\frac{\partial \Delta_{\text{vap}}H}{\partial T}\right)_\sigma \tag{22}$$

is obtained.

The *difference* between the heat capacities C_P and C_V may be derived as follows. Since

$$dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV \tag{23}$$

and

$$(\partial S/\partial V)_T = (\partial P/\partial T)_V \quad (24)$$

one obtains

$$C_P - C_V = TV\alpha_P\gamma_V \quad (25)$$

or, with Eq. 11,

$$C_P - C_V = TV\alpha_P^2/\beta_T \quad (26)$$

and

$$C_P - C_V = TV\beta_T\gamma_V^2 \quad (27)$$

respectively. With the compression factor $Z \equiv PV/RT$, alternatively the difference is given by [9]

$$C_P - C_V = R \frac{[Z + T(\partial Z/\partial T)_P]^2}{Z - P(\partial Z/\partial P)_T} \quad (28)$$

where R is the gas constant. Note that it is fully expressed in terms of PVT quantities.

The ratio of the heat capacities, $\kappa \equiv C_P/C_V$, is accessible via Eqs. 1 and 2:

$$\kappa \equiv \frac{C_P}{C_V} = \frac{(\partial S/\partial T)_P}{(\partial S/\partial T)_V} = \frac{(\partial S/\partial V)_P(\partial V/\partial T)_P}{(\partial S/\partial P)_V(\partial P/\partial T)_V}. \quad (29)$$

With

$$\frac{(\partial S/\partial V)_P}{(\partial S/\partial P)_V} = -\left(\frac{\partial P}{\partial V}\right)_S \quad (30)$$

and

$$\frac{(\partial V/\partial T)_P}{(\partial P/\partial T)_V} = -\left(\frac{\partial V}{\partial P}\right)_T = V\beta_T, \quad (31)$$

we obtain

$$\kappa \equiv \frac{C_P}{C_V} = -\left(\frac{\partial P}{\partial V}\right)_S V\beta_T. \quad (32)$$

At this juncture it is convenient to introduce, by definition, another auxiliary quantity, the *isentropic compressibility* β_S , often loosely called the adiabatic compressibility:

$$\beta_S \equiv -V^{-1}(\partial V/\partial P)_S = \rho^{-1}(\partial \rho/\partial P)_S. \quad (33)$$

Substituting $1/(V\beta_S)$ for $-(\partial P/\partial V)_S$ in Eq. 32 yields

$$\kappa \equiv C_P/C_V = \beta_T/\beta_S. \quad (34)$$

At low frequencies and small amplitudes, to an excellent approximation (i.e. neglecting dissipative processes, such as those associated with shear and bulk viscosity and thermal conductivity) the speed of ultrasound v_0 is related to β_S by [108, 109]

$$v_0^2 = \left(\frac{\partial P}{\partial \rho} \right)_S = \frac{1}{\rho \beta_S}. \quad (35)$$

Using Eq. 34, the speed of ultrasound may also be expressed as

$$v_0^2 = \frac{\kappa}{\rho \beta_T}. \quad (36)$$

Within the constraints indicated above [9], v_0 may be treated as a *thermodynamic equilibrium* property. However, at *higher* frequencies many liquids show sound speed dispersion due to thermal molecular relaxation and structural relaxation [108–112], i.e. the experimental sound speed is *larger* than the speed v_0 appearing in Eqs. 35 and 36. Thus, care must always be exercised in deciding whether the measured speed of ultrasound is indeed the quantity to be subsequently used in a *thermodynamic* analysis. In passing we note that β_S of liquids has also been determined by purely mechanical methods, i.e. by directly measuring the volume increase on sudden decompression [113–117], though this method is considerably less common and less accurate than that based on ultrasonics, Eq. 35.

Using Eq. 26 in conjunction with Eq. 36, the ratio of the heat capacities (or the ratio of the compressibilities) may now be calculated from

$$\kappa = 1 + \frac{TM_m \alpha_P^2 v_0^2}{C_P}. \quad (37)$$

This is one of the *most important* equations in thermophysics, since at low temperatures, where γ_V of liquids is *very* large, the *direct* calorimetric determination of C_V of *liquids* is not easy and requires sophisticated instrumentation, as evidenced by the careful work of Magee at NIST [118–123]. It becomes more practicable near the critical point where γ_V is much smaller. Most of the isochoric heat capacity data for liquids reported in the literature have been obtained *indirectly* through use of Eq. 37 from

$$C_V = C_P / \kappa, \quad (38)$$

that is to say, from experimentally determined isobaric heat capacities, isobaric expansivities and ultrasonic speeds at sufficiently low frequencies. With modern equipment, these three quantities may be measured accurately and speedily, thereby making the *indirect* method for determining C_V of liquids quite attractive.

In addition, Eq. 37 provides also a valuable alternative to the *direct* determination of β_T via *PVT* measurements, since

$$\beta_T = \kappa \beta_S. \quad (39)$$

Combining Eqs. 26 and 34, we obtain for the difference between the compressibilities

$$\beta_T - \beta_S = TV \alpha_P^2 / C_P, \quad (40a)$$

or

$$\beta_T - \beta_S = TV \alpha_P^2 / \kappa C_V, \quad (40b)$$

while

$$\beta_S^{-1} - \beta_T^{-1} = TV \gamma_V^2 / C_V. \quad (41)$$

Evidently, the most important use of liquid-state β_S data obtained via speed-of-sound measurements is the calculation of C_V and/or β_T using the appropriate equations given above. The *indirect* approaches for determining the isochoric heat capacity and the isothermal compressibility of liquids usually yield highly accurate results [3, 124, 125].

According to Eqs. 10, 34, 36 and 37, the isothermal pressure dependence of the density may be expressed as

$$\left(\frac{\partial \rho}{\partial P}\right)_T = \frac{1}{v_0^2} + \frac{TM_m \alpha_P^2}{C_P} \quad (42)$$

which gives upon integration at constant temperature [126–130]

$$\rho(T, P) = \rho(T, P_{\text{ref}}) + \int_{P_{\text{ref}}}^P v_0^{-2} dP + TM_m \int_{P_{\text{ref}}}^P \alpha_P^2 C_P^{-1} dP \quad (43)$$

where P_{ref} is a conveniently selected reference pressure, usually 0.1 MPa. Thus, by measuring the thermodynamic speed of ultrasound $v_0(T, P)$ as a function of temperature and pressure [131], and combining these results with data at ordinary pressure, that is $\rho(T, P_{\text{ref}})$ and $C_P(T, P_{\text{ref}})$, Eq. 43 provides a versatile alternative route to *high-pressure PVT* data and *high-pressure* heat capacity data. The first integral on the right-hand side may be evaluated directly by fitting the isothermal ultrasonic speed data $v_0(T, P)$ with suitably selected polynomials or Padé approximants, and for the second integral several successive integration algorithms have been devised, taking into account

$$(\partial \alpha_P / \partial P)_T = -(\partial \beta_T / \partial T)_P \quad (44)$$

and

$$(\partial C_P / \partial P)_T = -T(\partial^2 V / \partial T^2)_P = -TV[\alpha_P^2 + (\partial \alpha_P / \partial T)_P] \quad (45)$$

Equation 45 follows from

$$(\partial H / \partial P)_T = V - T(\partial V / \partial T)_P = V - TV\alpha_P \quad (46)$$

which in turn is obtained by differentiating the *Gibbs–Helmholtz* equation $H = G - T(\partial G / \partial T)_P$. The simplicity, rapidity and precision of this method makes it highly attractive for the determination of the density, isobaric expansivity, isothermal compressibility, isochoric thermal pressure coefficient, isobaric heat capacity and isochoric heat capacity of liquids at high pressures [132–138]. The most interesting results of these wide-temperature range/ wide-pressure range investigations of hydrocarbons, say, of heptane and toluene [133], are the proof of the existence of (shallow) *minima* of the isotherms $C_P = C_P(P)$ at elevated pressures, and of a substance-specific *crossing “point”* (or small crossing region?) of the isotherms $\alpha_P = \alpha_P(P)$. These two effects are closely related. For heptane, this crossing “point” is found at ca. 120 MPa, at which pressure $(\partial \alpha_P / \partial T)_P \approx 0$. Thus, for any given pressure lower than 120 MPa α_P of heptane *increases* with temperature, while at any given pressure higher than 120 MPa α_P *decreases* with temperature. For liquid water, recent high-precision measurements of the speed of sound over large temperature and pressure ranges have been communicated by Lin and Trusler [139] and by Baltasar et al. [140].

Note that

$$(\partial C_V / \partial V)_T = T(\partial^2 P / \partial T^2)_V = T(\partial \gamma_V / \partial T)_V, \quad (47)$$

which follows from

$$(\partial U / \partial V)_T = -P + T(\partial P / \partial T)_V = -P + T\gamma_V, \tag{48}$$

$$= -P + T\alpha_P / \beta_T. \tag{49}$$

In turn, Eq. 48 is obtained by differentiating the *Gibbs–Helmholtz* equation $U = F - T(\partial F / \partial T)_V$. Using Eqs. 35 and 37 yields the alternative expression

$$(\partial U / \partial V)_T = T\alpha_P \frac{C_P v_0^2 \rho}{C_P + TM_m \alpha_P^2 v_0^2} - P. \tag{50}$$

$(\partial U / \partial V)_T$ is called the *internal pressure* and is frequently given the symbol $\Pi(T, P)$. It is closely related to liquid structure and thus plays an important role in liquid-state physical chemistry [141–146]. Assuming the intermolecular pair potential energy $u(r)$ for a *simple* fluid to be spherically symmetric, as is the case, for instance, with a Mie (n, m) -type potential energy function (introduced in 1903 [147, 148]),

$$u(r) = \left(\frac{n}{m-n}\right) \left(\frac{n}{m}\right)^{m/(n-m)} \varepsilon \left[\left(\frac{\sigma}{r}\right)^n - \left(\frac{\sigma}{r}\right)^m \right], \tag{51}$$

and pairwise additive, the molar configurational internal energy U^c , which is equal to the molar *residual internal energy* $U^r = U - U^{pg}$, is related to the *pair distribution function* $g(r, T, \rho_n)$ by [78, 87],

$$\frac{U^c}{N_A k_B T} = \frac{2\pi\rho_n}{k_B T} \int_0^\infty u(r)g(r, T, \rho_n)r^2 dr, \tag{52}$$

Here, r is the distance between the molecules, n and m are positive constants associated with repulsion and attraction, respectively ($n > m$), ε is an intermolecular energy parameter characterizing the well-depth of the interaction energy function, i.e. $u(r_{\min}) = -\varepsilon$, σ is an intermolecular distance parameter characterized by $u(\sigma) = 0$, $\rho_n = N_A/V$ is the number density, N_A is the Avogadro constant, $k_B = R/N_A$ is the Boltzmann constant, and the superscript pg indicates the perfect-gas state (ideal-gas state), i.e. the real limiting state as $P \rightarrow 0$. Special cases of the Mie (n, m) function were introduced by Jones in 1924 and connected with gas viscosities [149], the equations of state of real gases [150], X-ray measurements on crystals [151], and quantum mechanics [152]. The most common form of the Lennard-Jones (12,6) function is [152]

$$u(r) = 4\varepsilon \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6 \right], \tag{53}$$

where $\sigma = 2^{-1/6}r_{\min}$.

By using a *chorostat* (constant volume piezometer), the internal pressure may be determined *directly*, according to Eq. 48, as the difference between the thermal (or kinetic) pressure $T\gamma_V$ and the total external pressure P , or *indirectly*, via Eqs. 49 or 50, respectively. Interestingly, isochoric thermal pressure coefficients γ_V of liquids have been measured far less frequently [153–163] than the other mechanical coefficients α_P and β_T , though direct determinations with a piezometer can be carried out with high accuracy. For normal liquids below the boiling point, $P \ll T\gamma_V$.

The *solubility parameter* δ [42, 43, 55, 72, 75, 141, 164–173] is a versatile quantity introduced by Hildebrand and by Scatchard. It is generally defined as the square-root of the cohesive energy density of a liquid and thus reflects the intermolecular interactions. While several definitions of the molar cohesive energy may be found in the literature, the most appropriate is

$$U_{\text{coh}}^{\text{L}}(T, P) \equiv U^{\text{pg}}(T) - U^{\text{L}}(T, P). \quad (54)$$

Thus, the solubility parameter is given by

$$\delta(T, P) = \left(\frac{U_{\text{coh}}^{\text{L}}(T, P)}{V^{\text{L}}(T, P)} \right)^{1/2}. \quad (55)$$

For $P = P_{\sigma}$, the molar cohesive energy is directly connected with the molar enthalpy of vaporization [46]:

$$\begin{aligned} U_{\text{coh}}^{\text{L}}(T, P_{\sigma}) &\equiv U^{\text{pg}}(T) - U^{\text{L}}(T, P_{\sigma}) \\ &= \Delta_{\text{vap}}H(T) - RT + P_{\sigma}V^{\text{L}}(T, P_{\sigma}) - \int_0^{P_{\sigma}} [V^{\text{V}}(T, P) - T(\partial V^{\text{V}}(T, P)/\partial T)_P] dP. \end{aligned} \quad (56)$$

The *PVT* behavior of the vapor phase at moderate pressures, say, at less than 0.3 MPa, is reasonably well approximated by a two-term virial equation in pressure,

$$Z^{\text{V}}(T, P) = 1 + \frac{B(T)}{RT}P, \quad (57)$$

which has practical advantages. Here, $B(T)$ is the second virial coefficient [44]. Insertion of this volume-explicit equation of state into Eq. 56 yields

$$U_{\text{coh}}^{\text{L}}(T, P_{\sigma}) \cong \Delta_{\text{vap}}H(T) - RT + P_{\sigma}V^{\text{L}}(T, P_{\sigma}) - P_{\sigma} \left(B(T) - T \frac{dB(T)}{dT} \right). \quad (58)$$

At sufficiently low vapor pressures and with the approximation of ideal-gas behavior of the vapor, Eq. 58 may be further simplified to

$$U_{\text{coh}}^{\text{L}}(T, P_{\sigma}) \approx \Delta_{\text{vap}}H(T) - RT, \quad (59)$$

and correspondingly the solubility parameter at saturation condition is

$$\delta(T, P_{\sigma}) \approx \left(\frac{\Delta_{\text{vap}}H(T) - RT}{V^{\text{L}}(T, P_{\sigma})} \right)^{1/2}. \quad (60)$$

The majority of the solubility parameters found in the literature is based on Eq. 60 and refers to 298.15 K. If the cohesive energy of a liquid is needed for $P > P_{\sigma}$, one has to integrate along the desired isotherm,

$$U_{\text{coh}}^{\text{L}}(T, P) = U_{\text{coh}}^{\text{L}}(T, P_{\sigma}) - \int_{V^{\text{L}}(T, P_{\sigma})}^{V^{\text{L}}(T, P)} \left(\frac{\partial U^{\text{L}}}{\partial V} \right)_T dV. \quad (61)$$

Concomitantly, the pressure dependence of V^L must be accounted for, for instance via the *modified Tait equation* (MTE), a versatile liquid-phase equation of state which is usually satisfactory for pressures up to about 100 MPa [26, 174, 175]:

$$V^L(T, P)/V^L(T, P_\sigma) = [1 + m_{\text{MTE}}(P - P_\sigma)\beta_T^L(T, P_\sigma)]^{-1/m}. \tag{62}$$

Here, $\beta_T^L(T, P_\sigma)$ is the isothermal compressibility of pure saturated liquid, and m_{MTE} is a pressure-independent parameter. For many liquid nonelectrolytes, experimental values cluster around $m_{\text{MTE}} = 10$, with only a weak temperature dependence. For recent work on the pressure dependence of the solubility parameter see Verdier and Andersen [176], and Rai et al. [177].

Based on ideas introduced by van Laar [178–180], for binary mixtures of essentially nonpolar molecules Hildebrand and Scatchard showed that the symmetrically normalized activity coefficients (Lewis–Randall convention, see below in Sect. 3) γ_i , $i = 1, 2$, can be expressed as

$$RT \ln \gamma_1 = V_1^{L*} \Phi_2^2 (c_{11} + c_{22} - 2c_{12}), \tag{63a}$$

and

$$RT \ln \gamma_2 = V_2^{L*} \Phi_1^2 (c_{11} + c_{22} - 2c_{12}), \tag{63b}$$

where V_1^{L*} is the molar volume of pure liquid component 1, V_2^{L*} is the molar volume of pure liquid component 2, and the corresponding volume fractions Φ_i are defined by

$$\Phi_i \equiv \frac{x_i V_i^{L*}}{x_1 V_1^{L*} + x_2 V_2^{L*}}, \quad i = 1, 2, \tag{64}$$

with x_i being the mole fraction of component i . The *cohesive energy densities* of the pure liquids are denoted by

$$c_{ii} \equiv \frac{U_{\text{coh},i}^{L*}}{V_i^{L*}}, \quad i = 1, 2. \tag{65}$$

where $U_{\text{coh},i}^{L*}$ is the cohesive energy of pure liquid component i , and c_{12} reflects the interaction between *unlike* molecules. Formally, this key quantity may be related to the cohesive energy densities of the pure liquids by

$$c_{12} = (c_{11}c_{22})^{1/2}(1 - k_{12}), \tag{66}$$

where k_{12} is a binary interaction parameter. As a first approximation, Scatchard and Hildebrand assume $k_{12} = 0$, whence with

$$\delta_i^2 \equiv c_{ii}, \tag{67}$$

the activity coefficients may be estimated using pure-component properties only:

$$RT \ln \gamma_1 = V_1^{L*} \Phi_2^2 (\delta_1 - \delta_2)^2, \tag{68a}$$

and

$$RT \ln \gamma_2 = V_2^{L*} \Phi_1^2 (\delta_1 - \delta_2)^2, \tag{68b}$$

yielding

$$G^E = RT \sum_i x_i \ln \gamma_i = (x_1 V_1^{L*} + x_2 V_2^{L*}) \Phi_1 \Phi_2 (\delta_1 - \delta_2)^2 \quad (69)$$

for the excess molar Gibbs energy. Only *positive* deviations from Raoult's law are predicted. The *regular-solution* equations Eqs. 68a and 68b may readily be generalized to multicomponent mixtures. For many solutions containing nonpolar components the regular-solution equations provide reasonable estimates provided that the temperature range of application is not large and that it is well below critical conditions.

For liquids, the graph P against T at constant volume is generally close to a straight line, i.e. the curvature of the isochores is very small, whence the density dependence of the isochoric heat capacity is very small (cf. Eq. 47), and its determination requires precision experiments. Starting with the pioneering work of Bridgman [181, 182] and, in particular, of Gibson and colleagues [183–187], we know that for organic solvents at ordinary temperatures $(\partial \gamma_V / \partial T)_V$, and hence $(\partial C_V / \partial V)_T$, is *negative*, which fact will be discussed below in another context.

In classical, direct high-pressure PVT measurements on fluids, isothermal compression is achieved by applying hydrostatic pressure and measuring the resulting volume changes. The value of β_T at saturation pressure, i.e. $\beta_T(T, P_\sigma(T))$, is then obtained through appropriate extrapolation of the (mean) experimental values over a fairly large pressure range, which needs careful attention to detail [188, 189]. On the other hand, vibrating-tube flow densimeters for the determination of $\rho(T, P)$ are widely used because they combine high precision and simple operation in the flow mode (involving fairly small samples). In addition, they allow a problem-oriented selection of the incremental pressure steps, which may be kept quite small. Based on the work of Kratky et al. [190] in the late 1960s and of Picker et al. [191] in 1974, Albert and Wood [192] presented a versatile high-pressure, high-temperature flow densimeter, and since then many new, improved designs have been introduced [193–199].

Equation 45 suggests still another method for obtaining heat capacities of fluids at elevated pressures. At constant T

$$C_P(T, P) = C_P(T, P_{\text{ref}}) - T \int_{P_{\text{ref}}}^P V(T, P) \left[\alpha_P^2(T, P) + \left(\frac{\partial \alpha_P(T, P)}{\partial T} \right)_P \right] dP, \quad (70)$$

with

$$V(T, P) = V(T_{\text{ref}}, P) \exp \left[\int_{T_{\text{ref}}}^T \alpha_P(T, P) dT \right], \quad (\text{constant } P). \quad (71)$$

Here, the isobaric expansivity is the *main* experimental property to be measured as a function of T and P . The other experimental properties are the molar volume $V(T_{\text{ref}}, P)$ as a function of pressure at a convenient low reference temperature T_{ref} and the molar isobaric heat capacity $C_P(T, P_{\text{ref}})$ as a function of temperature at a convenient low reference pressure P_{ref} . With a *scanning transitiometer* [200–203] it is possible to measure $\alpha_P(T, P)$ over wide ranges of temperature and pressure with an uncertainty of about 1–3 %, the reference volume isotherm with an uncertainty of about 0.6 %, and the reference heat capacity isobar with an uncertainty of about 0.3 %. Thus, the overall uncertainty of the

heat capacities of liquids at high pressures obtained by scanning transitiometry is estimated to be about 2 %. Again, perhaps the most interesting results are (i) the confirmation, for some organic liquids, of the existence of (shallow) *minima* of the isotherms of the isobaric heat capacity at elevated pressures, and (ii) the confirmation, for some organic liquids, of the existence of a *crossing “point”* (a crossing region?) of the isotherms $\alpha_P = \alpha_P(P)$ at elevated pressures. As concerns the experimental results for the isobaric expansivity obtained with this technique, we note that, say for liquid hexane [201], the isotherms $\alpha_P = \alpha_P(P)$ show a *crossing “point”* (a crossing region?) at about (65 ± 2) MPa, where $(\partial\alpha_P/\partial T)_P \approx 0$. However, the α_P isotherms of liquid hexan-1-ol [202] indicates a possible crossing region only at much higher pressure, i.e. around 280 MPa, whence the C_P isotherms of this hydrogen-bonded liquid do *not* show any minima at the conditions investigated. Closely related work has been reported by Romani’s group [204–207] in Spain.

The resolution of the variation of C_V^L of liquids along the *orthobaric curve*, i.e. along states with $V^L(T, P_\sigma(T))$, into contributions due to the increase of *temperature* and due to the increase of *volume*, respectively, is a highly interesting problem [1, 3, 7, 73, 104, 114–116]. It is important to realize that because of the close packing of molecules in a liquid, even a rather small change of the average volume available for their motion may have a considerable impact on the molecular dynamics: volume effects may become *more* important in influencing molecular motion in the liquid state than temperature changes. Since

$$\left(\frac{\partial C_V^L}{\partial T}\right)_\sigma = \left(\frac{\partial C_V^L}{\partial T}\right)_V + \left(\frac{\partial C_V^L}{\partial V}\right)_T V^L \alpha_\sigma^L, \quad (72)$$

in the absence of calorimetrically measured values of $(\partial C_V^L/\partial T)_V$, evaluation of this quantity requires knowledge of the *second* term of the right-hand-side of Eq. 72. At temperatures below the normal boiling point, the saturation expansivity α_σ^L is practically equal to α_P^L of the liquid (see Eqs. 8 or 9), and is frequently used instead. In principle, $(\partial C_V^L/\partial V)_T$ is accessible via precise *PVT* measurements, see Eq. 47, but measurements of $(\partial^2 P/\partial T^2)_V$ are also not plentiful. As indicated above, for simple organic liquids at ordinary temperatures, available data indicate that this quantity is small and *negative*, that is to say, at constant temperature C_V^L decreases with increasing volume. Alternatively, one may use [1, 3, 7, 73, 104]

$$\left(\frac{\partial C_V^L}{\partial V}\right)_T = \frac{T}{\beta_T^L} \left[\left(\frac{\partial \alpha_P^L}{\partial T}\right)_P - 2 \frac{\alpha_P^L}{\beta_T^L} \left(\frac{\partial \beta_T^L}{\partial T}\right)_P - \left(\frac{\alpha_P^L}{\beta_T^L}\right)^2 \left(\frac{\partial \beta_T^L}{\partial P}\right)_T \right]. \quad (73)$$

The last term in parenthesis on the right-hand side can be evaluated by means of a modified Tait equation [1, 3, 7, 26, 73, 104, 116, 174, 175, 208], see Eq. 62. Specifically,

$$\left(\frac{\partial \beta_T^L}{\partial P}\right)_T = -m_{\text{MTE}} (\beta_T^L)^2 \quad (74)$$

which relation holds remarkably well up to pressures of about 100 MPa (see above). For example, for liquid tetrachloromethane [3] at 298.15 K and corresponding $V^L(T, P_\sigma)$, the calculated value of $(\partial C_V^L/\partial V)_T$ amounts to $-0.48 \text{ J}\cdot\text{K}^{-1}\cdot\text{cm}^{-3}$, for cyclohexane $-0.57 \text{ J}\cdot\text{K}^{-1}\cdot\text{cm}^{-3}$ is obtained, and for 1,2-dichloroethane [4] $(\partial C_V^L/\partial V)_T = -0.60 \text{ J}\cdot\text{K}^{-1}\cdot\text{cm}^{-3}$. These results indicate a *substantial* contribution of $(\partial C_V^L/\partial V)_T V^L \alpha_\sigma^L$

to the change of C_V^L along the orthobaric curve (as well as to the corresponding change of the *residual* heat capacity, see below).

Equation 37 is a suitable starting point for a discussion of the temperature dependence of $\kappa^L \equiv C_P^L/C_V^L = \beta_T^L/\beta_V^L$ along the orthobaric curve [1, 3, 104]:

$$\left(\frac{\partial \kappa^L}{\partial T}\right)_\sigma = (\kappa^L - 1) \left[\frac{1}{T} + \frac{2}{\alpha_p^L} \left(\frac{\partial \alpha_p^L}{\partial T}\right)_\sigma + \frac{2}{v_0^L} \left(\frac{\partial v_0^L}{\partial T}\right)_\sigma - \frac{1}{C_p^L} \left(\frac{\partial C_p^L}{\partial T}\right)_\sigma \right]. \quad (75)$$

Usually, the second term in parenthesis on the right-hand-side of Eq. 75 is positive and the third term is negative [209]; the fourth term may contribute positively or negatively. Thus $\kappa^L(T, P_\sigma(T))$ of a liquid may increase or decrease with temperature.

From experimental heat capacities C_V^L of liquids, relatively simple approximate models may be used to extract information on the type of motion executed by molecules in the liquid state compared to the perfect or ideal gas state (pg). In general, they are based on the *separability* of contributions due to translation, rotation, vibration and so forth. Though none of the models is completely satisfactory, they have provided eminently useful insights and have thereby furthered theoretical advances. By following the pioneering work of Eucken [210, 211], Bernal [212], Eyring [213], Staveley [114, 115], Moelwyn-Hughes [116], Kohler [1, 214, 215], Bondi [216] and their collaborators, one may resolve the total molar heat capacity at constant volume of polyatomic non-associated liquids as follows [3, 7, 104]:

$$C_V^L = C_{tr}^L + C_{rot}^L + C_{int}^L + C_{or}^L. \quad (76)$$

The translational contribution C_{tr}^L arises from the motion of the centers of gravity of the molecules under the influence of all the other molecules in the system (movement within the respective free volumes). It is of the order $3R/2 + R$, R (the gas constant) being *roughly* the excess over the molar translational heat capacity associated with the perfect gas state. C_{rot}^L represents the contribution from the rotational movement of the molecules as a whole (overall molecular rotation). For nonlinear molecules, due to *hindered* rotation (often called libration), its value may be appreciably higher than its perfect-gas phase value of $3R/2$ (free rotation). The contribution from internal degrees of freedom, C_{int}^L , can be subdivided advantageously into a part C_{vib}^L , resulting from internal molecular vibrations which are *not* appreciably influenced by density changes (say, by going from the liquid to the perfect gas state), and another part, C_{conf}^L , resulting from internal rotations, i.e. conformational equilibria, which depend on changes in the surroundings of the molecules and hence on density [1, 4, 214–219]. Lastly, for polar substances there is a further contribution C_{or}^L from the change of the dipole–dipole orientational energy with temperature, which may become quite important [1, 4, 215, 219]. Here, the focus will be on liquids composed of quasi-rigid and not too anisotropic molecules, possessing no or only a small permanent dipole moment, of which tetrachloromethane, benzene and toluene are representatives. Preferably, all these contributions to C_V^L are discussed in terms of *residual* quantities in (T, V) -space [9], as elaborated in Refs. [3] and [7]. They provide the most direct measure of the contributions due to intermolecular interactions at any given state condition [76]. Note that when there is no risk of ambiguity, again for convenience quantities referring to the liquid will appear without a superscript L. The residual molar heat capacity $C_V^r(T, V)$ at constant volume of the liquid is directly obtained from *experimentally* determined isochoric liquid state heat capacities and subtracting the corresponding heat capacity for the substance in the perfect gas state:

$$C_V^r(T, V) \equiv C_V^L(T, V) - C_V^{pg}(T). \quad (77)$$

For fairly simple molecules, $C_V^{\text{pg}}(T)$ may be calculated using the frequencies of their normal modes of vibration [220–222], and extensive data compilations are available [45, 62, 223]. With the separability assumption

$$C_V^r(T, V) = C_{\text{tr}}^r(T, V) + C_{\text{rot}}^r(T, V) + C_{\text{int}}^r(T, V) \quad (78)$$

is obtained. For the class of liquids indicated above (i.e. quasi-rigid nonpolar or weakly polar non-associated molecules), to an excellent approximation

$$C_{\text{int}}^r(T, V) \equiv C_{\text{int}}^L(T, V) - C_{\text{int}}^{\text{pg}}(T) \approx 0, \quad (79)$$

whence Eq. 78 may be recast into

$$C_V^r(T, V) = C_{\text{tr}}^r(T, V) + C_{\text{rot}}^r(T, V). \quad (80)$$

Here,

$$C_{\text{tr}}^r(T, V) = C_{\text{tr}}^L(T, V) - 3R/2, \quad (81)$$

and for nonlinear molecules

$$C_{\text{rot}}^r(T, V) = C_{\text{rot}}^L(T, V) - 3R/2, \quad (82)$$

which quantity represents the excess over the (classical) perfect gas phase value due to *hindered* rotation in the liquid of the molecules as a whole. Using corresponding states arguments and focusing on orthobaric states, $C_{\text{tr}}^r(T, V_\sigma)$ may be approximated by the *orthobaric* $C_V^r(\text{Ar})$ of liquid argon [3, 73, 224] (where, of course, $C_{\text{int}}^r = 0$ as well as $C_{\text{rot}}^r = 0$) at the *same* reduced temperature $T_r = T/T_c$, where T_c denotes the critical temperature. Thus, semiquantitative estimates of the *residual molar rotational heat capacity* may be conveniently obtained from

$$C_{\text{rot}}^r(T, V_\sigma) \approx C_V^r(T, V_\sigma) - C_V^r(\text{Ar}), \quad (83)$$

and subsequently discussed in terms of any suitable model for restricted molecular overall rotation (hindered external rotation) in the liquid phase. An alternative scaling has been suggested by Harrison and Moelwyn-Hughes [116], who use the experimental value of C_V^L for mercury as giving C_{tr}^L for the polyatomic molecules at any “reduced” temperature Θ , which is defined in terms of the temperature of interest, the melting temperature T_{mp} and the normal boiling temperature T_{bp} :

$$\Theta = (T - T_{\text{mp}})/(T_{\text{bp}} - T_{\text{mp}}). \quad (84)$$

Focusing on the *entire* orthobaric liquid range, from the triple point (tr) temperature to the critical temperature, one may use instead

$$\theta = (T - T_{\text{tr}})/(T_c - T_{\text{tr}}). \quad (85)$$

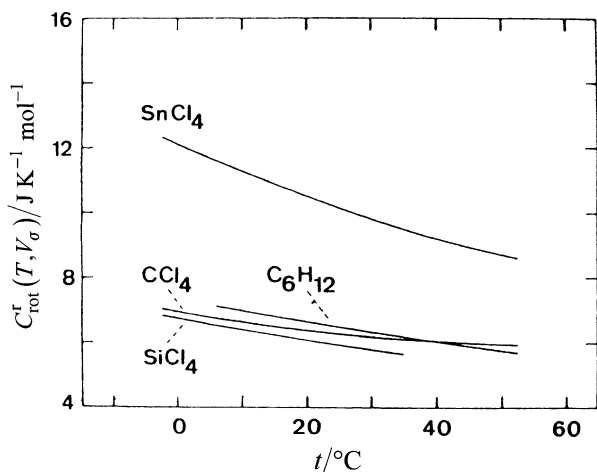
Figure 2 shows the residual molar rotational heat capacity $C_{\text{rot}}^r(T, V_\sigma)$ of the liquid quasi-spherical molecules tetrachloromethane, tetrachlorosilane, and tin tetrachloride as a function of temperature. Specifically, these three liquids were selected [3] to corroborate and quantify Sackmann’s geometry-based cogwheel model [225], in which interlocking of the tetrahalide molecules hinders free rotation. Whereas the results for CCl_4 and SiCl_4 are quite similar, amounting to $C_{\text{rot}}^r(T, V_\sigma) \approx 3R/4$ at 298.15 K, $C_{\text{rot}}^r(T, V_\sigma)$ for liquid SnCl_4 is distinctly larger, i.e. about $5R/4$: this is a clear indication of significantly *more hindered* external

molecular rotation in tin tetrachloride. Though originally developed by Pitzer and Gwinn [226] for molecules with restricted internal rotation, their model may be adopted to deal qualitatively with restricted external rotation (subscript *rr*) [3]. The resulting contributions C_{rr} depend on the barrier height U_0 hindering free rotation and on temperature. The available experimental data [3] suggest that at 298.15 K *all* the tetrahalides are already on the high-temperature decline, i.e. *past* the maximum of the Pitzer–Gwinn curve C_{rr} versus T .

For SnCl_4 , the experimental residual molar rotational heat capacity (see Fig. 2) at 298.15 K for one degree of freedom amounts to $C_{rot}^r/3R \approx 0.4$. Approximating this value with C_{rr}^r/R calculated via the Pitzer–Gwinn model indicates a barrier height of ca. $U_0 = 5.5 \text{ kJ}\cdot\text{mol}^{-1}$. For the other two tetrahalides where molecular rotation is less hindered, the experimental value (Fig. 2) at 298.15 K for one degree of freedom is $C_{rot}^r/3R \approx 0.25$, which corresponds to a barrier height of ca. $U_0 = 4.0 \text{ kJ}\cdot\text{mol}^{-1}$ [3]. For the volume dependence of U_0 of, say, CCl_4 at 298.15 K, $(\partial U_0/\partial V)_T \approx -100 \text{ J}\cdot\text{cm}^{-3}$ is obtained: increasing the molar volume by $1 \text{ cm}^3\cdot\text{mol}^{-1}$ results in the decrease of the barrier height responsible for hindered rotation by about $100 \text{ J}\cdot\text{mol}^{-1}$. In liquids, the nuclear spin relaxation rate via quadrupolar interaction is related to the rotational correlation time. From its temperature dependence in liquid CCl_4 , O'Reilly and Schacher [227] derived the rotational activation energy of $(5.4 \pm 0.4) \text{ kJ}\cdot\text{mol}^{-1}$. Relaxation times of ^{119}Sn in liquid SnCl_4 have been measured as a function of temperature by Sharp [228], yielding a distinctly higher activation energy of $7.8 \text{ kJ}\cdot\text{mol}^{-1}$, in satisfactory accord with our results.

Over the past four decades, liquids consisting of tetrahedral molecules in general, and liquid tetrachloromethane in particular, have been extensively studied by X-ray and neutron diffraction [229–240]. These studies indicate some common orientational order, as do computer simulations [236, 238, 241–246] and theoretical approaches [247–249] based on the reference interaction site model (RISM), though there are important differences in the details. For instance, it is found that the CCl_4 molecules form interlocking structures which give rise to significant orientational correlations between molecules in the dense liquid phase, extending up to the limit of the second solvation shell, i.e. up to about 14 \AA ($\text{\AA} = 10^{-10} \text{ m}$). According to Rey [244], of the configurations within the first solvation shell (which at ambient temperature reaches up to ca. 8 \AA and contains about 12 molecules) approximately 5 molecules belong to the *edge-to-edge* (2:2) configuration,

Fig. 2 Residual molar rotational heat capacity $C_{rot}^r(T, V_\sigma)$ as a function of temperature $t/^\circ\text{C} = T/\text{K} - 273.15$ of the liquid quasi-spherical molecules tetrachloromethane (CCl_4), tetrachlorosilane (SiCl_4), tin tetrachloride (SnCl_4), and cyclohexane ($c\text{-C}_6\text{H}_{12}$, not discussed in this review) for orthobaric conditions: $V_\sigma = V(T, P_\sigma(T))$ [3]



approximately 3 molecules belong to the *edge-to-face* (2:3) configuration, at least 2 to *corner-to-edge* (1:2), and at most 1 to *corner-to-face* (1:3). *Face-to-face* (3:3) and *corner-to-corner* (1:1) configurations share the remaining molecule. It is important to emphasize that this (or similar) pictures will be heavily influenced by the decrease of density when going along the saturation curve towards elevated temperatures [233, 234].

Combining the detailed analysis of molecular dynamics simulation results and the interpretation of neutron diffraction measurements using the reverse Monte Carlo method [250], it appears that the corner-to-face (1:3) type near-neighbor configuration (Sackmann's arrangement II [225], also known as the Apollo model [230]), which has been favored for the interpretation of structure in liquid CCl₄ for more than three decades, is quite rare, the occurrence being around 5 % [245]. We note, however, that at very short distances (<5.8 Å), where four molecules interlock *directly* with the central molecule [247], the face-to-face (3:3) configuration (Sackmann's arrangement I) becomes more important. Evidently, the orientational order in the liquid phase of tetrahedral molecules of type XCl₄ is much more complex and long ranged than previously thought.

3 Caloric Properties of Binary Liquid Mixtures Containing One Strongly Polar Aprotic Component

Mixtures/solutions of practical interest for the chemist, chemical engineer or biophysicist are usually quite complex, that is to say, the intermolecular potential energy functions characterizing the pure components differ strongly, and frequently cause pronounced nonideal thermodynamic behavior. 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 properties of mixtures/solutions in general, and on liquid-phase nonelectrolyte systems in particular. First and foremost, by systematically studying mixture/solution properties our knowledge of intermolecular *interaction* between different species in bulk liquid phases will improve. Second, the appearance of *new* physical phenomena in multicomponent systems is scientifically fascinating as well as challenging, and adds a new dimension to physico-chemical research. And third, the scientific insight gained allows the *practitioner* to deal efficiently (and pragmatically) with technologically important systems and processes.

Experiments are the fundament of science, yet the huge number of potentially interesting and useful mixture/solubility data connected with binary, ternary, quaternary, etc. systems at different temperatures and pressures effectively precludes their experimental determination for all but a few representative *key systems* of physico-chemical/technological interest. This is best illustrated by calculating the number of different multicomponent systems containing r components which can be formed out of, say, $n = 1000$ important chemicals. This r -combination is given by

$$C(n, r) = \binom{n}{r} = \frac{n(n-1) \cdots (n-r+1)}{r!}, \quad (86)$$

whence $C(1000, 2) = 4.995 \times 10^5$ different binaries may be formed, $C(1000, 3) = 1.66167 \times 10^8$ different ternary systems, $C(1000, 4) = 4.141712475 \times 10^{10}$ different quaternary systems, and so forth. Reliable and effective prediction methods for mixture/solution properties are thus indispensable tools of the trade, which are provided, for instance, by group contribution methods such as UNIFAC or DISQUAC [251–260], or the

new MOQUAC model [261], in which the effect of molecular orientation on molecular interaction is explicitly taken into account. While they work reasonably well for excess molar Gibbs energies G^E and excess molar enthalpies H^E over not too large temperature ranges, predicted results for activity coefficients at infinite dilution, aqueous solubilities of hydrocarbons and excess molar heat capacities at constant pressure, C_p^E , are frequently not satisfactory [262]. Similar comments apply to the COSMO-RS and related models [263–272]. This is not really surprising since mixture models are usually constructed at the *free-energy level*. If T , P and x_i are selected as independent canonical variables, $G^E = H^E - TS^E$ becomes a generating function for all the other excess molar quantities and the *activity coefficients* $\gamma_i(T, P, x_i)$ based on the *Lewis–Randall rule* (symmetric convention). This is perhaps best seen from the fundamental property relation

$$d(nG^E) = -(nS^E)dT + (nV^E)dP + RT \sum_i \ln \gamma_i dn_i, \quad (87)$$

whence,

$$\left(\frac{\partial G^E}{\partial T}\right)_{P,x} = -S^E, \quad (88)$$

$$\left(\frac{\partial G^E}{\partial P}\right)_{T,x} = V^E, \quad (89)$$

and

$$\left(\frac{\partial(nG^E)}{\partial n_i}\right)_{T,P,n_j \neq i} = G_i^E = RT \ln \gamma_i. \quad (90)$$

The excess heat capacity is related to the *second* derivative of G^E with respect to temperature, thus making it a *very important discriminatory property* for model evaluation:

$$C_p^E = (\partial H^E / \partial T)_{P,x} = T(\partial S^E / \partial T)_{P,x} = -T(\partial^2 G^E / \partial T^2)_{P,x}, \quad (91)$$

$$= -2RT \sum_i x_i (\partial \ln \gamma_i / \partial T)_{P,x} - RT^2 \sum_i x_i (\partial^2 \ln \gamma_i / \partial T^2)_{P,x}. \quad (92)$$

Here, S^E denotes the excess molar entropy, V^E is the excess molar volume, $x_i = n_i/n$ is the mole fraction of component i in a multicomponent system, n_i is the amount of substance of component i , the total amount of substance is given by $n = \sum_i n_i$, and $\sum_i x_i = 1$. Note, that

$$\left(\frac{\partial(G^E/RT)}{\partial T}\right)_{P,x} = -\frac{H^E}{RT^2}. \quad (93)$$

The partial molar excess Gibbs energy G_i^E of component i is the excess chemical potential, that is $G_i^E = \mu_i^E$, and since $RT \ln \gamma_i$ is a partial molar property with respect to G^E ,

$$G^E = \sum_i x_i G_i^E = RT \sum_i x_i \ln \gamma_i \quad (94)$$

see also Eq. 69. Derivation of useful relations for other excess *partial* molar properties in a constant-composition solution is straightforward.

In order to overcome their inherent difficulties, G^E -models may be combined with equations of state (EOS), such as the Soave–Redlich–Kwong (SRK) EOS or the Volume-Translated Peng–Robinson (VTPR) EOS, to yield predictive group contribution equations of state [268, 273–279]. A survey of many popular models used to describe phase equilibria was recently prepared by Lei et al. [280].

For the practically and theoretically important *global* thermodynamic description of liquid mixtures of nonelectrolytes [9], the excess molar isobaric heat capacities are pivotal quantities, and one can take advantage of the exact thermodynamic relations contained in Eq. 91 to effect a considerable economy in experimental effort. Given H^E and G^E at *one* suitably selected temperature T_{ref} and C_P^E as a function of temperature, integration at constant pressure of the relevant equations yields H^E , S^E and G^E over the temperature range of the heat capacity measurements. Well below the vapor–liquid critical region, C_P^E of a mixture of given composition and at constant pressure usually shows a simple functional dependence on temperature, for instance [9, 252]

$$\frac{C_P^E}{R} = a_3 + a_4\tau + a_5\tau^2, \quad (95)$$

where $\tau \equiv T_{\text{ref}}/T$. Starting from the differential equations of Eq. 91, integration over temperature at constant pressure and composition yields

$$\frac{H^E}{RT} = a_3 + (a_2 - a_3 + a_5)\tau - a_5\tau^2 - a_4\tau \ln \tau, \quad (96)$$

$$\frac{S^E}{R} = a_1 + a_4 + \frac{a_5}{2} - a_4\tau - \frac{a_5}{2}\tau^2 - a_3 \ln \tau, \quad (97)$$

and

$$\frac{G^E}{RT} = -a_1 + a_3 - a_4 - \frac{a_5}{2} + (a_2 - a_3 + a_4 + a_5)\tau - \frac{a_5}{2}\tau^2 + a_3 \ln \tau - a_4\tau \ln \tau. \quad (98)$$

The dimensionless coefficients $a_j = a_j(P, \{x_i\})$ are related to the corresponding excess quantities at $T_{\text{ref}}, P, \{x_i\}$ by

$$C_P^E(T_{\text{ref}}, P, \{x_i\})/R = a_3 + a_4 + a_5, \quad (99)$$

$$H^E(T_{\text{ref}}, P, \{x_i\})/RT_{\text{ref}} = a_2, \quad (100)$$

$$S^E(T_{\text{ref}}, P, \{x_i\})/R = a_1, \quad (101)$$

$$G^E(T_{\text{ref}}, P, \{x_i\})/RT_{\text{ref}} = a_2 - a_1. \quad (102)$$

Analogous expressions may be derived if C_P^E , at constant pressure and composition, is given by a polynomial in T instead of T^{-1} (see also Sect. 4 of this review). Global studies of this kind are, however, quite rare, with some of the most careful and extensive investigations being those of Ziegler and colleagues [281, 282].

Heuristically, a discussion of mixtures/solutions may be conducted in terms of differences in molecular size, shape anisotropy, dispersion energy, polarity, molecular polarizability, flexibility, and so forth. Figure 3 presents an overview of the most important aspects at the *molecular* level as well as the *bulk* level [7, 12, 43, 76, 87, 101, 283, 284]. In fact, in many liquid mixtures/solutions dipolar (and quadrupolar) interactions contribute significantly to the thermodynamic properties and may involve cooperative phenomena.

The principal obstacles for a comprehensive discussion of complex liquid mixtures/solutions are:

- Uncertainty concerning the intermolecular potential energy functions of the components, and insufficient knowledge about the potential energy functions characterizing *unlike* interaction, i.e. of *combining rules* [43, 87, 285–288];
- Difficulties encountered when two or more of the above-mentioned molecular aspects, say, shape anisotropy and a permanent electric dipole moment, are *present simultaneously* [43, 76, 87, 289–295];
- Meager knowledge of *many-body effects* [76, 78, 296–298], exemplified, for instance, by the correlation of molecular orientation and medium effects on conformational equilibria [1, 2, 4, 15, 214, 215, 217, 219, 299–305].

Additional aspects include molecular *association* via hydrogen bonds [306–308], or *charge transfer* interaction [309, 310], and if aqueous solutions are involved, *hydrophobic* and *hydrophilic* effects [311–317].

A dipolar substance is characterized by its permanent molecular electric dipole moment \mathbf{p} , though this quantity by itself is not sufficiently helpful in guiding the discussion of the impact of polarity on thermodynamic properties of pure liquids and liquid mixtures. For characterizing the *effective* polarity of a molecule, one may define a *reduced* dipole moment [7, 12, 76] according to

$$p'_r = [\mathbf{p}^2 / (4\pi\epsilon_0\sigma^3\epsilon)]^{1/2}, \quad (103)$$

where ϵ_0 is the permittivity of the vacuum, σ is an appropriate molecular size parameter, say, of a Mie-type intermolecular potential energy function, and ϵ is the corresponding interaction energy parameter (see Eqs. 51 and 53). Equivalently, by virtue of the corresponding states principle, we may use

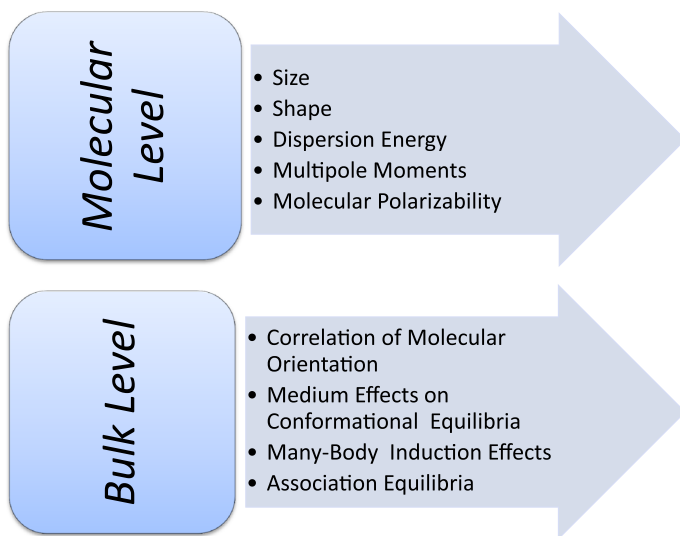


Fig. 3 Schematic summary of the most important physical aspects to be considered in a realistic description of pure liquids and liquid mixtures/solutions at the molecular level as well as on the bulk level [7, 12]

$$p_r = [\mathbf{p}^2 N_A / (4\pi\epsilon_0 V_c k_B T_c)]^{1/2}. \tag{104}$$

Evidently, a small dipole moment in a small molecule may cause as large a contribution to the interaction free energy as a large dipole moment in a large molecule [76]. However, even this quantity does not fully reflect the increase in effective polarity which results from an unsymmetrical disposition of the polar group within the molecule, i.e. from dipole moments exposed on the molecular periphery [7].

Here, I will only consider binary liquid systems of type [a polar aprotic component (1) + an aliphatic or alicyclic hydrocarbon (2)], where the focus is on dipolar orientational effects (caused by an appreciable dipole moment \mathbf{p}_1) and increasing non-randomness in the mixtures when the temperature is lowered. Following Pople’s treatment [318] of the thermodynamic effects of orientational forces in liquids, which includes, but is not restricted to, dipolar interactions, the total molar Helmholtz energy can be expressed as the sum of spherically symmetric central-force (cf) contributions and additional orientational (or) contributions:

$$F^{L*}(T, V^{L*}) = F_{cf}^{L*}(T, V^{L*}) + F_{or}^{L*}(T, V^{L*}). \tag{105}$$

Assuming a lattice model, the extra molar Helmholtz energy in a pure liquid due to the contribution of dipole–dipole interactions is given by [7]

$$F_{or}^{L*}/RT = -l[\mathbf{p}^2 N_A / (4\pi\epsilon_0 V^{L*} k_B T)]^2 = -l[p_r^2 / V_r^{L*} T_r]^2, \tag{106}$$

where $V_r^{L*} = V^{L*}/V_c$ is the reduced molar volume, $T_r = T/T_c$ is the reduced temperature, and l depends on the lattice selected. For a face-centered cubic lattice, including also interactions beyond the first coordination sphere, $l = 1.2045$. We note that the orientational contribution to the Helmholtz energy of a dipolar liquid is always *negative* and varies with $p^4 / (V^{L*} T)^2$.

Similarly, one may decompose the excess molar Gibbs energy of a binary liquid mixture containing one strongly polar aprotic component, say, component 1, into a central-force contribution and an orientational contribution caused by the permanent electric dipole moment \mathbf{p}_1 :

$$G^E(T, P, x_1) = G_{cf}^E(T, P, x_1) + G_{or}^E(T, P, x_1). \tag{107}$$

Again, assuming a face-centered cubic lattice and including interactions beyond the first coordination sphere, to a good approximation

$$\frac{G_{or}^E}{RT} = 1.2045 x_1 x_2 \left(\frac{N_A \mathbf{p}_1^2}{4\pi\epsilon_0 V^L k_B T} \right)^2, \tag{108}$$

where V^L is the molar volume of the mixture. Thus, when mixing a *dipolar* liquid with a *nonpolar* liquid, the net *destruction* of dipolar order results in a *positive* contribution to G^E which is proportional to the *fourth power* of \mathbf{p}_1 , or more precisely, it is proportional to $p_1^4 / (V^L T)^2$.

Alternatively, using a simple Guggenheim model [319] and including also contributions from molecular shape anisotropy, Kalali et al. [320] also showed that the order destruction leads to *positive* contributions to G^E , H^E and S^E , and to a *negative* contribution to C_p^E . In this model, the excess molar Gibbs energy is given by

$$G^E = x_1x_2W, \quad (109)$$

where

$$W = a + \frac{b}{T} \quad (110)$$

is the *molar cooperative free energy*, and a and b are constants characteristic for a given pair of substances, the excess molar enthalpy is

$$H^E = x_1x_2 \left(a + 2\frac{b}{T} \right), \quad (111)$$

the excess molar entropy is

$$S^E = x_1x_2 \frac{b}{T^2}, \quad (112)$$

and for the excess molar heat capacity at constant pressure one obtains

$$C_p^E = -2x_1x_2 \frac{b}{T^2} = -\frac{2(H^E - G^E)}{T}. \quad (113)$$

This latter relation appears to hold well for nonpolar or weakly polar mixtures. However, for mixtures of a strongly polar liquid with an essentially nonpolar liquid, say, an alkane, the experimental C_p^E is usually less negative than demanded by Eq. 113 [6, 7, 17, 320–322]. This indicates that some dipole–dipole orientations have considerably greater stability (one may regard this as weak association) than accounted for by the angle-averaging procedure involved. An intuitively appealing way of treating these *non-randomness* effects, based on Guggenheim's quasi-chemical theory, was suggested by Saint-Victor and Patterson [322]. To a reasonable approximation, the excess molar isobaric heat capacity is separated into a *random* (r) and a *non-random* (nr) contribution:

$$\begin{aligned} C_p^E/R &= C_p^E(r)/R + C_p^E(nr)/R \\ &= -x_1x_2TR^{-1}(d^2W/dT^2) \\ &\quad + (x_1x_2)^2 \left\{ 2[W - T(dW/dT)]^2\eta^2(zR^2T^2)^{-1} + (\eta^2 - 1)TR^{-1}(d^2W/dT^2) \right\} \end{aligned} \quad (114)$$

where $\eta = \exp(W/zRT)$, and z is the coordination number [6, 7, 12, 17]. Note that in their original expression, Eq. 7 of [322], the factor η^2 is missing from the first term inside the wavy brackets. Equation 114 is in agreement with the first-order result of the Taylor expansion of the full quasi-chemical expression as obtained by Cobos [323]. Clearly, the random term is *always negative* with a parabolic composition dependence, as expected for mixtures where dipole–dipole order is destroyed by the mixing process. In contradistinction, the non-random term is *always positive* and has *zero slope* against the mole fraction axis at both ends of the composition range. Thus, the superposition of the two contributions $C_p^E(r)$ and $C_p^E(nr)$ accounts qualitatively for the appearance of *W-shaped* curves C_p^E versus x . The *first* W-shaped $C_p^E(x)$ curves ever reported in the literature were for three mixtures of type (1,4-dioxane + an n -alkane) [10, 324], see Fig. 4. Since then, such mixture behavior has been found fairly often [17]. With decreasing temperature, the maximum caused by $C_p^E(nr)$ increases, thus making the W-shape more pronounced, which behavior

was confirmed by experiment [320, 322, 325–327]. For an analysis of W-shaped excess heat capacities in terms of the non-random two liquid (NRTL) model [328], see Troncoso et al. [329].

However, it is important to note that many of the mixtures showing W-shaped $C_p^E(x)$ curves are quite close to liquid–liquid phase separation with an upper critical solution temperature (UCST) T_{uc} . A liquid mixture near its upper critical consolute point has a *weak divergence* in its heat capacity at constant pressure when determined along a path of constant critical composition $x = x_{uc}$ [330–333]. Thus, for the approach through the homogeneous one-phase region ($T > T_{uc}$), the standard power law expression, including the first correction-to-scaling term for extending the theoretical description further away from the critical point [334], is

$$C_{p,x_{uc}} = B + Et + \frac{A^+}{\alpha} t^{-\alpha} (1 + D^+ t^{\Delta_1}). \quad (115)$$

Here, $t = |(T - T_{uc})/T_{uc}|$, is the reduced distance, temperature wise, from T_{uc} , B and E refer to the background heat capacity at constant pressure, A^+ is the amplitude of the leading divergence (homogeneous region), and D^+ is the amplitude of the first correction-to-scaling term; $\alpha = 0.11$ and $\Delta_1 = 0.5$ are universal critical exponents [320, 335–338]. Evidently, The quasi-chemical approximation underestimates the non-random contribution to the excess heat capacity and becomes *qualitatively incorrect* for $T \rightarrow T_{uc}$.

4 Caloric Properties of Dilute Solutions of Gases in Liquids

Solubility and related phenomena constitute one of the oldest and most important fields of physical chemistry. For more than a century, the study of the solubility of nonelectrolytes in liquids has contributed decisively to the development of the highly formalized general discipline of solution thermodynamics [34], a fact concisely summarized in 1950 by the introductory statement of Hildebrand and Scott to their monograph [141]: “*The entire history of chemistry bears witness to the extraordinary importance of the phenomenon of solubility.*”

Why, now, my long-term interest in the study of the solubility of gases in liquids? In addition to its profound theoretical interest, practical applications can be found in surprisingly diverse areas of the pure and applied sciences [20, 22, 26–28, 30–34, 339–347]: in other words, it is a fascinating area grounded in both theory and practice. Gas solubility data have led to useful estimates of *effective* Lennard-Jones parameters [348–350], which in turn allow successful predictions of Henry fugacities and related quantities for many gas–liquid systems over large temperature ranges using scaled particle theory [18, 22, 344, 351–354], ranging from aqueous [22, 23, 29, 355–357] to alcoholic systems [358] to the solubility of gases in perfluorinated hydrocarbons [19]. In particular, experimental solubilities determined in liquid water have been pivotal in developing modern views of hydrophobic effects [311, 312, 359–363], that is hydrophobic solvation and hydrophobic interaction, which field continues to be a highly active research area [313–317, 364–369].

It is far beyond the scope of this review to discuss available experimental methods tailored for determining caloric properties of dilute solutions in general (enthalpies of solution, heat capacity changes on solution), and of solutions of gases in liquids in particular. Those potentially interested in precision apparatus are referred to my review articles covering this topic, say, Refs. [22, 26, 30]. Let it suffice to point out that flow

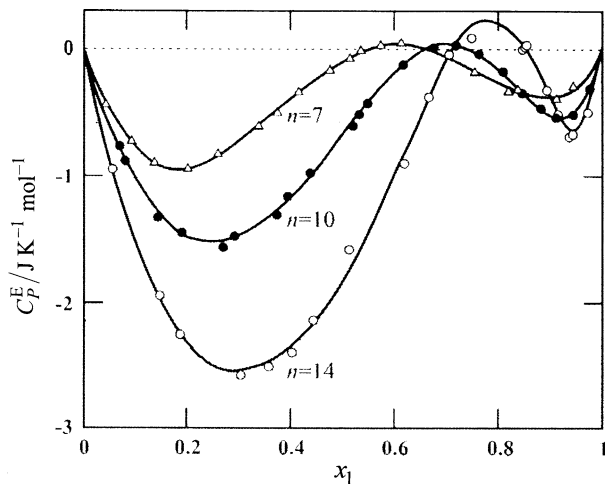


Fig. 4 Excess molar heat capacities C_p^E at constant pressure of three liquid mixtures of type $\{x_1, 1, 4\text{-C}_4\text{H}_8\text{O}_2 + x_2\text{C}_n\text{H}_{2n+2}\}$, $n = 7, 10$ and 14 , at 298.15 K and ambient pressure. The *circles* and *triangles* are experimental points obtained with a Picker flow-calorimeter [10, 324]

calorimetry involves fairly direct measurement techniques, and despite sophisticated designs they require relatively little additional thermophysical information and data manipulation to obtain the desired quantities from the primary experimental results. In contradistinction to this situation, to obtain thermodynamically well-defined and reliable caloric properties from gas solubility measurements, besides sophisticated instruments, data reduction is *more complex* and requires more auxiliary thermophysical data. A comprehensive discussion of this so-called *van't Hoff approach* and of the relevant thermodynamic fundamentals was recently presented in Refs. [30, 33, 34].

By way of example, I will focus on data reduction associated with the use of our high-precision *analytic* gas solubility apparatus [23, 24, 29, 356, 357]. By and large, the method adopted for use with our medium-precision *synthetic*, fully automated Ben-Naim/Baer-type instrument, is similar [370–375]. In this context, high-precision implies an average random error (imprecision) of about $\pm 0.05\%$ in conjunction with a maximum systematic error (inaccuracy) of about $\pm 0.05\%$ or less. The imprecision associated with the Ben-Naim/Baer-type apparatus is roughly $\pm 0.5\%$, and the corresponding systematic error is estimated to be also about $\pm 0.5\%$. Our high-precision analytical method is based on earlier work of Benson and Krause [376, 377]. The technique used to degas the solvent has been described [378]. In order to obtain fully reproducible results, we usually use equilibration times of up to 48 h. The temperature drift of the large water thermostat during equilibration never exceeds ± 0.003 K.

After attaining vapor–liquid equilibrium at T and $P > P_{\sigma,1}$, vapor phase and liquid phase samples of precisely known volumes are isolated, and the quantities of gas contained in each are transferred to the manometric system to determine the amounts of pure gas by classical *PVT* measurements. From the measured quantities, the *Henry fugacity* $h_{2,1}(T, P_{\sigma,1}(T))$, also known as the Henry's law (HL) constant, of solute 2 (gas) dissolved in liquid solvent 1 at the experimental temperature and at the corresponding vapor pressure of the pure solvent $P_{\sigma,1}(T)$ is obtained through straightforward though tedious *isothermal* extrapolation $P \rightarrow P_{\sigma,1}(T)$, and concomitantly decreasing *liquid phase* mole fraction of

dissolved gas, $x_2 \rightarrow 0$, and decreasing mole fraction of gas in the coexisting *vapor phase*, $y_2 \rightarrow 0$, according to

$$h_{2,1}(T, P, \sigma, 1(T)) = \lim_{x_2 \rightarrow 0} \left(\frac{f_2^L(T, P, x_2)}{x_2} \right) = \lim_{\substack{x_2 \rightarrow 0 \\ y_2 P \rightarrow 0}} \left(\frac{\phi_2^V(T, P, y_2) y_2 P}{x_2} \right), \text{ constant } T. \quad (116)$$

Here, $f_2^L(T, P, x_2)$ is the fugacity of the solute in the liquid phase, and $\phi_2^V(T, P, y_2)$ is the vapor phase component fugacity coefficient of the gaseous solute. Equation 116 is directly obtained from the general criterion for phase equilibrium in *PVT* systems of uniform temperature and pressure, which is formulated advantageously in terms of the equality of the *fugacity* of each constituent component *i* in *all* coexisting phases [42, 43]. For the *solute* ($i = 2$) in a binary solution this reads [26, 30, 31, 34]

$$f_2^L(T, P, x_2) = f_2^V(T, P, y_2), \quad (117)$$

where the *liquid phase* fugacity may be expressed by

$$f_2^L(T, P, x_2) = \gamma_2^{HL}(T, P, x_2) x_2 h_{2,1}(T, P), \quad (118)$$

and the *vapor phase* fugacity by

$$f_2^V(T, P, y_2) = \phi_2^V(T, P, y_2) y_2 P. \quad (119)$$

Note that the limiting behavior of the *unsymmetrically* normalized activity coefficient based on Henry’s law is

$$\lim_{x_2 \rightarrow 0} \gamma_2^{HL} = 1, \quad \text{constant } T, P. \quad (120)$$

While the mole fractions are experimentally determined quantities, $\phi_2^V(T, P, y_2)$ has to be calculated with a suitable equation of state. For measurements at such low pressures as in our work ($P < 120$ kPa), the virial equation in pressure at the second-virial-coefficient level,

$$Z^V(T, P, \{y_i\}) = 1 + \frac{B(T, \{y_i\})}{RT} P, \quad (121)$$

is entirely adequate and most convenient for the description of real gas behavior: Hence, in a binary vapor mixture

$$\ln \phi_i^V = \frac{P}{RT} (B_{ii} + y_j^2 \Delta_{12}), \quad i, j = 1, 2, i \neq j, \quad (122)$$

with

$$\Delta_{12} = 2B_{12} - (B_{11} + B_{22}). \quad (123)$$

B_{11} and B_{22} are the second virial coefficients of the pure components, B_{12} designates the composition-independent interaction virial coefficient (cross-coefficient), and the second virial coefficient of the mixture may be expressed as

$$B = y_1 B_{11} + y_2 B_{22} + y_1 y_2 \Delta_{12}. \quad (124)$$

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

$$\ln \phi_2^{V\infty} = \frac{P}{RT} (2B_{12} - B_{11}), \quad (125)$$

and the fugacity coefficient of pure component 2 by

$$\ln \phi_2^{V*} = \frac{P}{RT} B_{22}. \quad (126)$$

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

In brief, the auxiliary quantities needed for a thermodynamically rigorous data reduction of gas solubility measurements in liquids at low pressures with our high-precision apparatus are the vapor pressure of the solvent, the second virial coefficients of the pure components, the second virial cross-coefficient, the molar volume of the pure liquid solvent [23], and the partial molar volume of the gas at infinite dilution in the liquid phase [23] (see also below). Frequently, no experimental data are available for one or more of these properties. Thus for vapor–liquid equilibrium (VLE) data reduction in general, and for gas solubilities in liquids in particular, one depends heavily on semiempirical estimation methods, which are predominantly based on the *extended corresponding states theorem*. For details I refer to the original articles and to the pertinent reviews [26, 30, 33, 34].

Once experimental Henry fugacities $h_{2,1}(T, P_{\sigma,1}(T))$ for a given solute/solvent system have been collected over a certain temperature range (but not too close to the critical temperature of the solvent), the question arises as to their most satisfactory mathematical representation as a function of temperature. In the absence of theoretically well-founded models of general validity, one has to rely on essentially empirical correlating equations, subject, however, to some important thermodynamic constraints. Depending on the choice of variables, that is T or $1/T$, for expanding the enthalpy of solution (see later), either the *Clarke–Glew* (CG) equation [379–381]

$$\ln[h_{2,1}(T, P_{\sigma,1}(T))/\text{Pa}] = A_0 + A_1(T/\text{K})^{-1} + A_2 \ln(T/\text{K}) + \sum_{i=3}^n A_i (T/\text{K})^{i-2} \quad (127)$$

or the *Benson–Krause* (BK) equation [376, 377]

$$\ln[h_{2,1}(T, P_{\sigma,1}(T))/\text{Pa}] = \sum_{i=0}^m a_i (T/\text{K})^{-i} \quad (128)$$

are obtained. Both correlating equations are widely used, but on the basis of the ability to fit high-precision Henry fugacities over fairly large temperature ranges, and of simplicity, the BK power series in $1/T$ appears to be superior. In passing we note that the 3-term version of Eq. 127 is the well-known Valentiner equation [382].

At this juncture I would like to emphasize again that the frequently found sweeping statement “the solubility of a gas in a liquid decreases with increasing temperature” is misleading/incorrect when the entire liquid range between the triple point and the critical point of the solvent is considered. For many systems, the following behavior is well documented: at low temperatures (starting at the solvent triple point), $h_{2,1}(T, P_{\sigma,1})$ *increases* with increasing temperature, passes through a *maximum*, and then *decreases* towards its *finite* limiting value at the solvent’s critical point:

$$\lim_{\substack{T \rightarrow T_{c,1} \\ P_{\sigma,1} \rightarrow P_{c,1}}} h_{2,1}(T, P_{\sigma,1}) = \phi_2^{V\infty}(T_{c,1}, P_{c,1}) P_{c,1}, \quad (129)$$

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

$$\phi_2^{V\infty}(T_{c,1}, P_{c,1}) = \phi_2^{L\infty}(T_{c,1}, P_{c,1}). \tag{130}$$

Here, $\phi_2^{V\infty}(T_{c,1}, P_{c,1})$ and $\phi_2^{L\infty}(T_{c,1}, P_{c,1})$ are the fugacity coefficients of component 2 at infinite dilution in the vapor phase and the liquid phase, respectively, at the critical point. Clearly, under these conditions Eq. 125 is no longer adequate and has to be replaced by an expression appropriate for elevated pressures/elevated densities. As I have shown some time ago [12, 25–27, 30, 33–35, 383, 384], this exact limiting value follows directly from the generally valid relation

$$\phi_i^{L\infty}(T, P) = \frac{h_{i,j}(T, P)}{P}. \tag{131}$$

An example of the solubility behavior of gases in liquid water is provided by Fig. 5, where the Henry fugacities, i.e. $\ln[h_{2,1}(T, P_{\sigma,1})/\text{GPa}]$, of methane dissolved in liquid water, and of krypton dissolved in liquid water, are plotted against temperature [23, 385]. The system {water (1) + methane(2)} plays an important role in discussions of hydrophobic effects [311, 312] as well as in the exploration of offshore oil fields [386].

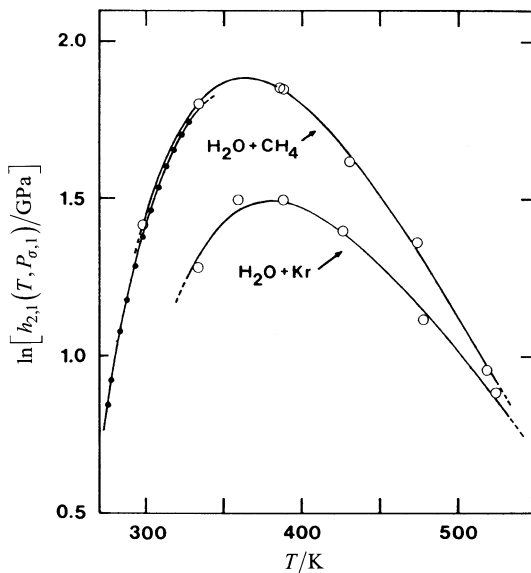


Fig. 5 Plot of $\ln[h_{2,1}(T, P_{\sigma,1})/\text{GPa}]$ against temperature T for krypton and methane dissolved in liquid water. $h_{2,1}(T, P_{\sigma,1})$ denotes the Henry fugacity (Henry’s law constant) at temperature T and corresponding pressure $P_{\sigma,1}(T)$, the vapor pressure of water. *Open circles* experimental results of Crovetto et al. [385]: the average percentage deviation of the Henry fugacities from the values calculated via BK-type fitting equations is about $\pm 2\%$. *Filled circles* experimental results of Rettich et al. [23]: the average percentage deviation of the Henry fugacities from the values calculated via the correlating BK function, Eq. 128, is about $\pm 0.05\%$. The temperature where the Henry fugacity exhibits a maximum is about 382 K for $\text{H}_2\text{O} + \text{Kr}$, and about 363 K for $\text{H}_2\text{O} + \text{CH}_4$. The limiting values of the respective Henry fugacities $h_{2,1}(T, P_{\sigma,1})$ as $T \rightarrow T_{c,1}$ and $P_{\sigma,1} \rightarrow P_{c,1}$ are finite and given by Eq. 129, the limiting slope of the curves is $-\infty$, see Eq. 132

While the Henry fugacity remains *finite* at $T_{c,1}$, for *volatile* solutes the *limiting slope diverges* to $-\infty$:

$$\lim_{\substack{T \rightarrow T_{c,1} \\ P \rightarrow P_{c,1}}} \frac{d \ln [h_{2,1}(T, P_{\sigma,1})/\text{Pa}]}{dT} = -\infty \quad (132)$$

when the critical point of the solvent is approached along the coexistence curve [387, 388].

Nonclassically, the temperature derivative diverges as $\left| (T - T_{c,1})/T_{c,1} \right|^{\beta-1}$, with a critical exponent $\beta = 0.326$.

Until the mid 1980s, high-precision measurements of Henry fugacities over temperature ranges large enough to permit *van't Hoff-type* data treatment constituted the only reliable source of information on *partial molar enthalpy changes on solution*,

$$\Delta H_2^\infty(T, P_{\sigma,1}) = H_2^{L\infty}(T, P_{\sigma,1}) - H_2^{\text{pg}*}(T), \quad (133)$$

and a fortiori on *partial molar heat capacity changes on solution*,

$$\Delta C_{P,2}^\infty(T, P_{\sigma,1}) = C_{P,2}^{L\infty}(T, P_{\sigma,1}) - C_{P,2}^{\text{pg}*}(T). \quad (134)$$

Here, $H_2^{L\infty}$ is the partial molar enthalpy of the solute at infinite dilution in the liquid solvent, $H_2^{\text{pg}*}$ is the molar enthalpy of the pure solute in the perfect gas state, $C_{P,2}^{L\infty}$ is the partial molar heat capacity at constant pressure of the solute at infinite dilution in the liquid solvent, and $C_{P,2}^{\text{pg}*}$ is the molar heat capacity at constant pressure of the pure solute in the perfect gas state. Since the temperature dependence of the Henry fugacity is given by

$$\left(\frac{\partial \ln h_{2,1}(T, P)}{\partial T} \right)_P = -\frac{\Delta H_2^\infty(T, P)}{RT^2}, \quad (135)$$

and its pressure dependence by

$$\left(\frac{\partial \ln h_{2,1}(T, P)}{\partial P} \right)_T = \frac{V_2^{L\infty}(T, P)}{RT}, \quad (136)$$

where $V_2^{L\infty}$ is the partial molar volume of the gas at infinite dilution in the liquid solvent, we obtain [23, 26–28, 30–34, 383],

$$\frac{\Delta H_2^\infty(T, P_{\sigma,1})}{RT} = -T \frac{d \ln [h_{2,1}(T, P_{\sigma,1})/\text{Pa}]}{dT} + \frac{V_2^{L\infty}}{R} \frac{dP_{\sigma,1}}{dT}, \quad (137)$$

and by analogous arguments

$$\begin{aligned} \frac{\Delta C_{P,2}^\infty(T, P_{\sigma,1})}{R} &= \frac{d\Delta H_2^\infty(T, P_{\sigma,1})}{RdT} - \frac{1}{R} \left[V_2^{L\infty} - T \left(\frac{\partial V_2^{L\infty}}{\partial T} \right)_P \right] \frac{dP_{\sigma,1}}{dT} \\ &= -2T \frac{d \ln [h_{2,1}(T, P_{\sigma,1})/\text{Pa}]}{dT} - T^2 \frac{d^2 \ln [h_{2,1}(T, P_{\sigma,1})/\text{Pa}]}{dT^2} \end{aligned} \quad (138a)$$

$$+ 2 \frac{T}{R} \left(\frac{\partial V_2^{L\infty}}{\partial T} \right)_P \frac{dP_{\sigma,1}}{dT} + \frac{T}{R} \left(\frac{\partial V_2^{L\infty}}{\partial P} \right)_T \left(\frac{dP_{\sigma,1}}{dT} \right)^2 + \frac{TV_2^{L\infty}}{R} \frac{d^2 P_{\sigma,1}}{dT^2}. \quad (138b)$$

The ordinary differential quotients in Eqs. 137 and 138a, 138b indicate differentiation while maintaining *orthobaric* conditions: the first term on the right-hand-side of Eq. 137 as

well as the first and the second term on the right-hand-side of Eq. 138b may be obtained from any one of the selected fitting equations, say the BK equation Eq. 128. The additional terms on the right-hand-side, containing $V_2^{L\infty}$ and its derivatives with respect to T and P together with $dP_{\sigma,1}/dT$ and $d^2P_{\sigma,1}/dT^2$, are referred to in the literature [388, 389] as *Wilhelm terms*. For aqueous solutions, say, of the rare gases below 100 °C, their contributions are small, usually smaller than the experimental error associated with current precision measurements. However, their contributions increase rapidly with increasing temperature. In fact, 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, see Wood et al. [390, 391], and the partial molar enthalpy at infinite dilution will diverge in exactly the same manner. The partial molar isobaric heat capacity at infinite dilution, $C_{p,2}^{L\infty}$, diverges in a more complex way and much stronger than either $V_2^{L\infty}$ or $H_2^{L\infty}$ [392–396]. The important experiments of Wood et al. confirm the theoretical expectations. The influences of these divergences are felt relatively far from the critical point.

As pointed out above, *direct* calorimetric determinations of the high-dilution partial molar enthalpy change when a gas is dissolved in a liquid have been carried out by only a very limited number of research groups, primarily due to the *very* small heat effects involved. Besides calorimetric sensitivity, achieving the dissolution of an accurately known amount of gas in a time interval compatible with the stability of the calorimeter is another important experimental problem. Battino and Marsh [397] used a modified isothermal displacement calorimeter to measure $\Delta H_2^\infty(T, P_{\sigma,1})$ of argon and nitrogen in tetrachloromethane, cyclohexane and benzene at 298.15 K, and of carbon dioxide, methane, ethane, ethene and propane in the same three solvents at 298.15 K and 318.15 K, and derived reasonable $\Delta C_{p,2}^\infty(T, P_{\sigma,1})$ values from

$$\Delta C_{p,2}^\infty(T, P_{\sigma,1}) \cong \frac{d\Delta H_2^\infty(T, P_{\sigma,1})}{dT}. \quad (139)$$

The *major* step forward for measuring $\Delta H_2^\infty(T, P_{\sigma,1})$ over extended temperature ranges with a precision high enough to allow the reliable determination of $\Delta C_{p,2}^\infty(T, P_{\sigma,1})$ is based on the development of microcalorimeters (batch or flow) by I. Wadsö's group at the Thermochemistry Laboratory in Lund, Sweden, and by S. J. Gill in the Chemistry Department of the University of Colorado in Boulder, Colorado, USA [398, 399]. There exist only *seven sets* of *directly* determined heat capacities of gases dissolved in liquid water, all originating from R. H. Wood's laboratory at the University of Delaware, Newark, Delaware, USA [394–396]. Regrettably, so far no other research groups have continued work in this field.

Recently, Wilhelm [28, 30] and Wilhelm and Battino [32] presented comprehensive compilations of calorimetrically determined results for $\Delta H_2^\infty(T, P_{\sigma,1})$ and $\Delta C_{p,2}^\infty(T, P_{\sigma,1})$ for many gases dissolved in liquid water at $T = 298.15$ K and $P_{\sigma,1}(298.15 \text{ K}) = 3.1691$ kPa, together with van't Hoff-derived enthalpy changes on solution and heat capacity changes on solution. As representative examples, Table 1 shows such a comparison for argon [22, 357, 376, 389, 394, 400–403], oxygen [22, 29, 376, 377, 398, 399, 401, 405] and methane [22, 23, 396, 401, 406–408]. Evidently, comparing van't Hoff derived enthalpy changes (*one* differentiation step with respect to T) and heat capacity changes (*two* differentiation steps with respect to T) with high-precision calorimetric results constitutes a severe quality test of solubility data. For nearly all solutions, agreement between these two approaches is entirely satisfactory, that is it is usually within the

Table 1 Partial molar enthalpy changes on solution $\Delta H_2^\infty(T, P_{\sigma,1})$ and partial molar heat capacity changes on solution $\Delta C_{p,2}^\infty(T, P_{\sigma,1})$ of argon, oxygen and methane dissolved in liquid water at $T = 298.15$ K and $P_{\sigma,1} = 3.1691$ kPa: comparison of values obtained via *van't Hoff*-type analysis of precision gas solubility measurements (see Eqs. 137 and 138a, 138b) with values obtained by *calorimetric* methods

| Gas dissolved in liquid water at 298.15 K | From solubilities (van't Hoff-type analysis) | | From calorimetry | |
|---|---|---|---|---|
| | $\Delta H_2^\infty(T, P_{\sigma,1})$ (kJ·mol ⁻¹) | $\Delta C_{p,2}^\infty(T, P_{\sigma,1})$ (J·K ⁻¹ ·mol ⁻¹) | $\Delta H_2^\infty(T, P_{\sigma,1})$ (kJ·mol ⁻¹) | $\Delta C_{p,2}^\infty(T, P_{\sigma,1})$ (J·K ⁻¹ ·mol ⁻¹) |
| Ar | -11.95 [376] ^a | 186 [376] ^a | -12.01 [401] | 200 [401] |
| | -11.92 [389] | 195 [389] | -11.94 [402] | 185 [394] ^c |
| | -11.96 [357] | 192 [357] | -12.00 [403] | |
| | -12.27 [22] ^b | 178 [22] ^b | | |
| O ₂ | -12.19 [376] | 192 [376] | -12.00 [401] | 205 [401] |
| | -12.09 [405] | 138 [405] | -12.06 [398] | |
| | -12.01 [377] | 196 [377] | -12.03 [399] | |
| | -11.97 [29] | 200 [29] | | |
| | -12.06 [22] ^b | 200 [22] ^b | | |
| CH ₄ | -13.19 [23] | 237 [23] | -13.06 [401] | 242 [401] |
| | -13.79 [22] ^b | 207 [22] ^b | -13.12 [406] | 209 [406] |
| | | | -13.18 [407] | 218 [408] |
| | | | 212 [396] ^c | |

^a In their quoted article, Benson and Krause [376] recalculated the original experimental data of Murray and Riley [400]

^b For the sake of comparison, I included van't Hoff values obtained from older measurements as published in the review article by Wilhelm et al. [22] more than 35 years ago. These values are the result of our critical evaluation of the extant literature at that time, and the agreement with more modern results is satisfactorily good

^c After extrapolating the calorimetrically determined apparent molar heat capacity to 298.15 K and setting it approximately equal to $C_{p,2}^{L,\infty}(T, P_{\sigma,1})$, as suggested by the authors [394, 396], Eq. 134 was used with $C_{p,2}^{pgs}(\text{Ar}) = 20.79$ J·K⁻¹·mol⁻¹ and $C_{p,2}^{pgs}(\text{CH}_4; 298.15 \text{ K}) = 35.79$ J·K⁻¹·mol⁻¹, respectively, taken from Landolt-Börnstein [404] in (1961), to obtain the $\Delta C_{p,2}^\infty(T, P_{\sigma,1})$ values reported in the table

combined experimental errors. What a credit to the experimental ingenuity, perseverance and skills of solution thermodynamicists!

5 Concluding Remarks and Outlook

By common consent, the liquid state of matter still houses by far the largest group of unsolved/crudely solved problems in modern physical chemistry. Research on pure liquids continues to be an active field, and water is definitely the most enigmatic solvent. When studying liquid mixtures/solutions, the appearance of *new* phenomena not present in the pure components constitutes a most stimulating theoretical challenge and is of enormous practical importance: these aspects provide the principal reasons for investing so much experimental and theoretical work in the investigation of mixture/solution properties. When combined with advances in the *statistical-mechanical treatment* and increasingly sophisticated *computer simulations*, new insights and important connections at the microscopic, mesoscopic and macroscopic level are obtained. Pride of place, of course, is

held by aqueous solutions, which are of central importance in biophysics and biophysical chemistry [368, 409–412]. And, of course, studies of aqueous interfaces and of the behavior of solutes therein (in particular ionic solutes) [413–421] have greatly profited from recent advances in surface selective spectroscopic techniques.

Calorimetry, *PVT* measurements and *VLE* determinations (and liquid–liquid equilibrium determinations and solid–liquid equilibrium determinations) are the most fundamental and also the oldest experimental disciplines of physical chemistry. Although simple in principle, enormous effort and ingenuity had to be invested into the construction of scientific instruments to provide the vast array of apparatus now at our disposal for the high-precision determination of caloric, *PVT* and ultrasonic properties of pure and mixed fluids over large ranges of temperature and pressure, and for vapor–liquid, liquid–liquid and solid–liquid equilibrium studies. The major driving forces for progress in instrumentation are the desire to (I) increase the area of applicability (larger temperature and pressure ranges, ever smaller concentrations, etc.), to (II) improve precision and accuracy (in particular for testing and developing theories), to (III) increase the speed of measurements, and to (IV) facilitate application, data management and data transfer. Undoubtedly, automation of instruments will continue, and so will miniaturization. In summary, *chemical thermodynamics* of liquids and liquid mixtures/solutions in general, and of aqueous systems in particular, will continue to be an exciting, developing field, and cross-fertilization with other disciplines, notably with molecular biology and molecular medicine, will become increasingly important. A rich research area lies ahead with *many new and fascinating vistas of importance for mankind*, and here the “*end of scientific discovery*” [422] is nowhere in sight.

The field of chemical thermodynamics has grown too big to be covered in one modest review article, but for the three subsections treated above (to which I have contributed over the years) I hope to have succeeded in providing a feeling for their scope, position in the development of science, and potential. It is a pleasure to acknowledge the many years of fruitful scientific collaboration with my former PhD advisor, Friedrich Kohler (†), with Rubin Battino, now Emeritus Professor at Wright State University (WSU), Dayton, Ohio, USA, with Jean-Pierre E. Grolier, now Emeritus Professor at Université Blaise Pascal, Clermont-Ferrand, France, with Henry V. Kehiaian (†), with Augustinus Asenbaum, now Retired Professor of Experimental Physics at the University of Salzburg, Salzburg, Austria, and about 80 colleagues, post-doctoral fellows and students from 17 countries. Without them, many projects would have been difficult to carry out. My association with chemical thermodynamics led to two extended stays in the United States of America at WSU, Dayton, Ohio, of about 4 years altogether, which I greatly enjoyed, and to more than 5 years, altogether, in France, first at the CRMT/CNRS, Marseille, and then at the Université Blaise Pascal, Clermont-Ferrand, which I also greatly enjoyed. Fortunately, over the years the University of Wien (Vienna), Wien, Austria, was generous enough to grant repeatedly extended *Leaves of Absence* for scientific research abroad.

6 Glossary of Symbols

In most cases I have adhered to the nomenclature/symbols suggested by IUPAC (see Green Book, *Quantities, Units and Symbols in Physical Chemistry* [423]). Deviations are due to my desire to present a concise, unequivocal and logically consistent notation in compliance with usage preferred by the scientific community interested in this review’s topics, *i.e.* by physical chemists, physicists and chemical engineers. Such an approach is in accord with

the spirit of the Green Book expressed so admirably by Martin Quack in his *Historical Introduction* on p. XII of its 3rd edition, 2007: *It is not the aim to present a list of recommendations in form of commandments. Rather we have always followed the principle that this manual should help the user in what may be called “good practice of scientific language”*. Two quantities in particular I would like to single out to comment on: the Helmholtz energy (Helmholtz function) F and the pressure P . Sometimes the Helmholtz energy is denoted by A , which symbol is, however, almost universally used for the *affinity* of a chemical reaction as introduced by Th. De Donder in 1922, as quoted by Prigogine and Defay [424]. In addition, when surfaces are involved, A usually denotes the surface area. The symbol P for pressure is now accepted by IUPAC as an alternative to p , as indicated in Tables 2.2 and 2.10 of the Green Book. The reason why I (and many others) prefer P is the following. Temperature and pressure are *both* intensive quantities, and together with the composition they form a set of basic thermodynamic variables advantageously used for *homogeneous* fluids in equilibrium states. They are not perceived primarily as properties of the fluids but as conditions imposed on/exhibited by them with the valuable bonus of being (in principle) easily measured and controlled. In other words, temperature and pressure are quantities of “*equal rank*”, which fact should be reflected in the symbols we use, that is to say *capital T* and *capital P*. For heterogeneous PVT systems consisting of several phases in equilibrium with each other, temperature and pressure are identical in the coexisting phases. We note that Griffiths and Wheeler [425] call such variables *fields* (in contradistinction to variables that are in general *not* equal in coexisting phases, such as volume, enthalpy and entropy, which they call *densities*).

Some of the symbols listed below may be *modified* further, with obvious meaning, by adding appropriate subscripts, such as σ (saturation or orthobaric condition), and/or superscripts, such as * (pure substance), ∞ (infinite dilution), and L (liquid) or V (vapor). The *capital* superscript letters are used because (i) they are easy to read, (ii) they are frequently used in the chemical engineering literature, including important monographs (for instance, Prausnitz et al. [43], Poling et al. [55]) and volumes published under the auspices of the International Union of Pure and Applied Chemistry (IUPAC) [69], and (iii) vapor–liquid equilibrium is usually abbreviated by VLE, and not by vle. The values for some fundamental physical constants listed in the glossary below are CODATA recommended values [107, 426].

Variables

- a Parameter in the expression for the molar cooperative free energy, Eq. 110
- a_j $=a_j(P, \{x_i\})$, $j = 1, 2, 3, \dots$ dimensionless coefficients used to describe the temperature dependence of C_p^E/R , S^E/R , H^E/RT , and G^E/RT , Eqs. 95–98
- a_i $i = 0, 1, 2, \dots$ dimensionless coefficients used to describe the temperature dependence of the Henry fugacity, i.e. of $\ln[h_{2,1}(T, P_{\sigma,1}(T))/\text{Pa}]$, Eq. 128 (BK)
- A_i $i = 0, 1, 2, \dots$ dimensionless coefficients used to describe the temperature dependence of the Henry fugacity, i.e. of $\ln[h_{2,1}(T, P_{\sigma,1}(T))/\text{Pa}]$, Eq. 127 (CG)
- A^+ Amplitude of the leading critical divergence in the homogeneous one-phase region above the upper critical solution temperature T_{uc} for a path at constant critical composition x_{uc} : see the power law describing the weak divergence of $C_{p,x_{uc}}$, Eq. 115

| | |
|---------------------------|---|
| b | Parameter in the expression for the molar cooperative free energy, Eq. 110 |
| B | Non-diverging background term in the power law describing the weak divergence of $C_{P,x_{uc}}$, Eq. 115 |
| B | Second virial coefficient of a gaseous mixture |
| B_{11}, B_{22} | Second virial coefficients of the pure gaseous components 1 and 2 when using the volume-explicit virial equation in pressure $Z \equiv PV/RT = 1 + B_{ii}P/RT$, $i = 1$ or 2 |
| B_{12} | Vapor-phase interaction virial coefficient (cross-coefficient) |
| c_{ii} | Cohesive energy density of pure liquid i , Eqs. 65 and 67 |
| C_P^L, C_P^V | Molar heat capacity at constant pressure (molar isobaric heat capacity) of the liquid (L) or of the vapor (V), respectively |
| $C_{P,2}^{L\infty}$ | Partial molar heat capacity at constant pressure of solute 2 at infinite dilution in a liquid (L) solvent 1 |
| $\Delta C_{P,2}^{\infty}$ | Partial molar heat capacity change on solution of a gas (2) in a liquid (1) at infinite dilution |
| C_V^L, C_V^V | Molar heat capacity at constant volume (molar isochoric heat capacity) of the liquid (L) or the vapor (V), respectively |
| C_σ^L | Molar heat capacity of a liquid (L) maintained at all temperatures in equilibrium with an infinitesimal amount of vapor (or shorter: molar heat capacity of a liquid at saturation) |
| C_σ^V | Molar heat capacity of a saturated vapor (superscript V) |
| $C_{P,2}^{pg*}(T)$ | Molar heat capacity at constant pressure of a pure fluid in the perfect-gas (ideal-gas) state |
| $C_V^{pg}(T)$ | $= C_P^{pg}(T) - R$, Molar heat capacity at constant volume of a fluid in the perfect-gas (ideal-gas) state |
| C_P^E | Excess molar heat capacity at constant pressure |
| C_V^r | Residual molar heat capacity at constant volume in (T, V) -space |
| C_{tr}^L | Translational contribution to C_V^L arising from the motion of the centers of gravity of the molecules under the influence of all the other molecules in the liquid system |
| C_{rot}^L | Contribution to C_V^L originating from the rotational movement of the molecules as a whole; includes contributions due to <i>hindered</i> rotation (libration) |
| C_{int}^L | Contribution to C_V^L originating from internal degrees of freedom |
| C_{or}^L | Contribution to C_V^L originating from the change of the dipole–dipole orientational energy with temperature |
| D^+ | Amplitude of the <i>first</i> correction-to-scaling term (Wegner term), see Eq. 115 |
| E | Parameter referring to the background heat capacity of a liquid mixture, see Eq. 115 |
| f | Fugacity |
| f_i | Fugacity of component i in solution (liquid phase or vapor phase) |
| f_i^{V*} | $= \phi_i^{V*}P$, fugacity of pure substance i in the vapor phase |
| F | Molar Helmholtz energy |
| $g(r, T, \rho_n)$ | Pair distribution function |
| G | Molar Gibbs energy |
| G^E | Excess molar Gibbs energy |

| | |
|----------------------------|---|
| G_{or}^{E} | Orientational contribution to the excess molar Gibbs energy caused by a permanent electric dipole moment of one of the components |
| G_i^{E} | $=\mu_i^{\text{E}} = RT\ln\gamma_i$, excess partial molar Gibbs energy of component i of a mixture/solution, also known as excess chemical potential |
| $h_{i,j}$ | $=h_{i,j}(T, P)$, Henry fugacity (or Henry's law constant) of component i dissolved in solvent j . Usually, experimental data are reported at pressures $P = P_{\sigma,j}$, the vapor pressure of the solvent |
| H | Molar enthalpy |
| H^{E} | Excess molar enthalpy |
| $\Delta_{\text{vap}}H$ | Molar enthalpy of vaporization |
| ΔH_2^{∞} | Partial molar enthalpy change on solution of a gas (2) in a liquid (1) at infinite dilution |
| k_{B} | $=R/N_{\text{A}} = 1.380\,650\,4(24) \times 10^{-23} \text{ J}\cdot\text{K}^{-1}$, Boltzmann constant |
| k_{12} | Scatchard–Hildebrand binary interaction parameter, Eq. 66 |
| l | $=1.2045$, lattice-specific constant in the Pople model (face-centered cubic), Eq. 106; for a body-centered cubic lattice $l = 1.5317$ |
| m | Mass |
| m, n | Mie parameters, Eq. 51; when $m = 6$ and $n = 12$ they are called Lennard-Jones parameters, Eq. 53 |
| m_{MTE} | Dimensionless parameter in the modified Tait equation, Eq. 62; for many liquid nonelectrolytes at ordinary temperatures $m_{\text{MTE}} \approx 10$ |
| M_{m} | $=m/n$, molar mass |
| n | $=\sum_i n_i$, total amount of substance |
| n_i | Amount of substance of component i of a mixture/solution |
| N_{A} | $=6.022\,141\,79(30) \times 10^{23} \text{ mol}^{-1}$, Avogadro constant |
| p | Permanent molecular electric dipole moment |
| p_{r} | Reduced dipole moment, Eq. 104 |
| P | Pressure |
| P_{c} | Critical pressure |
| P_{σ} | Vapor pressure |
| P_{ref} | Suitably selected reference pressure, frequently $10^5 \text{ Pa} = 0.1 \text{ MPa}$ |
| r | Distance between molecules |
| R | $=8.314\,472(15) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$, (molar) gas constant |
| S | Molar entropy |
| S^{E} | Excess molar entropy |
| t | $= (T - T_{\text{uc}})/T_{\text{uc}} $, dimensionless variable measuring the reduced distance, temperature-wise, from the upper critical solution temperature T_{uc} |
| T | Thermodynamic temperature |
| T_{c} | Critical temperature |
| T_{r} | Reduced temperature |
| T_{ref} | Suitably selected reference temperature |
| T_{mp} | Melting (fusion) temperature |
| T_{tr} | Triple point temperature |
| T_{bp} | Normal boiling temperature |
| T_{uc} | Upper critical solution temperature |
| $u(r)$ | Pair-potential-energy function |
| U | Molar internal energy |
| U^{r} | Molar residual internal energy |

| | |
|-------------------------------------|---|
| U^c | Molar configurational internal energy |
| $U_{\text{coh}}^L(T, P)$ | Molar cohesive energy density of a liquid, Eq. 54 |
| $(\frac{\partial U}{\partial V})_T$ | $\equiv \Pi(T, P)$, internal pressure |
| v_0 | Thermodynamic speed of ultrasound (at low frequencies) |
| V | Molar volume |
| V_c | Critical molar volume |
| V^E | Excess molar volume |
| $\Delta_{\text{vap}}V$ | Molar volume change on vaporization |
| W | Cooperative free energy in the simple Guggenheim model, see Eq. 110 |
| x_i | $= n_i^L/n^L$, liquid-phase mole fraction of component i of a mixture/solution, $\sum_i n_i^L = n^L$; $\sum_i x_i = 1$ |
| x_{uc} | Critical composition, pertaining to an upper critical solution point (liquid–liquid equilibrium) with an upper critical solution temperature (UCST) T_{uc} |
| y_i | $= n_i^V/n^V$, vapor-phase mole fraction of component i of a mixture/solution, $\sum_i n_i^V = n^V$; $\sum_i y_i = 1$ |
| Z | $\equiv PV/RT$, compression factor |

Greek letters

| | |
|-------------------------|---|
| α | ≈ 0.11 , universal nonclassical critical exponent pertaining to the weak divergence of C_V of <i>pure liquids</i> along the critical isochore, or universal nonclassical critical exponent pertaining to the weak divergence of C_P of a liquid <i>mixture</i> when determined along a path of constant critical composition x_{uc} as described by the power law, Eq. 115 |
| α_P | $\equiv V^{-1}(\partial V/\partial T)_P$, isobaric expansivity |
| α_{σ}^L | $\equiv (V^L)^{-1}(\partial V^L/\partial T)_{\sigma}$, expansivity of a pure liquid (L) in contact with its vapor (saturation expansivity) |
| β_S | $\equiv -V^{-1}(\partial V/\partial P)_S$, isentropic compressibility |
| β_T | $\equiv -V^{-1}(\partial V/\partial P)_T$, isothermal compressibility |
| γ_V | $\equiv (\partial P/\partial T)_V = \alpha_P/\beta_T$, isochoric thermal pressure coefficient |
| γ_{σ} | $\equiv (\partial P/\partial T)_{\sigma}$, slope of the vapor pressure curve, dP_{σ}/dT |
| γ_i | $= \gamma_i(T, P, x_i)$, activity coefficient of component i of a mixture/solution based on the symmetric Lewis–Randall (LR) convention |
| γ_i^{HL} | $= \gamma_i^{\text{HL}}(T, P, x_i)$, activity coefficient of component i of a mixture/solution based on the unsymmetric Henry’s law (HL) convention |
| $\delta(T, P)$ | Solubility parameter, Eq. 55 |
| $\delta(T, P_{\sigma})$ | Solubility parameter at saturation condition, Eq. 60 |
| Δ_1 | $= 0.5$, universal critical exponent associated with the <i>first</i> correction-to-scaling term (Wegner term [334]), Eq. 115 |
| Δ_{12} | $= 2B_{12} - (B_{11} + B_{22})$ |
| ε | Intermolecular energy parameter characterizing the well-depth of the interaction energy function, say, of the Mie function, Eq. 51 |
| ε_0 | $= 8.854187... \times 10^{-12} \text{ F}\cdot\text{m}^{-1}$, permittivity of vacuum (electric constant) |
| η | $= \exp(W/zRT)$, used in Eq. 114 which is based on Guggenheim’s quasi-chemical theory |
| Θ | “Reduced” temperature, Eq. 84 (Harrison and Moelwyn-Hughes [116]) |
| θ | “Reduced” temperature, Eq. 85 (Wilhelm, this work) |

| | |
|---------------|--|
| κ | $\equiv C_p/C_V = \beta_T/\beta_S$, ratio of heat capacities or compressibilities, respectively |
| μ_i | Chemical potential of component i of a mixture/solution |
| μ_i^E | $\equiv G_i^E = RT \ln \gamma_i$, excess chemical potential of component i of a mixture/solution, LR convention |
| $\Pi(T, P)$ | Internal pressure |
| ρ | $\equiv M_m/V = m/(nV)$, mass density |
| ρ_n | $\equiv N_A/V$, number density |
| σ | Intermolecular distance parameter of the Mie intermolecular pair-potential-energy function, see Eq. 51; it is characterized by $u(\sigma) = 0$ |
| τ | $\equiv T_{\text{ref}}/T$ |
| ϕ_i | Fugacity coefficient of component i in solution (liquid phase or vapor phase) |
| ϕ_i^{V*} | Fugacity coefficient of pure substance i in the vapor phase |
| Φ_i | $\equiv x_i V_i^{L*} / (x_1 V_1^{L*} + x_2 V_2^{L*})$, $i = 1, 2$, volume fraction of component i in solution |

Superscripts

| | |
|----------|---|
| E | Excess quantity |
| HL | Indicates ideal-solution behavior based on Henry's law |
| L | Liquid phase |
| LR | Indicates ideal-solution behavior based on the Lewis–Randall rule |
| pg | Perfect-gas state (ideal-gas state) |
| r | Residual quantity in (T, V) -space |
| V | Vapor phase |
| * | Indicates a pure-substance property |
| ∞ | Infinite dilution |

Subscripts

| | |
|-----------|--|
| c | Critical property |
| cf | Central-force contribution |
| i, j, k | General indices; usually i denotes a component of a mixture/solution |
| int | Internal |
| or | Orientalional |
| r | Reduced quantity |
| rot | Rotational |
| tr | Translational |
| σ | Saturation (orthobaric) condition |

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