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DETERMINATION OF CALORIC QUANTITIES OF DILUTE LIQUID SOLUTIONS*

EMMERICH WILHELM

*Institut für Physikalische Chemie, Universität Wien,
Währingerstraße 42, A-1090 Wien, Austria*

ABSTRACT

This article reviews recent advances in the experimental determination of caloric quantities, for instance heat capacities, of dilute liquid nonelectrolyte solutions. *Direct* methods, i.e. calorimetric methods, as well as *indirect* methods, i.e. vapor-liquid equilibrium studies as a function of temperature, are considered.

1. INTRODUCTION

The subject of this review is the experimental determination of certain caloric quantities of dilute liquid nonelectrolyte solutions, with emphasis on enthalpy changes and heat capacity changes upon solution. This topic has been included in several recent state-of-the-art surveys, though with greatly differing coverage and from a variety of viewpoints.[1-21] Besides purely descriptive presentations of results, of pertinent instruments and of corresponding experimental techniques, the focus has been, for instance, on McMillan-Mayer or Kirkwood-Buff type analysis of data, application of group-contribution methods, critical behavior, order/disorder phenomena, hydrophobic effects in "simple" model solutions of biological relevance, aqueous micellar systems and interactions of biomolecules with water. The preponderance of work on aqueous systems is evident - it simply reflects the fact that water is our environment's primary and indispensable solvent.

Within the restricted scope of this article, only a few aspects can be considered. In particular, I will focus upon the concise formulation of the relevant thermodynamics for binary solutions, recent progress in instrumentation, and data treatment. Only a small number of experimental results will be presented: besides quantities obtained directly from calorimetric experiments, I will include quantities obtained via van't Hoff analysis of high-precision vapor-liquid equilibrium (VLE) studies. The emphasis will be on

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dilute aqueous solutions of "simple" nonelectrolytes, such as the rare gases or hydrocarbons of low molecular mass.

During the last decade, the statistical-mechanical theory of the liquid state has evolved rapidly. Together with results obtained from Monte Carlo and/or molecular dynamics calculations on model systems, it has furthered considerably our understanding of solutions in general, and of dilute aqueous solutions in particular. These topics, however, will only be touched upon. In passing we note that their combined impact has produced new and challenging demands for high-precision experiments to be used as discriminators in model evaluation. Figure 1 illustrates schematically the relative positions of experiment, theory and computer simulation by showing what may be gained from a comparison of respective results (under idealized conditions).

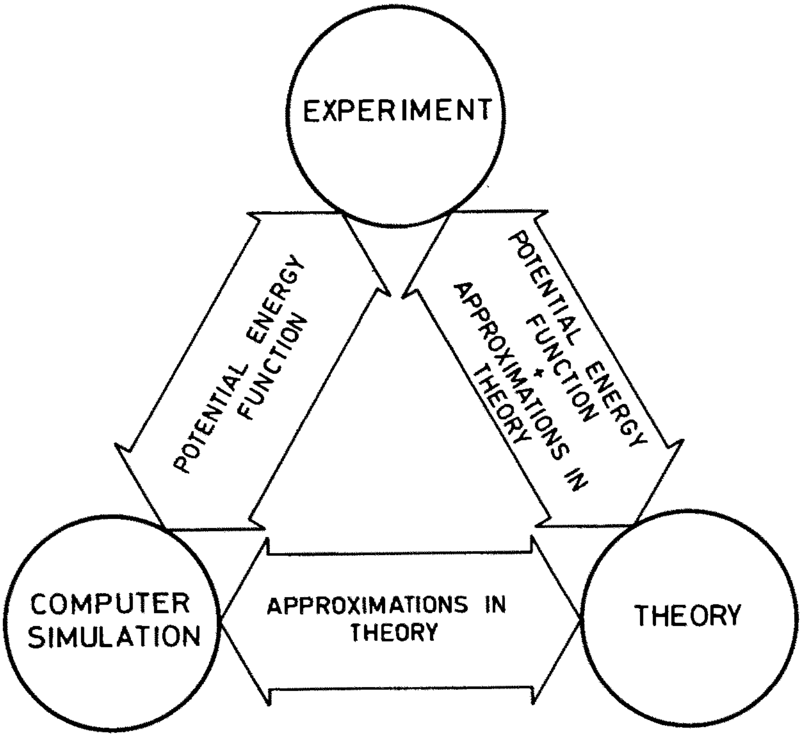

FIGURE 1. Relative positions of experiment, theory and computer simulation: the arrows signify possible comparisons and indicate the "objects" to be tested.

2. THERMODYNAMICS[13,14,18,21,22]

The thermodynamic description [*)] of dilute liquid two-component solutions of nonelectrolytes is advantageously based upon the *unsymmetric convention*, which rests on the two phenomenological limiting laws commonly known as the Lewis-Randall (LR) rule and Henry's law (HL). Let the fugacity of pure component i (= 1 or 2) be denoted by $f_i^* = f_i^*(T,P)$, the Henry fugacity (referring to a solution of i in j) by $H_{i,j} = H_{i,j}(T,P)$, were $i = j$, the fugacity of the binary solution by $f = f(T,P,x_i)$, where $x_i = n_i/\sum n_i$ is the mole fraction, and the component fugacity in solution by $f_i = f_i(T,P,x_i)$. At constant temperature T and pressure P we have for each component

$$\lim_{x_i \to 1} (f_i/x_i) = (df_i/dx_i)_{x_i=1} = f_i^* \quad \ldots \mathrm{LR}\,, \tag{1}$$

and

$$\lim_{x_i \to 0} (f_i/x_i) = (df_i/dx_i)_{x_i=0} = H_{i,j} \ldots \mathrm{HL}\,. \tag{2}$$

LR-based activity coefficients are defined by

$$\gamma_i \equiv f_i/x_i f_i^*\,, \tag{3}$$

and HL-based activity coefficients by

$$\gamma_i' \equiv f_i/x_i H_{i,j}\,. \tag{4}$$

Thus, when the unsymmetric convention is selected, we have for the component present in large excess, i.e. for the solvent (i = 1), $\gamma_1 = f_1/x_1 f_1^*$, and for the solute (i = 2), $\gamma_2' = f_2/x_2 H_{2,1}$. The corresponding excess molar Gibbs energy is given by

$$G^{E'}/RT = x_1 \ln\gamma_1 + x_2 \ln\gamma_2'\,. \tag{5}$$

[*)] Throughout this article molar properties are indicated by capital letters. The corresponding extensive properties, indicated by small letters, are obtained through multiplication with $n = m/M = \sum n_i$, the total amount of substance (m is the mass and M the molar mass). Pure-substance properties are indicated by a superscript*, $^{\circ}$ identifies a perfect-gas-state quantity, and $^{\infty}$ indicates infinite dilution. A subscript c denotes a critical quantity.

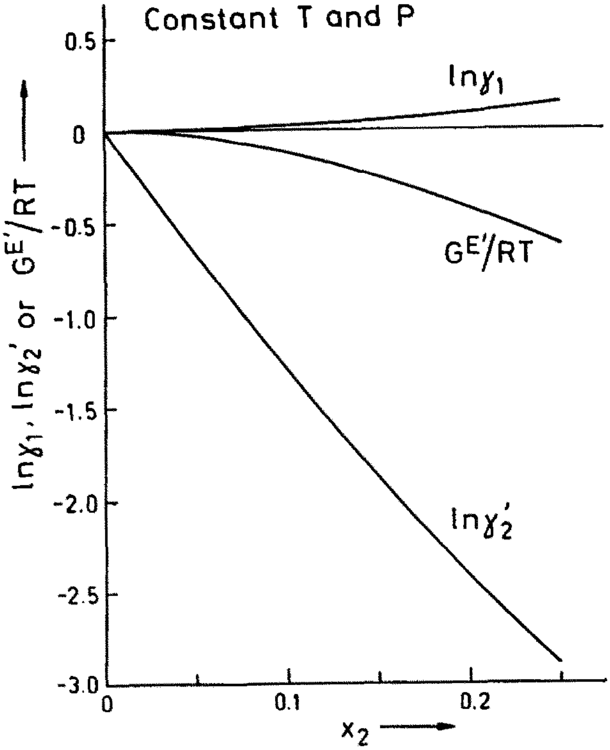

FIGURE 2. Composition dependence (schematic) of $\ln\gamma_1$ and $\ln\gamma_2'$ of a binary solution (*unsymmetric* convention) at constant T and P. Also included is the corresponding dimensionless quantity $G^{E'}/RT$, eq.(5).

A schematic representation of the composition dependence of $\ln\gamma_1$, $\ln\gamma_2'$ and $G^{E'}/RT$ is provided by figure 2.

The treatment based on the unsymmetric convention for the standard states is, of course, rigorously related to the symmetric convention (where *all* activity coefficients are defined by eq.(3)). The corresponding excess molar Gibbs energy is given by

$$G^E/RT = x_1 \ln\gamma_1 + x_2 \ln\gamma_2 \ . \tag{6}$$

From eqs.(2) through (4) we have

$$\gamma_i^\infty = \lim_{x_i \to 0} \gamma_i = H_{i,j}/f_i^* = \gamma_i/\gamma_i' \ , \tag{7}$$

whence the following relations hold:

$$(G^E - G^{E'})/RT = x_2 \ln(\gamma_2/\gamma_2') = x_2 \ln(H_{2,1}/f_2^*) = x_2 \ln \gamma_2^\infty \ . \tag{8}$$

Because of the unsymmetric normalization, $G^{E'}$ vanishes at infinite dilution with respect to the solute, that is for $x_2 \rightarrow 0$, but *not* for $x_1 \rightarrow 0$, where $G^{E'}(x_2 = 1)/RT = -\ln(H_{2,1}/f_2^*) = -\ln \gamma_2^\infty$. Physically, this reflects the fact that the ideal-solution model to which $G^{E'}$ refers is infinitely dilute in component 2. It is thus predominantly the *self-interaction* of solute 2 which causes deviations from Henry's law behavior; the unlike-species interactions exert their influence only indirectly through interference of the solute-solvent interactions of the solute species.

The link with the equation-of-state (EOS) formalism is established as follows. The fugacity coefficient of pure substance i, of a solution and of component i in solution are defined, respectively, by

$$\phi^* \equiv f_i^*/P \ , \tag{9}$$

$$\phi \equiv f/P \ , \tag{10}$$

and

$$\phi_i \equiv f_i/x_i P \ . \tag{11}$$

Thus, according to eq.(2) we have

$$\phi_i^\infty = \lim_{x_i \rightarrow 0} \phi_i = H_{i,j}/P \ . \tag{12}$$

Combination of eqs.(9),(11) and (12) with eqs.(3) and (4) yields

$$\gamma_i = \phi_i/\phi_i^* \ , \tag{13}$$

$$\gamma_i' = \phi_i/\phi_i^\infty \ , \tag{14}$$

and

$$\gamma_i^\infty = \phi_i^\infty/\phi_i^* \ . \tag{15}$$

In view of

$$\ln \phi = \sum_i x_i \ln \phi_i \tag{16}$$

and

$$\Delta \ln\phi \equiv \ln\phi - \left(x_1 \ln\phi_1^* + x_2 \ln\phi_2^*\right) , \tag{17}$$

$$\Delta \ln\phi' \equiv \ln\phi - \left(x_1 \ln\phi_1^* + x_2 \ln\phi_2^\infty\right) , \tag{18}$$

we obtain from eqs.(5) and (6)

$$G^E/RT = x_1 \ln(\phi_1/\phi_1^*) + x_2 \ln(\phi_2/\phi_2^*) = \Delta \ln\phi , \tag{19}$$

$$G^{E'}/RT = x_1 \ln(\phi_1/\phi_1^*) + x_2 \ln(\phi_2/\phi_2^\infty) = \Delta \ln\phi' , \tag{20}$$

and

$$(G^E - G^{E'})/RT = \Delta \ln\phi - \Delta \ln\phi' = x_2 \ln(\phi_2^\infty/\phi_2^*) . \tag{21}$$

The fugacity coefficients introduced above may be calculated from any adequate equation of state, either pressure-explicit or density-explicit, by simple, well-known expressions. In turn they may be used to obtain activity coefficients and excess molar Gibbs energies for both conventions.

We turn now to the temperature and pressure dependence of some of the quantities introduced above. For a constant-composition solution

$$\left(\frac{\partial \ln\phi_i}{\partial T}\right)_{P,x} = -\frac{H_i - H_i^o}{RT^2} , \tag{22}$$

$$\left(\frac{\partial \ln\phi_i}{\partial P}\right)_{T,x} = \frac{V_i - V_i^o}{RT} , \tag{23}$$

whence

$$\left(\frac{\partial \ln H_{i,j}}{\partial T}\right)_P = -\frac{H_i^\infty - H_i^o}{RT^2} \equiv -\frac{\Delta H_i^\infty}{RT^2} , \tag{24}$$

$$\left(\frac{\partial \ln H_{i,j}}{\partial P}\right)_T = \frac{V_i^\infty}{RT} , \tag{25}$$

$$\left(\frac{\partial \ln\gamma_i}{\partial T}\right)_{P,x} = -\frac{H_i - H_i^*}{RT^2} \equiv -\frac{H_i^E}{RT^2} , \tag{26}$$

$$\left(\frac{\partial \ln\gamma_i'}{\partial T}\right)_{P,x} = -\frac{H_i - H_i^\infty}{RT^2} \equiv -\frac{H_i^{E'}}{RT^2} , \tag{27}$$

$$\left(\frac{\partial \ln \gamma_i}{\partial P}\right)_{T,x} = \frac{V_i - V_i^*}{RT} \equiv \frac{V_i^E}{RT} \quad , \tag{28}$$

$$\left(\frac{\partial \ln \gamma_i'}{\partial P}\right)_{T,x} = \frac{V_i - V_i^\infty}{RT} \equiv \frac{V_i^{E'}}{RT} \quad , \tag{29}$$

where all the symbols have their usual significance. For instance, H_i and H_i^∞ are, respectively, the partial molar enthalpy of component i at a given composition and at infinite dilution, H_i^o is the molar enthalpy of pure i in the perfect-gas reference state, H_i^* is the molar enthalpy of pure i, ΔH_i^∞ is known as the partial molar enthalpy change upon solution, H_i^E is the excess partial molar enthalpy of i in solution defined according to the symmetric convention, and $H_i^{E'}$ is the excess partial molar enthalpy appropriate for the unsymmetric convention. Clearly,

$$\left(\frac{\partial \ln \gamma_i^\infty}{\partial T}\right)_P = - \frac{H_i^\infty - H_i^*}{RT^2} \equiv - \frac{H_i^{E\infty}}{RT^2} \tag{30}$$

$$= - \frac{H_i^E - H_i^{E'}}{RT^2} \quad , \tag{31}$$

and

$$\left[\frac{\partial (G^{E'}/RT)}{\partial T}\right]_{P,x} = - \frac{H^{E'}}{RT^2} = - \frac{x_1 H_1^E + x_2 H_2^{E'}}{RT^2} \quad . \tag{32}$$

Finally, with obvious notation, we obtain for the partial molar heat capacity change upon solution (at infinite dilution)

$$\Delta C_{P,i}^\infty = C_{P,i}^\infty - C_{P,i}^o = \left(\frac{\partial \Delta H_i^\infty}{\partial T}\right)_P = - \frac{R}{T^2}\left(\frac{\partial^2 \ln H_{i,j}}{\partial (1/T)^2}\right)_P \quad . \tag{33}$$

Equations (24) to (33) form the basis for comparisons of calorimetrically determined values (*direct* methods), say ΔH_2^∞, with those obtained from van't Hoff analysis of high-precision VLE data (*indirect* method). The next section will be devoted to recent contributions to both approaches.

3. EXPERIMENT

During the last decade, major advances in experimental techniques, as applied to dilute solutions, have been reported in the literature. As already stated in the introduction, it is far beyond the scope of this review to attempt to catalog, let alone to discuss, available experimental methods for

VLE studies or calorimetry. This section is merely intended to be a brief guide to recent publications by focussing upon a few, selected contributions to either

(1) novel designs of apparatus which significantly improve experimental precision and accuracy, and/or

(2) designs which increase the accessible pressure and temperature ranges.

The selection is, admittedly, somewhat biased and reflects to a significant degree current interests of the author. For more comprehensive surveys see refs. 11,12,14,15 and 23 through 27.

3.1. Vapor-Liquid Equilibria

An interesting automated apparatus, allowing the rapid and precise determination of vapor pressure-composition isotherms of dilute solutions by a *synthetic* method, has been conceived and constructed by Tucker. Conceptually, the design is simple.[28,29] It has four primary components:

(1) the vapor pressure sample chamber of known volume, containing a known amount of pure liquid solvent;

(2) the solute inlet system, which consists of a 6-port high-pressure liquid-chromatography valve with an external sample loop (ca. 20 mm^3) for transferring accurately known quantities of the volatile liquid solute into the measuring chamber;

(3) a quartz Bourdon-tube pressure gauge fitted with a BCD shaft encoder (minimum resolution of 0.13 Pa over the pressure range 0 to 40 000 Pa);

(4) a microcomputer reading pressure data via a BCD interface and sending control signals via a parallel output port.

The LC valve and the vapor pressure sample chamber are housed in a thermostat bath, the overnight temperature variations of which are of the order of ± 0.003 K. Figure 3 shows a photograph of the entire apparatus (courtesy of Professor Tucker).

In a typical experiment, successive amounts of liquid solute (which is stored in an external reservoir) are added to a degassed and thermostatted amount of solvent via the computer-actuated sample-addition valve. The pressure is read at preset time intervals, the final equilibrium vapor pressure is recorded, and the next solute increment is added. This sequence is repeated as often as desired. From the experimental data, that is from vapor pressure-composition isotherms, Henry fugacities and activity coefficients may be obtained. When repeated at several temperatures, appropriate thermodynamic manipulations, as indicated in section 2, lead to ΔH_2^{∞}, $\Delta C_{P,2}^{\infty}$ and so forth.

The use of this automated apparatus generally yields a large number of precise results, typically hundreds of sets P vs. x_2, for the dilute solution

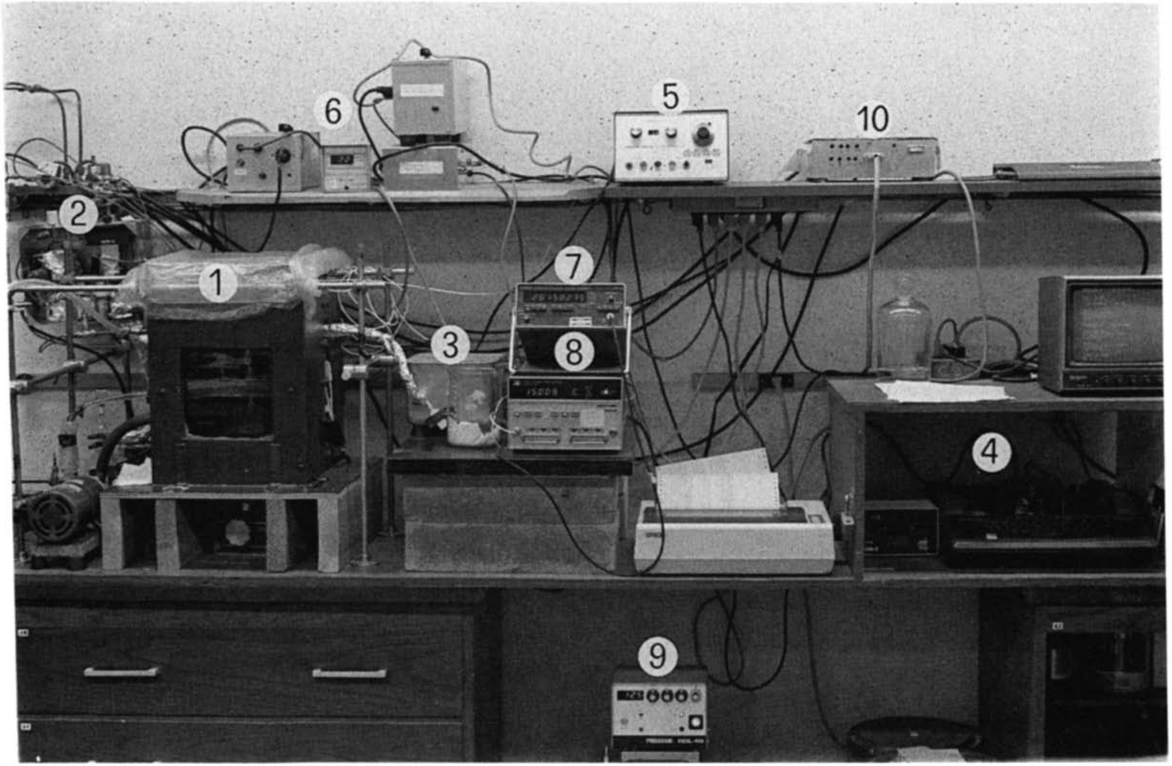

FIGURE 3. Automated vapor pressure apparatus as described in the text (for details see refs. 28 and 29): (1) sample chamber control bath; (2) solute reservoir and HPLC valve; (3) pressure transducer; (4) control computer; (5) sample bath temperature control; (6) temperature control and power supplies for HPLC valve and pressure transducer; (7) transducer readout; (8) quartz thermometer; (9) refrigeration circulator; (10) relay box for solenoids.

region. In order to retrieve physically meaningful power-series coefficients from ($P_{s,1}$ is the vapor pressure of pure solvent)

$$P = P_{s,1} + ax_2 + bx_2^2 + cx_2^3 + \cdots , \tag{34}$$

a numerical-derivative method, employing a running cubic spline, has been developed by Christian and Tucker.[30,31] Subsequently, these coefficients may be converted to McMillan-Mayer osmotic pressure virial coefficients, which are of central importance in the theory of dilute solutions.[21,32-34] Particularly interesting is the study of solutions of benzene in water,[29,35] an important model system for the discussion of hydrophobic effects. The good agreement of ΔH_2^∞ and $\Delta C_{P,2}^\infty$ so obtained with direct calorimetric results[36-38] (see below) is gratifying.

Similar in spirit is the automated apparatus of Tominaga et al.[39] for the determination of Ostwald coefficients. Both pressure control and measurement of the volume of gas dissolved in a given amount of liquid solvent are effected by a microprocessor. This design combines easy handling with automated data retrieval, and is totally mercury-free. From the experimental results, Henry fugacities may be evaluated rigorously,[8,13,14] and from their temperature dependence ΔH_2^∞ etc. may be obtained (see below).

An *analytical* high-precision method for VLE measurements on dilute solutions of gases in liquids has been developed by Rettich, Battino and Wilhelm (RBW), refs. 40 through 42. It is based on earlier work by Benson and Krause.[43,44] The compositions of the liquid phase and the vapor phase in equilibrium are determined via classical PvT measurements, and Henry fugacities are obtained rigorously according to

$$H_{2,1}(T, P_{s,1}) = \lim_{x_2 \to 0} \left(y_2 P \phi_2^V / x_2 \right) . \tag{35}$$

A schematic representation of the experimental situation is provided by figure 4.

The imprecision of the RBW approach is usually about ± 0.05%. Its reliability has been impressively demonstrated by

(1) the interlab accord for $H_{2,1}$ of oxygen dissolved in water: between 275 and 328 K the average difference between the values reported by us[40] and those reported by Benson and Krause[44] amounts to about 0.1%;

(2) the agreement of ΔH_2^∞ and $\Delta C_{P,2}^\infty$ obtained for several gases dissolved in water (H_2O + Ar, + N_2, + O_2, + CO, + CH_4, + C_2H_6, + C_2H_4, and + C_3H_8, see refs. 40-42, 45-47) with calorimetrically determined enthalpy and heat capacity changes[48-57] (see below).

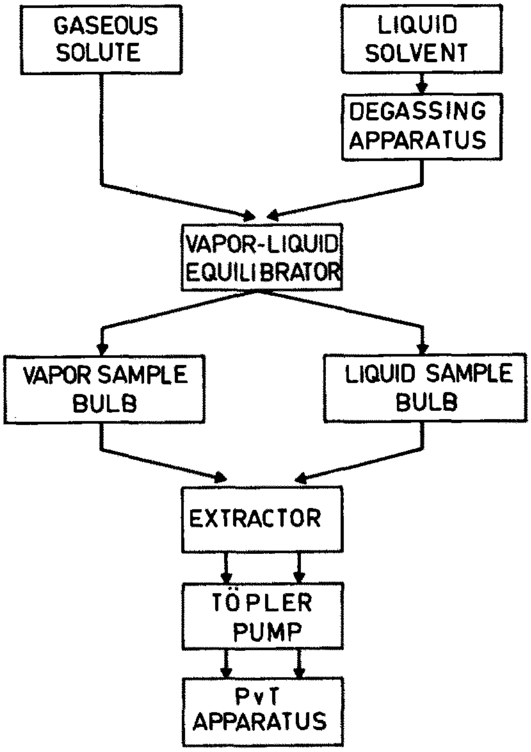

FIGURE 4. Block diagram of the experimental arrangement used in the RBW high-precision gas-solubility apparatus.[14,40-42,45-47]

When a comparison between, say, van't Hoff enthalpy changes and calorimetric measurements is desired, the empirical fitting equation representing the temperature dependence of the Henry fugacity has to be judiciously selected. Usually, either a Clarke-Glew type expression[58] or a power series in 1/T, as suggested by Benson and Krause,[43,44] is used. It is essential that some appropriate statistical criterion of goodness of fit is applied. For instance, the number of terms in either series should be based upon the F-test in conjunction with a *realistic attitude* as to the precision attainable with a particular experimental *method*.[58-60] Henry fugacities $H_{2,1}(T,P_{s,1})$ determined at different temperatures refer, of course, to different pressures $P_{s,1}(T)$. Thus the partial molar enthalpy change upon solution (see eq.(24)) is rigorously given by[8,13,14,18,40]

$$\Delta H_2^{\infty}(T,P_{s,1})/RT = \frac{d\ln[H_{2,1}(T,P_{s,1})/\mathrm{Pa}]}{Td(1/T)} + \frac{V_2^{\infty}}{R}\frac{dP_{s,1}}{dT} , \qquad (36)$$

with analogous expressions for $\Delta C_{P,2}^{\infty}$ and the higher derivatives. The first term on the rhs of eq.(36) is obtained from one of the selected fitting equations. The second term is usually overlooked, despite the fact that it increases rapidly with increasing temperature. Its evaluation requires a reliable vapor pressure equation for the solvent and information on the partial molar volume V_2^{∞} at infinite dilution.[14,61] At temperatures far below the critical temperature of the solvent, $T_{c,1}$, the second term will frequently, but not necessarily, be rather small as compared to the magnitude of the first term. Consider, for instance, methane dissolved in water.[40,62] Evidently, at the minimum-solubility temperature $T_m \approx 363$ K, that is the temperature where $H_{2,1}(T,P_{s,1})$ vs. T shows a maximum, the first term is exactly zero, and $\Delta H_2^{\infty}(T = T_m, P_{s,1})$ is entirely due to the second term.

Most of the measurements of $H_{2,1}$ reported in the literature have been performed at or close to 298.15 K, and data extending to temperatures near $T_{c,1}$ are rather scarce. This is even the case for gases dissolved in the most important liquid of all, water. Recent contributions to the measuring technique at elevated temperatures and pressures are due to Brass et al.,[63] Crovetto et al.,[62,64] Gerth,[65] and Japas and Franck.[66,67]

3.2. Calorimetry

For the direct calorimetric determination of enthalpies of solution of slightly soluble liquids in water, some years ago Gill, Nichols and Wadsö[36,37] reported on a flow microcalorimeter capable of measuring essentially ΔH_2^{∞} of benzene (and other hydrocarbons) in water at different temperatures. A new and substantially improved version has recently been presented by Nilsson and Wadsö.[38] While the design has been chosen with particular reference to water as solvent, it can be used for any liquid of low viscosity. It uses very small quantities of liquid solute, which may be very slightly soluble or easily soluble. In the latter case the instrument's precision approaches the level attainable by high-precision macrocalorimetric equipment. The syringe technique of injecting the solute into the solvent flow is simple and makes the measurement and calculation procedures amenable to automation. For details we refer to the original literature, refs. 36-38.

Until very recently, precision measurements of $H_{2,1}(T,P_{s,1})$ over sufficiently large ranges of temperature constituted the only reliable source of information on enthalpy changes upon solution, and *a fortiori* on heat capacity changes upon solution of sparingly soluble gases in liquids (see the preceding sections). The direct calorimetric determination of ΔH_2^{∞} for gases in liquids has been pioneered by Battino and Marsh,[68] Gill and Wadsö,[48] and Dec and Gill,[49] that of $\Delta C_{P,2}^{\infty}$ by Wood and collaborators.[56,57] In general, agreement with values obtained from van't Hoff analysis of high-precision solubility results is excellent[18] and may be taken as a tribute to both experimental ingenuity and state-of-the-art data reduction.

For measuring the heat effects associated with the process of dissolving a slightly soluble gas into water, two flow-microcalorimetric techniques[48,49] have been developed. The principle of the *steady-state* method is to bring together, within a heat-conduction calorimeter, accurately determined flows of gas and water, thereby forming a system in steady state of gas dissolution. The attainment of the steady state is brought about by computer control of the gas flow rate. The power generated by the continuously dissolving gas is detected by a semiconductor thermopile whose voltage output is proportional to the power. The calorimeter is calibrated electrically with an imprecision of 0.2% for power levels of 150-450 μW. Successive measurements of enthalpies of solution are reproducible within ± 1%. For details of the construction and operation of the most recent design we refer to the work of Dec and Gill.[49] When using the *batch-type* calorimeter reaction cell,[48] gas is added batchwise, that is by injecting a gas bubble containing a known amount of solute, into the water flow. The enthalpy change on solution is then determined by integration of the power against the time required for the gas to dissolve completely. Here too, electric calibration is used. The integration of the calorimeter recordings is made through use of a microprocessor.

Both methods give now results of comparable precision, though the steady-state method is potentially more advantageous when measurements at high temperatures and elevated pressures are intended.

The first direct calorimetric determination of the heat capacity of an aqueous solution of a slightly soluble gas has been published[56] at the end of 1985. The measurements on (H_2O + Ar) at about P = 17 MPa covered the range 306 to 578 K. The measuring principle is similar to that of the conventional Picker flow microcalorimeter.[69-72] Specifically, the power ratio W_S/W_W between the heaters in the sample cell (solution, S) and in the reference cell (water, W) is measured, from which the ratio of the corresponding specific heat capacities ($\hat{C}_P = C_P/M$) may be calculated using[73]

$$\hat{C}_{P,S}/\hat{C}_{P,W} = (1 + \ell \Delta W/W_W)\rho_W/\rho_S \ . \tag{37}$$

Here, $\Delta W \equiv W_S - W_W$, ρ_W and ρ_S are the densities at the experimental pressure and temperature of the sample loop, and ℓ is a heat loss correction factor, which must be determined at each temperature.[74]

The temperature dependence of $\Delta C_{p,2}^{\infty}/R$ of argon dissolved in water is shown in figure 5. In preparing this graph it was assumed that the concentrations of argon used in the study of Biggerstaff et al.[56] are small enough so that, within experimental error, apparent molar heat capacities $C_{p,2,\phi}$ are equal to the partial molar heat capacities $C_{p,2}^{\infty}$ at infinite dilution.

Two points deserve special attention. First we note the excellent agreement between $\Delta C_{p,2}^{\infty}$ values measured directly (I),[56,57] results obtained from the temperature dependence of calorimetrically determined ΔH_2^{∞} (II),[51] and values determined via van't Hoff analysis of $\ln H_{2,1}$ vs. T (III),[43,47,75] as indicated by eq.(33). The latter approach imposes severe demands upon the precision of the VLE data, since they have to survive *two* differentiation steps with respect

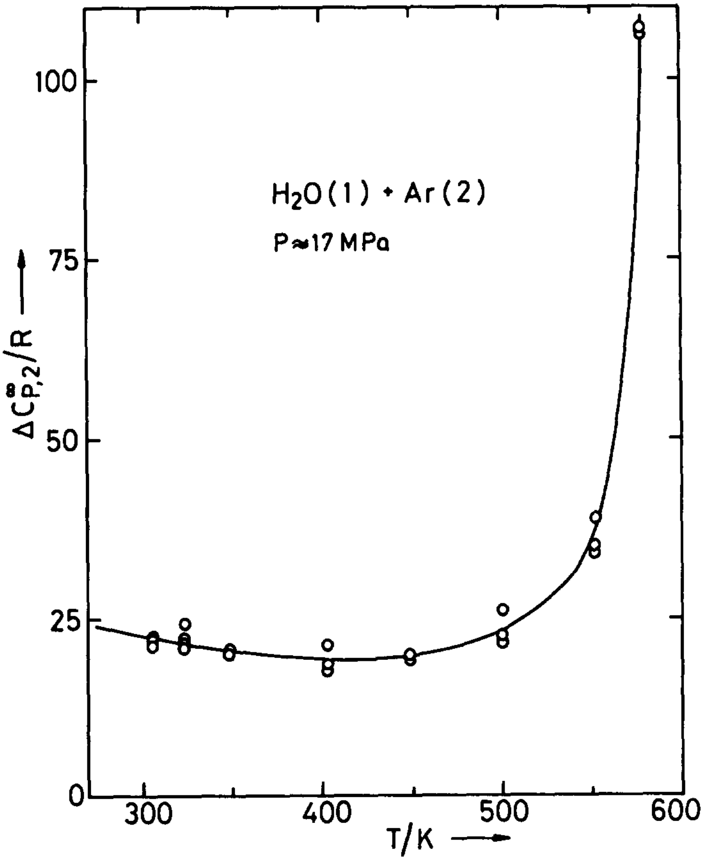

FIGURE 5. Plot of the heat capacity change on solution $\Delta C_{p,2}^{\infty} = (C_{p,2}^{\infty} - C_{p,2}^{o})$ of argon dissolved in water vs. temperature T at ca. 17 MPa total pressure.[56]

to temperature. Specifically, for argon dissolved in water at 298.15 K the following results for the partial molar heat capacity change at infinite dilution have been reported:

(I) $\Delta C_{P,2}^{\infty}(P=17.2\ \mathrm{MPa})/R = 22.76$; (II) $\Delta C_{P,2}^{\infty}(P=0.1\ \mathrm{MPa})/R = 24.05$;
(III) $\Delta C_{P,2}^{\infty}(P=P_{s,H_2O})/R = 22.39$.

Second we note the steep increase of $\Delta C_{P,2}^{\infty}/R$ for $T \rightarrow T_{c,H_2O}$;[19,76] that it begins at such a relatively *low* temperature ($T_{c,H_2O} = 647$ K) is rather surprising. As shown recently by Biggerstaff and Wood,[57] at 32 MPa $C_{P,2,\phi}$ reaches a sharp maximum (ca. 5000 $\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$) at about 665 K and decreases then rapidly to a sharp minimum (ca. -5000 $\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$) at about 685 K. The same behavior but with *opposite sign* is theoretically expected for dilute aqueous solutions of *electrolytes* and has recently been confirmed by experiment.[77]

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