Thermochimica Acta, 69 (1983) 1–44
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

CALORIMETRY: ITS CONTRIBUTIONS TO MOLECULAR THERMODYNAMICS OF FLUIDS*

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ABSTRACT

This article reviews recent contributions of fluid phase calorimetry to the theory of pure fluids and fluid mixtures. Selected examples serve to illustrate the use of experimental results for the development of rational prediction techniques for thermodynamic quantities, which are of importance for the chemical engineer. For instance, the following topics are dealt with in some detail:

- Low density fluids: virial coefficients;
- Pure liquids: isothermal compressibility, heat capacity at constant volume;
- Liquid mixtures: data correlation, group contribution methods;
- Dilute solutions: enthalpy of solution.

1. INTRODUCTION

During the last decade, calorimetry in general and calorimetry as applied to fluids in particular has experienced impressive advances. Besides novel designs of apparatus which significantly improved experimental precision, considerable effort has been directed toward increasing the accessible pressure and temperature range of methods as well as toward simplifying and accelerating data acquisition. Details concerning design and operation of calorimeters have been recently reviewed, for instance, in various chapters of ref. 1, by Becker[2] and by Hemminger and Höhne[3], and will *not* be considered here to any extent (additional brief surveys may be found in more general reviews on the thermodynamics of fluids, such as refs. 4-7). As concerns the

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* Communicated in part as a plenary lecture at the "5. Ulmer Kalorimetrietage", Ulm, F.R.G., 21 to 22 March 1983.

0040-6031/83/$03.00

scope of this article, we will focus attention upon a few selected areas to whi calorimetry has contributed significantly, and present the relevant physics together with representative recent results. The topics considered will include studies of theoretical importance as well as more application oriented work, wi the bias resulting from the author's current research interests. For instance, will first discuss calorimetric measurements which have been instrumental in th elucidation of intermolecular forces, such as measurements of Joule-Thomson coefficients and excess enthalpies at low fluid densities. Indirect determinati of the key thermophysical quantities isothermal compressibility and heat capacity at constant volume of dense fluids will be treated next in some detail which topics are in turn followed by an appraisal of problems associated with the correlation of various thermodynamic excess quantities of liquid mixtures as functions of temperature and composition. Finally, recent results of calorimetric measurements on very dilute solutions, both aqueous and non-aqueous, will be discussed, the former being of interest in the study of hydrophobic interaction.

2. GAS IMPERFECTIONS

For more than a century, experimental studies of real-gas behavior at low or moderate densities (i.e. PVT measurements) have held a prominent position in physical chemistry. They were motivated, and still are, either by the need to solve practical problems - such as those encountered in reduction of vapor-liquid equilibrium (VLE) data - or by their potential usefulness as sources of information on intermolecular forces in both pure gases and gaseous mixtures.

At low to moderate molar densities $\rho \equiv V^{-1}$, the pressure-explicit virial equation of state[8]

$$Z(T,\rho) \equiv \frac{P}{\rho R T} = 1 + \sum_{n=2}^{\infty} B_n \rho^{n-1} \quad ,$$

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

is appropriate for the description of real-gas behavior[1]. Here, V represents

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[1] We exclude strongly associating fluids, such as alkanoic acids. For such substances appropriate "chemical" theories have been developed[9,10].

the molar volume, P is the pressure, T is the temperature, R is the gas constant, and in the case of mixtures, the subscript x indicates constant composition expressed in mole fractions. The coefficients $B_2 \equiv B$, $B_3 \equiv C$ etc. are known as the second virial coefficient, the third virial coefficient and so forth, and are functions of temperature and composition only. The general manner of the variation of B and C with temperature is indicated in Fig. 1, the curves

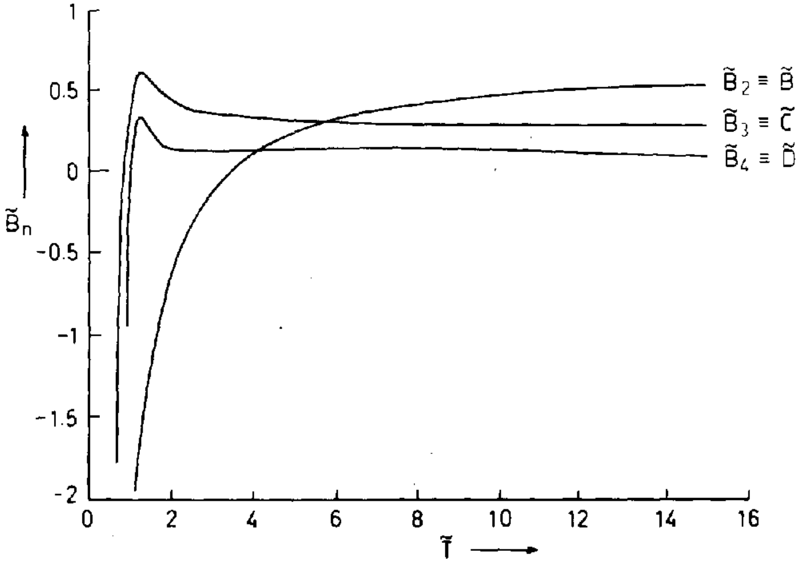

FIGURE 1. Reduced virial coefficients $\tilde{B}_n = B_n/b_0^{n-1}$ as function of reduced temperature $\tilde{T} = kT/\varepsilon$ from the Lennard-Jones (6,12) potential, see eq. 21 and Fig. 2. $b_0 = (2/3)\pi\sigma^3 N_A$. They were computed[21] with the pairwise additivity assumption. $\tilde{B}_2$ has a maximum at about $\tilde{T} = 25$.

of which have been calculated for a Lennard-Jones (6,12) pair potential depicted in Fig. 2. We note, however, that experimental evidence for the temperature behavior of C at low temperatures, that is to say left of the maximum, is rather weak.

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

$$Z(T,P) = 1 + \sum_{n=2}^{\infty} B'_n P^{n-1} \quad ,$$

$$B'_n = \frac{1}{(n-1)!}\left(\frac{\partial^{n-1} Z}{\partial P^{n-1}}\right)_{T, x_i, P=0} \quad ,$$

where the virial coefficients $B'_2 \equiv B'$, $B'_3 \equiv C'$ etc. of the density- (or volume-explicit equation of state eq. 3 are also functions of temperature and composit only. The coefficients of these two infinite series are closely related 2), i.e.

$$B' = B/RT \quad ,$$

$$C' = (C - B^2)/(RT)^2 \quad ,$$

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

For theoretical as well as practical reasons, the virial equation in density, eq. 1, is often preferred[8,12,13] over the pressure series eq. 3. Other virial-type series are possible. A rather comprehensive comparative study of the rate of convergence of several such series, including the pressure-explicite series eq. 1 and the density-explicit series eq. 3, is given in ref. 14, together witl the appropriate conversion formulae in terms of the B_n defined by eq. 2.

For a mixture of n components, each with mole fraction x_i, statistical mechanics provides the following exact mixing rules for the virial coefficient B(T,x), C(T,X) etc.

$$B(T,x) = \sum_{i}^{n} \sum_{j}^{n} x_i x_j B_{ij}(T) \quad ,$$

$$C(T,x) = \sum_{i}^{n} \sum_{j}^{n} \sum_{k}^{n} x_i x_j x_k C_{ijk}(T) \quad .$$

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2) In practice, evaluation of virial coefficients from experimental PVT data is limited to the determination of B and C, and occasionally D. As a consequenc eqs. 5-7 are only approximations for converting *measured* virial coefficient from the truncated density-series representation to the truncated pressure-series representation and vice versa. For an illustration of this point, see for example Scott and Dunlap's work on n-butane[11].

On the rhs of eqs. 8 and 9, coefficients with identical subscripts refer to pure substances, whereas mixed subscripts designate composition-independent interaction virial coefficients (or cross-coefficients) characterizing the molecular interaction between molecules of species i with those of species j (B_{ij}), of species i with those of species j and k (C_{ijk}) and so forth. A valuable compilation of virial coefficients of pure gases and binary mixtures has recently been prepared by Dymond and Smith[15].

Residual thermodynamic functions (also called departure functions)[8,12] are defined as the differences between the actual value of a thermodynamic property X and the value of the same property for the fluid in its perfect-gas state, X^{pg}, both evaluated at the same temperature, pressure and composition$^{3)}$:

$$X^*(T,P,x) \equiv X(T,P,x) - X^{pg}(T,P,x) \quad . \tag{10}$$

We designate residual functions by a superscript asterisk. They may be expressed in terms of the PVT equation of state and hence, at low or moderate densities, in terms of the appropriate virial coefficients and their temperature derivatives. For instance, when the pressure-explicit equation of state $Z = Z(T,\rho)$ is used, we obtain for the residual molar enthalpy, including terms up to $O(\rho^2)$

$$\begin{aligned} H^*/RT &= -T\int_0^{\rho}\left(\frac{\partial Z}{\partial T}\right)_{\rho}\rho^{-1}d\rho + Z - 1 \\ &= \left(B - T\frac{dB}{dT}\right)\rho + \left(C - \frac{T}{2}\frac{dC}{dT}\right)\rho^2 + \cdots \quad , \end{aligned} \tag{11}$$

for the residual molar entropy

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3) Alternatively, it may sometimes be more convenient to define a residual function as the difference between the actual value of X for the real substance and the value X^{pg} referring to the substance in the perfect-gas state at the same temperature, density and composition:

$$X^*(T,\rho,x) \equiv X(T,\rho,x) - X^{pg}(T,\rho,x) \quad .$$

In general $X^*(T,P,x) \neq X^*(T,\rho,x)$, unless the property X^{pg} of the perfect gas is independent of density at constant temperature, such as U, H, C_V, and C_P. Note, that instead of X^{pg} often X° is used.

$$S^*/R = -\int_0^\rho \left[T\left(\frac{\partial Z}{\partial T}\right)_\rho + Z - 1\right]\rho^{-1}d\rho + \ln Z$$

$$= -\left[\left(B + T\frac{dB}{dT}\right)\rho + \frac{1}{2}\left(C + T\frac{dC}{dT}\right)\rho^2 + \cdots\right] + \ln Z\ ,$$

and for the residual molar heat capacities

$$C_V^*/R = -T\int_0^\rho \left[T\left(\frac{\partial^2 Z}{\partial T^2}\right)_\rho + 2\left(\frac{\partial Z}{\partial T}\right)_\rho\right]\rho^{-1}d\rho$$

$$= -\left[T\left(2\frac{dB}{dT} + T\frac{d^2B}{dT^2}\right)\rho + \frac{T}{2}\left(2\frac{dC}{dT} + T\frac{d^2C}{dT^2}\right)\rho^2 + \cdots\right]\ ,$$

$$C_P^*/R = C_V^*/R - 1 + \left[T\left(\frac{\partial Z}{\partial T}\right)_\rho + Z\right]^2 \Big/ \left[\rho\left(\frac{\partial Z}{\partial \rho}\right)_T + Z\right]$$

$$= -\left\{T^2\frac{d^2B}{dT^2}\rho + \left[-\left(B - T\frac{dB}{dT}\right)^2 + C - T\frac{dC}{dT} + \frac{T^2}{2}\frac{d^2C}{dT^2}\right]\rho^2 + \cdots\right\}.$$

The fugacity f is defined by $f \equiv P\cdot\exp(G^*/RT)$, where the residual molar Gibb energy is $G^* = H^* - TS^*$. Hence for the fugacity coefficient $\phi \equiv f/P$ we obtai

$$\ln\phi = \int_0^\rho (Z-1)\rho^{-1}d\rho + Z - 1 - \ln Z$$

$$= -\ln Z + 2B\rho + \frac{3}{2}C\rho^2 + \frac{4}{3}D\rho^3 + \cdots\ .$$

We repeat that eqs. 10-15 are valid for pure fluids as well as constant composition mixtures.

An alternative set of formulae for volume-explicit equations of state, su as the pressure series eq. 3, may easily be derived. Since pressure and temperature are the most common experimental parameters, these expressions h some computational advantage. For convenience, we give the relation for the fugacity coefficient, viz.

$$\ln\phi = \int_0^P (Z-1)P^{-1}dP$$

$$= B'P + \frac{1}{2}C'P^2 + \frac{1}{3}D'P^3 + \cdots\ .$$

To round out this introduction, we briefly summarize the relations of the virial coefficients with the intermolecular potential energy function. For a spherically symmetric (i.e. angle-independent) pair potential u(r), as depicted in Fig. 2, it can be shown[12,16] that the second virial coefficient of a pure fluid is given by

$$B(T) = -2\pi N_A \int_0^\infty \left\{ \exp[-u(r)/kT] - 1 \right\} r^2 dr \quad , \qquad (17)$$

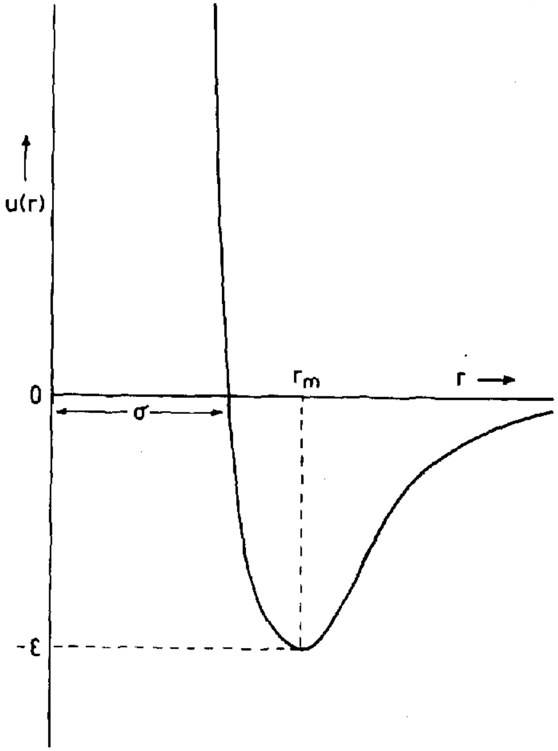

FIGURE 2. Schematic representation of the potential energy of interaction between two spherically symmetric molecules, u(r), as function of intermolecular separation r (see, for instance, the Lennard-Jones potential eq. 21).

where N_A is Avogadro's constant and $k = R/N_A$. Eq. 17 can be transformed through integration by parts into

$$B(T) = -\frac{2\pi N_A}{3kT}\int_0^\infty \exp[-u(r)/kT]\,\frac{du(r)}{dr}\,r^3 dr \quad . \qquad (1$$

Another equivalent form is[17]

$$B(T) = \exp(\varepsilon/kT)\,\frac{2\pi N_A}{3kT}\int_0^\infty \Delta(\psi)\exp[-\psi(r)/kT]\,d\psi(r) \quad , \qquad (1$$

where ε is the maximum depth of the potential energy well (see Fig. 2), and $\psi(r) = u(r) + \varepsilon$. The well-width function is defined by

$$\Delta(\psi) = \begin{cases} r_l^3(\psi) - r_r^3(\psi) & \text{for} \quad \psi \leqslant \varepsilon \\ r_l^3(\psi) & \text{for} \quad \psi > \varepsilon \quad , \end{cases} \qquad (2$$

where r_l and r_r are, respectively, the inner and outer coordinate of the potent well at energy ψ. Thus we note that although there exist direct and fairly simple relations between $u(r)$ and B, eqs. 19 and 20 indicate a formal limitatio on efforts to obtain *uniquely* the pair potential from experimental virial coefficients[4)]. In general, $B(T)$ determines $u(r)$ only for $\psi(r) > \varepsilon$, i.e. $u(r) > 0$ whilst for $\psi(r) \leqslant \varepsilon$, i.e. $u(r) \leqslant 0$, data inversion yields information as to the well width as function of the well depth. However, rather sophisticated inversi techniques have been developed recently[18,19] to circumvent this obstacle. This topic has been carefully reviewed by Maitland and collaborators[20].

The conventional approach to the problem of how to extract information on the pair potential is based on the use of model functions with two or more adjustable parameters, which are optimized by fitting to experimental data obtained over *large* temperature ranges. A fairly simple and reasonably realisti model function for spherical, non-polar molecules is the popular and widely used Lennard-Jones (6,12) pair potential function (see Fig. 2)

$$u(r) = 4\varepsilon\left[(\sigma/r)^{12} - (\sigma/r)^6\right] \quad . \qquad (21$$

[4)] Note that $\frac{3}{2}kTB(T)/[\pi N_A \cdot \exp(\varepsilon/kT)]$ is the Laplace-transform of $\Delta(\psi)$,

$$\mathcal{L}[\Delta(\psi)] = f(s) = \int_0^\infty e^{-s\psi}\Delta(\psi)\,d\psi \quad ,$$

with $s = 1/kT$.

Here, σ is that value of r for which $u(r) = 0$, and ε is the depth of the potential well at $r_m = 2^{1/6}\cdot\sigma$, i.e. at the minimum of $u(r)$. A numerical method for evaluating virial coefficients assuming pairwise additivity of the potential function (see below) is given in ref. 21. Its results were used for Fig. 1. Details concerning the use of more complicated model functions as well as limitations of this approach may be found in refs. 12, 20, and 22, which also contain sections on angle-dependent potential functions.

For convenience, we give here the numerical values for a few hard-sphere virial coefficients[12] (σ is the hard-sphere diameter): $B_{hs} = (2/3)\cdot\pi\sigma^3 N_A \equiv b_0$, $C_{hs}/b_0^2 = 5/8$, and $D_{hs}/b_0^3 = 0.2869$.

The second virial coefficient of a mixture is given by eq. 8, where B_{ii} is due to interactions i-i, and is related to the pair potential via eq. 17. Similarly B_{ij} characterizes interactions of type i-j, and is related to the pair potential $u_{ij}(r)$ between unlike, spherical, non-polar molecules by an expression analogous to eq. 17, the only difference being the replacement of $u(r)$ by $u_{ij}(r)$. Thus the mixture problem is reduced to the calculation of the interaction virial coefficients and hence to the calculation of u_{ij} in terms of the pure-fluid potential functions u_{ii} and u_{jj}. Conversely, experimental results on B_{ij} are frequently used to obtain information on u_{ij}, which in turn may be exploited to establish semi-empirical methods for its estimation from the known potential functions of the pure fluids. Such recipes are generally known as combining rules, and will be discussed further at the end of this section.

We conclude this introduction to the theory of virial coefficients with a few remarks concerning third virial coefficients. Even for pure fluids, reliable results on C(T) are not plentiful, and virial cross-coefficients C_{ijk} for mixtures are exceedingly scarce. While B(T) contains information on two-body molecular interactions, C(T) is potentially useful for the elucidation of contributions due to three-body molecular interactions. In order to obtain C(T) from statistical mechanics, the three-body potential energy u_3 for a trio of molecules must be evaluated. Formally, we may write

$$u_3(r_{12}, r_{13}, r_{23}) = u(r_{12}) + u(r_{13}) + u(r_{23}) + \Delta u(r_{12}, r_{13}, r_{23}) \quad , \qquad (22)$$

where the first three terms on the rhs of eq. 22 represent the so-called pairwise-additivity assumption, which in more general terms is expressed as

$$u_N = \sum_{i<j}^{N} u(r_{ij}) \quad , \qquad (23)$$

where u_N denotes the n-body potential energy.

Δu is a correction term representing the non-additivity contributions. Eq. 22 then leads to

$$C(T) = C^{add}(T) + \Delta C(T) \quad , \qquad (2$$

where $C^{add}(T)$ is the value obtained[12] assuming $\Delta u = 0$:

$$C^{add}(T) = -\frac{8\pi^2 N_A^2}{3}\iiint f_{12} f_{13} f_{23} r_{12} r_{13} r_{23} \, dr_{12} dr_{13} dr_{23} \quad . \qquad (2$$

Here, $f_{ij} \equiv \exp\left[-u(r_{ij})/kT\right]-1$, and r_{ij} is the distance between molecules i and j. Estimation of the non-additivity contribution $\Delta C(T)$ may be based, for instance, on the work of Sherwood and Prausnitz[23].

Several successful predictive methods for evaluating C_{ijk} of mixtures from pure component third virial coefficients are based on extended versions of corresponding-states theory (CST), such as those due to Chueh and Prausnitz[13,1 and of de Santis and Grande[25], respectively.

We now turn to our "Leitmotiv" *calorimetry* by inquiring as to its contributi toward improved knowledge of virial coefficients. At a first glance, direct experimental determination of virial coefficients by conventional precision PVT measurements appears to be straightforward. In practice, however, the situation is far less satisfactory, and current experimental techniques allow only measurement of B and C, and occasionally D. Though PVT methods undoubtedly account for the bulk of data on virial coefficients, indirect methods have recently attracted considerable interest. The main advantage of many of these methods is the possibility of obtaining reliable results even under conditions where adsorption would be a serious problem with conventional methods, that is to say at low reduced temperatures.

In principle, experimental determination of any property whose value depends on gas imperfection, and hence on the equation of state, may be used to determi virial coefficients. Perhaps the most important technique to date is the flow-calorimetric measurement of the isothermal Joule-Thomson coefficient[26-31] $\varphi \equiv (\partial H/\partial P)_T$, which quantity is related to the (isenthalpic) Joule-Thomson coefficient $\mu \equiv (\partial T/\partial P)_H$ according to

$$\mu C_P = -\varphi \quad . \qquad (2$$

Consider an adiabatic flow calorimeter fitted with a throttle, a heater and appropriate thermometers and manometers as shown schematically in Fig. 3.

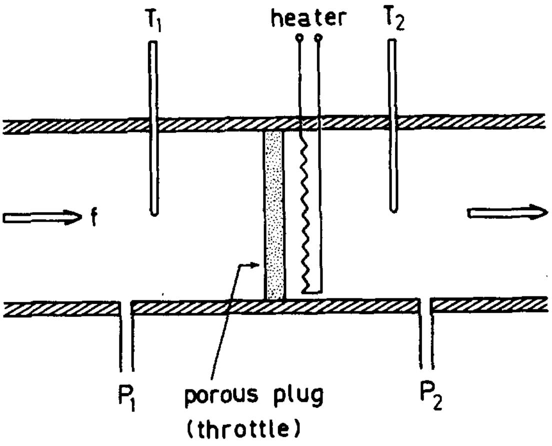

FIGURE 3. Adiabatic flow calorimeter (schematic) equipped with throttle, electric heater, thermometers (T_1, T_2) and manometers (P_1, P_2).

When no power W is supplied by the heater to the fluid flowing with a molar flow rate f, this throttling experiment is isenthalpic and

$$\mu = \lim_{P_2 \to P_1} \frac{T_2 - T_1}{P_2 - P_1} \quad . \tag{27}$$

On the other hand, when the power input is adjusted so as to maintain isothermal conditions across the pressure gradient (isothermal throttling), we obtain

$$\varphi = \lim_{P_2 \to P_1} \frac{W}{f \cdot (P_2 - P_1)} \quad . \tag{28}$$

Note that with the throttle removed we have a flow calorimeter for measuring essentially the heat capacity at constant pressure,

$$C_P = \lim_{T_2 \to T_1} \frac{W}{f \cdot (T_2 - T_1)} \quad . \tag{29}$$

The quantity measured in an actual isothermal throttling experiment may be expressed in terms of virial coefficients

$$\frac{H(T,P_2)-H(T,P_1)}{P_2-P_1} = B - T\frac{dB}{dT} + \left[-2B\left(B - T\frac{dB}{dT}\right) + 2C - T\frac{dC}{dT}\right]\frac{\bar{P}}{RT} + \cdots,$$ (3

where $\bar{P} = (P_1 + P_2)/2$ is the mean pressure. Thus, when plotted against $\bar{P}$, the intercept is the zero pressure isothermal Joule-Thomson coefficient

$$\varphi^\circ = B - T\frac{dB}{dT} \quad ,$$ (31

while the initial slope yields information on the third virial coefficient, see eq. 30. Evidently, eq. 31 may be integrated between a suitable reference temperature T_{ref} and T to yield

$$\frac{B(T)}{T} = \frac{B(T_{ref})}{T_{ref}} - \int_{T_{ref}}^{T} \frac{\varphi^\circ}{T^2}\,dT \quad .$$ (32

Precise flow calorimeters for measuring μ and C_p have recently been designed by Bier and coworkers[30], who measured these quantities for ethane and propene[31], and subsequently determined the compressibility factor, entropy, enthalpy etc. For instance, the latter quantity may be obtained by integrating

$$dH = C_p dT - \mu C_p dP \quad ,$$ (33a

and by integrating φ/T^2 over T, differences of Z may be determined:

$$Z(T,P) - Z(T_{ref},P) = -\frac{P}{R}\int_{T_{ref}}^{T} \varphi(T,P)T^{-2}\,dT \quad .$$ (33b

Today, flow calorimetry is the commonly used method for measuring the heat capacity at constant pressure of gases and vapors[32,33], and isothermal measurements of C_p as a function of pressure are usually performed to obtain th heat capacity C_p° in the perfect-gas state, i.e. at zero pressure (see Table 1). We note that

$$\lim_{P\to 0}\left(\frac{\partial C_p}{\partial P}\right)_T = -T\frac{d^2B}{dT^2} \quad .$$ (34

TABLE 1. Vapor heat capacity $C_p/JK^{-1}mol^{-1}$ of benzene[35] and hexafluorobenzene[36] as function of temperature and pressure.

P/kPa	$C_p/JK^{-1}mol^{-1}$ of C_6H_6 at				
	333.15 K	368.15 K	403.15 K	473.15 K	527.15 K
202.65			117.44	134.45	145.48
101.32		106.39	115.85	133.79	145.99
50.66		105.13	115.01	133.30	145.82
25.33	94.23	104.59	114.69	133.09	145.70
12.67	93.76	104.26	114.47		
$C_p^\circ/JK^{-1}mol^{-1}$	93.32	103.98	114.29	132.94	145.39

	$C_p/JK^{-1}mol^{-1}$ of C_6F_6 at				
	335.15 K	368.15 K	403.15 K	473.15 K	527.15 K
202.66			190.53	201.81	210.55
101.32		180.24	186.70	200.21	209.61
50.66		177.47	185.01	199.38	209.14
25.33	168.48	176.29	184.33	199.23	209.08
12.67	167.35				
$C_p^\circ/JK^{-1}mol^{-1}$	166.27	174.95	183.40	198.76	208.78

These results may then be used to obtain the residual heat capacities $C_p^* = C_p - C_p^\circ$, and $C_V^* = C_V - C_p^\circ + R$, which quantities are of central importance in fluid phase thermodynamics. As an example of estimation techniques for C_p°, which are based on group contribution methods, we refer to the work of Benson and collaborators[34].

Calorimetric measurements of the molar enthalpy of vaporization $\Delta_l^g H$ are also a useful source of information on second virial coefficients. Starting with the rigorous Clapeyron equation

$$\frac{dP_s}{dT} = \frac{\Delta_l^g H}{T\Delta_l^g V} , \qquad (35)$$

where $\Delta_l^g V = V_{g,s} - V_{l,s}$ denotes the molar volume change on vaporization, we obtain, after rearrangement and assuming negligible influence of virial coefficients other than B,

$$Z_s = 1 + B\rho_{g,s}$$

$$= \frac{P_s \Delta_l^g H}{RT^2(dP_s/dT)} + \frac{P_s}{\rho_{l,s}RT} \quad . \qquad (3$$

Here, $Z_s = P_s/(\rho_{g,s}RT)$ is the compressibility factor of the vapor phase at saturation conditions. Since both vapor pressure P_s and orthobaric liquid molar density $\rho_{l,s} = 1/V_{l,s}$ are usually known with great precision as function of temperature, eq. 36 permits evaluation of B. Concurrent determinations of C_P° and B as functions of temperature via calorimetric measurements of vapor heat capacity and enthalpy of vaporization have been used extensively by Hossenlopp and Scott at the Bartlesville Research Center, Oklahoma, now part of the U.S. Department of Energy. For many substances such a treatment provides the only information on second virial coefficients. Representative articles, for instance on the IUPAC - recommended reference material benzene, are given in refs. 35 and 36.

The speed of sound at zero frequency w_0 is related to the equation of state and hence to the virial coefficients by

$$w_0^2 = -\frac{\kappa V^2}{M}\left(\frac{\partial P}{\partial V}\right)_T \quad , \qquad (3$$

where $\kappa = C_P/C_V = \beta_T/\beta_S$. $\beta_T = -V^{-1}(\partial V/\partial P)_T$ and $\beta_S = -V^{-1}(\partial V/\partial P)_S$ are, respectively, the isothermal and the isentropic compressibility, and M is the molar mass. Correct to the second virial coefficient we thus obtain

$$w_0^2 = (w_0^\circ)^2 \cdot (1 + A_1\rho + \cdots) \quad , \qquad (3$$

where w_0° is the speed of sound in the perfect-gas state

$$(w_0^\circ)^2 = \kappa^\circ RT/M \quad , \qquad (3$$

$$\kappa^\circ = C_P^\circ/C_V^\circ = 1 + R/C_V^\circ \quad , \qquad (4$$

and

$$A_1 = 2B + 2(\kappa^\circ - 1)T\frac{dB}{dT} + \frac{(\kappa^\circ-1)^2}{\kappa^\circ}T^2\frac{d^2B}{dT^2} \quad . \tag{41}$$

Thus, measurement of the sound speed[37] as function of density or pressure will yield information on B together with its first and second temperature derivatives. Though κ° (or C_V°) may as well be obtained through extrapolation of measured w_0^2 to zero density, another approach is to combine precise calorimetric results for the heat capacity in the perfect-gas state, $C_V^\circ = C_p^\circ - R$, with isothermal measurements of w_0 as function of density: this method of determining B is both rapid and unaffected by adsorption, and may be applied in a large temperature range[38].

Most of the methods so far discussed for pure substances may equally well be used for constant-composition mixtures and will then yield B(T,x) etc. Consider, for example, a binary gas mixture containing components 1 and 2 with mole fractions x_1 and x_2, respectively. According to eq. 8[5)]

$$B(T,x) = x_1^2B_{11} + 2x_1x_2B_{12} + x_2^2B_{22} \quad , \tag{42}$$

and once B(T,x) is known through some experiment, B_{12} may be calculated, though with a larger uncertainty than that associated with the pure substance values. Calorimetric determination of the molar enthalpy of mixing H^E of two gases is yet another source of information on the interaction virial coefficients. At low pressures this quantity is closely related to the excess second virial coefficient

$$\mathcal{E} \equiv B_{12} - \frac{1}{2}(B_{11} + B_{22}) \, . \tag{43}$$

Specifically,

$$H^E/x_1x_2 = 2\left(\mathcal{E} - T\frac{d\mathcal{E}}{dT}\right)P + O(P^2) \quad , \tag{44}$$

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5) For the cross-coefficients certain symmetry relations apply, e.g.

$$B_{ij} = B_{ji} \quad ,$$

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

where the second-order term is a fairly involved function of second and third pure-component and interaction virial coefficients[6], and of their temperature derivatives. Thus, when plotting $H^E/(x_1x_2P)$ against P, the intercept yields $\mathcal{E}-Td\mathcal{E}/dT$, or equivalently the excess zero-pressure isothermal Joule-Thomson coefficient $\left[\varphi^\circ_{12} - \frac{1}{2}(\varphi^\circ_{11} + \varphi^\circ_{22})\right]$; here the cross-term Joule-Thomson coefficien is $\varphi^\circ_{12} = B_{12} - (TdB_{12}/dT)$, and φ°_{11} and φ°_{22} are the pure-component coefficient (see eq. 31)[7], which may be obtained either by direct measurements or from the temperature dependence of the second virial coefficients of the pure substances

In contrast to PVT experiments, there are no adsorption errors. Since H^E for most gas mixtures is positive, a flow calorimeter may be operated isothermally by balancing the cooling with electrical heating. As a consequence heat leaks can be made very small. Pioneering design of equipment as well as a large number of investigated mixtures are due to Wormald and coworkers[39,40].

As already indicated, virial cross-coefficients measured in one way or another serve a dual purpose. Clearly, they are of importance in practical problems associated with real gas behavior, including data reduction of low- or medium-pressure VLE measurements[13]; these topics will not be pursued further. On the other hand, with the restrictions discussed above, cross coefficients permit the testing and development of so-called combining rules, that is to say of methods designed to characterize unlike-pair interactions in terms of like interactions. The simplest prescription for two-parameter pair potentials is the classical Lorentz-Berthelot rule,

$$\sigma_{12} = (\sigma_{11} + \sigma_{22})/2 \ , \tag{45a}$$

$$\varepsilon_{12} = (\varepsilon_{11}\varepsilon_{22})^{1/2} \ . \tag{45b}$$

---

[6] In analogy to eq. 43, it is convenient to define two excess third virial coefficients, viz. $\mathcal{F}_{112}$ and $\mathcal{F}_{122}$, according to

$$\mathcal{F}_{ijk} = C_{ijk} - \frac{1}{3}\left(C_{iii} + C_{jjj} + C_{kkk}\right) .$$

[7] Note that the zero-pressure isothermal Joule-Thomson coefficient of a binary mixture is given by

$$\begin{aligned}\varphi^\circ(T,x) &= x_1^2\varphi^\circ_{11} + 2x_1x_2\varphi^\circ_{12} + x_2^2\varphi^\circ_{22}\\ &= B(T,x) - T\frac{dB(T,x)}{dT} .\end{aligned}$$

The first relation, eq. 45a, is exact for hard spheres, and the second is seen to follow from a simplified treatment of the dispersion energy. For real substances neither relation is valid and results obtained via eq. 45 are generally rather unsatisfactory. Thus, it is common practice to introduce parameters η and ξ to describe deviations from this rule, viz.

$$\sigma_{12} = \eta(\sigma_{11} + \sigma_{22})/2 \ , \tag{46a}$$

$$\varepsilon_{12} = \xi(\varepsilon_{11}\varepsilon_{22})^{1/2} \ . \tag{46b}$$

Several of the more popular semi-theoretical expressions for ξ are given in Table 2. A successful new combining rule for ξ *and* η which is applicable to spherically symmetric two-parameter pair potentials, has recently been

TABLE 2. Combination rules for the interaction energy parameter $\varepsilon_{12} = \xi(\varepsilon_{11}\varepsilon_{22})^{1/2}$, where ξ is of the form $\xi = [2\sqrt{X_{11}X_{22}}/(X_{11} + X_{22})]^n[2\sqrt{\sigma_{11}\sigma_{22}}/(\sigma_{11} + \sigma_{22})]^6$ (that is to say with the assumption $\eta = 1$)

	X	Reference
n = 1	$(N/\alpha)^{1/2}$: N is the (effective) electron number, and α is the mean polarizability	J.C. Slater and J.G. Kirkwood, Phys. Rev., 1931, 37, 682.
	θ/α : θ is the diamagnetic susceptibility	J.G. Kirkwood, Phys. Z., 1932, 33, 57. A. Müller, Proc. Roy. Soc. (London), Ser.A, 1936, 154, 624.
	I : first ionization potential	G.H. Hudson and J.C. McCoubrey, Trans. Faraday Soc., 1960, 56, 761.
	$\varepsilon\sigma^6/\alpha^2$	F. Kohler, Monatsh. Chem., 1957, 88, 857.
n = 2	$(N/\alpha)^{1/2}$	D.R. Pesuit, J. Chem. Phys., 1977, 67, 5341; Ind. Eng. Chem. Fundam., 1978, 17, 235.

suggested by Kohler, Fischer and Wilhelm[41]. It is based on the senior author's earlier work[42] and includes as a novel aspect the constraint of additivity of t *temperature-dependent effective* hard-sphere diameters (instead of σ)

$$d_{ii} = \int_0^{r_m} \left\{ 1 - \exp[-\psi(r)/kT] \right\} dr \ , \qquad (4$$

with $\psi(r) = u(r) + \varepsilon$. Even for rather complicated mixtures, such as $(CH_4 + CF_4)$, satisfactory results are obtained for B_{12}.

On a somewhat less fundamental level, experimental data on B_{12} as a function of temperature, may be used to establish as well as improve correlations based on extended CST. Consider, for instance, Tsonopoulos' method[43] for calculating the reduced second virial cross-coefficient at a reduced temperature $T_r = T/T_{c,12}$:

$$B_{12}(T_r) P_{c,12}/RT_{c,12} = B^{(0)}(T_r) + \omega_{12} B^{(1)}(T_r) \ , \qquad (4$$

where $B^{(0)}(T_r)$ and $B^{(1)}(T_r)$ are functions of inverse powers of T_r. The characteristic parameters $T_{c,12}$ and $P_{c,12}$ are related to the pure-component critical quantities $T_{c,i}$, $P_{c,i}$ and $V_{c,i}$ through the mixing rules

$$T_{c,12} = (1 - k_{12})(T_{c,1}\, T_{c,2})^{1/2} \ , \qquad (4$$

$$P_{c,12} = 4 T_{c,12} (P_{c,1} V_{c,1}/T_{c,1} + P_{c,2} V_{c,2}/T_{c,2}) (V_{c,1}^{1/3} + V_{c,2}^{1/3})^{-3} \ , \qquad (5$$

$$\omega_{12} = (\omega_1 + \omega_2)/2 \ . \qquad (5$$

Here, ω is the acentric factor of pure i, and k_{12} is a binary interaction parameter (usually much smaller than unity); $1-k_{12}$ is somewhat similar to ξ of eq. 46b. For any given type of mixtures, say (N_2 + a hydrocarbon), k_{12} may be correlated with appropriate quantities characterizing these mixtures, for instance with the number of C-atoms or with the critical volume of the hydrocarbon. Thus, provided a reasonable number of k_{12} values has been determined experimentally, B_{12} of a specific mixture of the same type, for which no experimental PVT data are available, may be estimated with some confidence by this procedure.

3. PURE LIQUIDS AND LIQUID MIXTURES

This section is devoted essentially to two topics:

(a) Determination of the isothermal compressibility β_T and the molar heat capacity at constant volume C_V, and a few selected areas of application.

(b) The use of data on molar excess enthalpies H^E and molar excess heat capacities C_P^E in the development of data correlations, in particular in the development of group contribution theories.

An appraisal of contributions of calorimetry toward an improved understanding of dilute solutions is deferred to Section 4.

3.1. ISOTHERMAL COMPRESSIBILITY AND ISOCHORIC HEAT CAPACITY

Isothermal compressibility β_T and isochoric heat capacity C_V are key thermophysical quantities, and accurate data are needed in many areas of physics, chemistry and the engineering sciences. However, reliable data for pure liquids are not plentiful, and a fortiori this is the case for mixtures. Traditionally, isothermal compressibilities have been obtained by direct methods, that is to say by conventional PVT measurements at relatively high pressures. A careful discussion of some pitfalls associated with such an approach has been presented by Hayward[44]. With the availability of relatively fast high-precision calorimetric equipment[45] in conjunction with modern techniques for measuring volumetric properties of liquids[46], the indirect method for determining β_T via measurement of the heat capacity at constant pressure C_P, the speed of sound w_0, the thermal expansivity $\alpha_P = V^{-1}(\partial V/\partial T)_P$, and the molar volume V has attracted renewed interest. The relevant relations are

$$\beta_T = \beta_S + TV\alpha_P^2/C_P \quad , \tag{52}$$

$$\beta_S = V/(Mw_0^2) \quad . \tag{53}$$

Indeed, it has been shown that results obtained with eqs. 52 and 53 are reliable to within a few tenth of a percent[47,48], and are thus comparable with the very best data measured directly (see Table 3). C_V is obtained from C_P according to

$$C_V = C_P\beta_S/\beta_T \quad . \tag{54}$$

The corresponding imprecision is of similar magnitude as for β_T, arising mainly from the experimental uncertainty associated with α_P.

TABLE 3. Isothermal compressibility β_T at 298.15 K of tetrachloromethane, benz and cyclohexane: comparison with selected literature data[a] (values obtained by indirect method are italicized)

	Asenbaum & Wilhelm[48]	Literature
CCl_4	*1075.5*	1066[b], 1059[c], 1077[d], 1089[e], *1077.9*[f], *1074.6*[g]
C_6H_6	*970.5*	967[h], 968[d], 944[e], 971[i], 966[j], *973.2*[k], *969.7*[f], *969.2*[g]
C_6H_{12}	*1129.9*	1110[c], 1140[d], 1130[i], 1120[j] *1127.7*[ℓ], *1130.2*[f], *1126.6*[g]

[a] No attempt was made to distinguish between results obtained for saturation an atmospheric pressure.

[b] R.E. Gibson and O.H. Loeffler, J.Am.Chem.Soc., 1941, 63, 898. [c] M. Diaz Peña M.L.McGlashan, Trans.Faraday Soc., 1961, 57, 1511. [d] G.A. Holder and E. Whalle Trans.Faraday Soc., 1962, 58, 2095. [e] H.W. Schamp, J.R. Hastings, and S. Weiss Phys.Fluids, 1965, 8, 8. [f] O. Kiyohara, C.J. Halpin and G.C. Benson, J.Chem. Thermodyn., 1978, 10, 721. [g] Ref. 47. [h] R.E. Gibson and J.F. Kincaid, J.Am.Che Soc., 1938, 60, 511. [i] M.B. Ewing, K.N. Marsh and R.H. Stokes, J.Chem.Thermody 1972, 4, 637. [j] E. Aicart, G. Tardajos, and M. Diaz Peña, J.Chem.Thermodyn., 1 12, 1085. [k] E. Rajagopal and S.V. Subrahmanyam, J.Chem.Thermodyn., 1974, 6, 87 [ℓ] E. Rajagopal and S.V. Subrahmanyam, J.Chem.Thermodyn., 1980, 12, 797.

Correlations of data concerning the volumetric behavior of liquids under hydrostatic compression are based on essentially semi-empirical equations of state. Up to several tens of megapascals, one of the simplest and most versatile equations is the so-called modified Tait equation

$$V(T,P)/V_{ref}(T,P_{ref}) = \left[1 + n(P - P_{ref})\beta_{T,ref}(T,P_{ref})\right]^{-1/n} , \qquad ($$

where $\beta_{T,ref}$ and V_{ref} denote the isothermal compressibility and the molar volume, respectively, at an arbitrary reference pressure P_{ref}. For convenience this reference pressure is often taken either as 100 kPa or as P_s, the orthobaric pressure. n is a pressure-independent parameter.

For many organic liquids experimental values of n cluster around 10, with no or very small temperature dependence[49,50]. From eq. 55 it follows that

$$1/\beta_T(T,P) = 1/\beta_{T,ref}(T,P_{ref}) + n(P - P_{ref}) \quad , \tag{56}$$

which relation is identical with the linear tangent-modulus equation[8)].

For liquids composed of polyatomic molecules, the residual isochoric heat capacity C_V^* may serve as the starting point for a semi-quantitative discussion of density-dependent external hindered rotation (or libration) of molecules. This approach is based on the reasonable assumption, that for more or less rigid molecules without internal rotations[9)] the Hamiltonian can be separated into contributions corresponding to the various degrees of freedom of the molecules[47,48,50-57]. Specifically, the canonical partition function for the liquid may formally be written as[58]

$$Z = \frac{1}{N!}\left(\frac{1}{\Lambda^3}\right)^N (z_{vib})^N (z_{el})^N Z_{hrot} Q_0 \quad , \tag{57}$$

$$\Lambda = \left(\frac{h^2}{2\pi m k T}\right)^{1/2} \quad . \tag{58}$$

Λ is called the thermal de Broglie wavelength associated with a molecule of mass m at temperature T, h is Planck's constant, z_{vib} and z_{el} are the molecular vibrational and electronic partition functions, and Z_{hrot} denotes the density-dependent partition function for hindered rotation of the molecules as a whole. The configuration integral

$$Q_0 = \int \cdots \int \exp\left[-U_0(\vec{r}_1, \ldots, \vec{r}_N)/kT\right] d\vec{r}_1 \cdots d\vec{r}_N \tag{59}$$

---

8) Several useful expressions may easily be derived from eqs. 52 and 53, such as

$$n = -\beta_T^{-2}(\partial \beta_T/\partial P)_T \quad ,$$

$$\beta_T/\beta_{T,ref} = (V/V_{ref})^n \quad .$$

9) Pure liquids and liquid mixtures where constituent molecules show internal rotation (e.g. 1,2-dichloroethane) have been discussed in refs. 50-53.

incorporates only the *angle-independent* part u_0 of the total potential energy, and $d\vec{r}_i \equiv dx_i dy_i dz_i$. This approach is similar to that of Beret and Prausnitz[59].

The link with thermodynamics is established through

$$F = -kT\ln Z \quad , \tag*{(6}$$

where F is the molar Helmholtz free energy, and $C_V = -T(\partial^2 F/\partial T^2)_V$. In most cases of interest the residual quantity $C^*_{el} = 0$, and often $C^*_{vib} \approx 0$ (see for instance ref. 48), whence the residual molar isochoric heat capacity[10)] of a saturated liquid at a reduced temperature T_r may be expressed as

$$C^*_V(T_r) = C^*_{hrot}(T_r) + C^*_{V,Ar}(T_r) \quad . \tag*{(6}$$

The residual heat capacity of argon $C^*_{V,Ar}(T_r)$ represents the contribution due to Q_0, which approximation is based on corresponding states theory[48,56]. $C^*_{hrot}(T_r)$ represents the excess over the perfect gas rotational heat capacity. This excess is due to hindered rotation (or libration) of the molecules as a whole in the liquid phase, i.e. $C^*_{hrot}(T_r) = C^l_{hrot}(T_r) - C^{pg}_{rot}(T_r)$. Fig. 4 shows the residual rotational heat capacity C^*_{hrot} for several liquids as a function

---

[10)] The canonical partition function for a polyatomic perfect gas (free rotatic is

$$Z^{pg} = \frac{1}{N!}\left(\frac{V}{\Lambda^3}\right)^N (z_{rot})^N (z_{vib})^N (z_{el})^N \; ,$$

where classically, for linear molecules

$$z_{rot} = 8\pi^2 I kT/(h^2\hat{\sigma}) \; ,$$

and for non-linear molecules

$$z_{rot} = (8\pi^2 kT/h^2)^{3/2}(I_x I_y I_z \pi)^{1/2}/\hat{\sigma} \; .$$

Here, I denotes the moment of inertia (I_x, I_y, I_z are principal moments of inertia), and $\hat{\sigma}$ is the symmetry number of the molecule. Classically, $C^{pg}_{rot} = R$ for linear molecules, and $C^{pg}_{rot} = 3R/2$ for non-linear molecules.

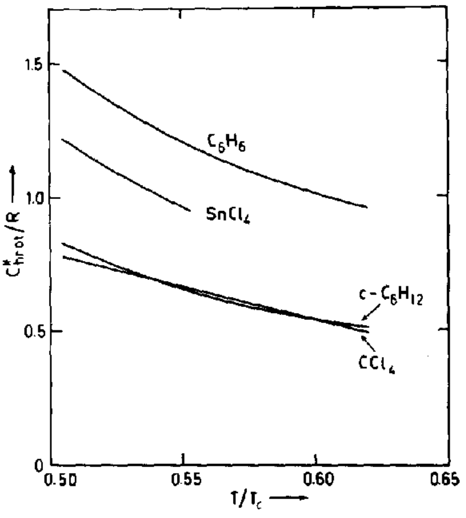

FIGURE 4. Residual rotational heat capacity C^*_{hrot}/R as function of reduced temperature T/T_c of cyclohexane[48], benzene[48], tetrachloromethane[48] and tin tetrachloride[56] along the saturation curve.

of reduced temperature (orthobaric conditions). These results may now be discussed in terms of any suitable model for hindered external molecular rotation, for instance by adopting Pitzer's non-classical treatment[60] of hindered internal rotation[48,56]. As specific examples, we quote rotational barrier heights so determined at 298.15 K for liquid carbon tetrachloride, U_0= 4 kJ/mol, and for liquid tin tetrachloride, U_0= 5.5 kJ/mol. These values are in reasonable agreement with results obtained by other methods, and indicate appreciable interlocking of these tetrahedral molecules (see also ref. 61). Extension of this kind of discussion to mixtures is possible.

3.2. EXCESS ENTHALPY H^E AND EXCESS HEAT CAPACITY C_P^E

The theory of liquid mixtures of non-electrolytes has greatly profited from *systematic* investigations of (molar) excess quantities G^E, H^E, S^E, V^E and C_p^E as functions of both temperature and composition[62,63]; the influence of pressure has been investigated to a much smaller extent. An excess quantity is defined by

$$X^E = X^{real} - X^{ideal} \qquad (\text{same } P, T, x) \quad ,$$

that is to say it is defined as the difference between the actual molar prope value X^{real} and the value calculated for an ideal mixture X^{ideal} at the same temperature, pressure and composition. For example, the molar excess heat capacity at constant pressure of a binary mixture is given by

$$C_P^E = C_P - (x_1 C_{P,1}^{\circ} + x_2 C_{P,2}^{\circ}) \quad ,$$

where C_P, $C_{P,1}^{\circ}$ and $C_{P,2}^{\circ}$ are the molar heat capacities of the mixture, and of the pure components 1 and 2, respectively. For an overview of progress concerning experimental techniques for measuring excess quantities, we refer the pertinent review articles and monographs cited in the Introduction.

The most satisfactory strategy for a comprehensive thermodynamic investigation of liquid mixtures is exemplified by the work of Ziegler and coworkers[64]. These authors determined, by adiabatic calorimetry, the molar he capacities C_P and excess heat capacities C_P^E of selected mixtures as a functic of composition and temperature over ranges exceeding 100 K (in general, the experimental data were fitted to polynomials in temperature). In conjunction with experimental results for H^E and $G^E = H^E - TS^E$ at suitably selected temperatures (at or near 298.15 K), these heat capacity data were then used to calculate H^E, S^E and G^E in the temperature range of the calorimetric measurements by integrating

$$(\partial H^E/\partial T)_{P,x} = C_P^E$$

and

$$(\partial S^E/\partial T)_{P,x} = C_P^E/T \quad .$$

For instance, this method has been applied to various binary mixtures of type (alcohol + hydrocarbon) . Subsequently, the whole set of thermodynamic excess functions was compared with predictions of various chemical association models, which is indeed a severe test of any theory.

Measurements of this type play an important role in the development of generalized classification schemes of liquid non-electrolyte mixtures. The most recent activity in this field is due to Kohler and Gaube[65], and was stimulated by Bittrich's work[66] of the mid-sixties. The former authors plot G^E against H^E for binary mixtures at $x= 0.5$, and indicate the changes with increasing temperature by arrows, thereby distinguishing qualitatively various mixture types.

Outside the critical region, the influence of pressure on excess quantities is rather small, though modern instrumentation allows, for instance, the measurement of enthalpies of mixing at elevated pressures[67-69]. Since

$$(\partial H^E/\partial P)_{T,x} = V^E - T(\partial V^E/\partial T)_{P,x} \quad , \tag{66}$$

eq. 66 is frequently used for testing the consistency of such calorimetric measurements by means of volumetric data and vice versa.

Quantitative information on phase equilibria is essential for designing separation processes such as distillation, partial condensation, absorption and extraction. Phase equilibrium calculations in multicomponent PVT-systems of uniform temperature and pressure are conveniently based on the rigorous thermodynamic criterion of equality of the fugacities $f_i(T,P,x_1,\ldots,x_n)$ for each component i in all phases involved. The link with practice is generally established by either one of two equivalent methods. In the first, the condition for equilibrium is rewritten in terms of fugacity coefficients $\phi_i \equiv f_i/(x_iP)$ and thus requires an equation of state which accurately describes the volumetric properties of all phases. In the second method, the fugacities in the liquid phase(s) are expressed in terms of liquid-phase activity coefficients $\gamma_i \equiv f_i/(x_if_i^\circ)$, where f_i° is an appropriate standard-state fugacity. For vapor-liquid equilibria this approach yields

$$y_i\phi_iP = x_i\gamma_if_i^\circ \tag{67}$$

as equilibrium condition, where y_i is the mole fraction in the vapor phase and x_i the mole fraction in the liquid phase. For temperatures below the critical temperature, f_i° is usually taken to be the fugacity of pure liquid i at T and P of the mixture. This method is particularly useful for the description of VLE at low or moderate pressures. For liquid-liquid equilibria, with f_i° being the same in both liquid phases α and ß, we obtain

$$x_i^\alpha\gamma_i^\alpha = x_i^\beta\gamma_i^\beta \quad . \tag{68}$$

The activity coefficient is directly related to the molar excess Gibbs energy G^E through

$$\ln \gamma_i = \frac{1}{RT}\left[\frac{\partial(nG^E)}{\partial n_i}\right]_{T,P,n_{j\neq i}} , \tag{6}$$

where $n = \sum_i n_i$ denotes the total amount of substance, and

$$G^E/RT = \sum_i x_i \ln \gamma_i \quad . \tag{7}$$

Considerable effort was - and still is - invested in the development of efficient models for G^E of *complex liquid mixtures*. Ideally, they should allow evaluation of γ_i at any desired composition and temperature. If sufficient experimental data are available for a given mixture, the emphasis is on *interpolation* (or on extrapolation over *small* ranges of composition or temperature). Several well-known essentially empirical relations, such as Redlich-Kister, generalized Myers-Scott[70], van Laar etc., when necessary with temperature-dependent parameters, may be adopted. Occasionally, spline-fit techniques are indicated[71]. However, if no data are known, *prediction* is preferably based on one or the other of the existing group contribution theories. These theories are based on the intuitively appealing assumption that "group properties" are essentially invariant, that is to say they are supposed to be independent of the type and the number of other groups present in the molecule. It is clear that this assumption can never be strictly valid, but in many cases of interest (and with judiciously defined groups) it is a reasonable approximation. The usefulness of group contribution methods lies in the fact, that with only a few groups a great variety of molecules of potential interest may be constructed.

The quantitative performance of a given group contribution theory depends crucially on the underlying statistical-thermodynamical mixture model. For instance, the Guggenheim-Barker-Kehiaian (GBK) theory[72,73] is based on the rigid quasi-lattice model and considers interactions in terms of group surfaces. The geometrical parameters "relative molecular volume" r_i and "relative molecular surface" q_i of molecule i are calculated[11)] by adding appropriate group increments as determined by Bondi's method[57]. In the simplest version of the GBK theory, that is to say in the random-mixing (or zeroth)

[11)] Here, "relative" means with respect to methane (arbitrary choice).

approximation, the molar excess Gibbs energy of a multicomponent mixture is given by

$$G^E = G^E_{comb} + G^E_{int} \quad , \tag{71}$$

where the combinatorial term is calculated with the simple Flory-Huggins equation

$$G^E_{comb} = RT\sum_i x_i \ln\left(\gamma_i / x_i\right) \quad , \tag{72}$$

and the interaction term is

$$G^E_{int} = \frac{1}{2}\left(\sum_i q_i x_i\right)\sum_i\sum_j \xi_i \xi_j g_{ij} \quad , \tag{73}$$

$$g_{ij} = -\frac{1}{2}\sum_s\sum_t (\alpha_{si} - \alpha_{sj})(\alpha_{ti} - \alpha_{tj}) g_{st} \quad . \tag{74}$$

Here, the volume fraction γ_i of component i is defined as

$$\gamma_i = r_i x_i \Big/ \sum_i r_i x_i \quad , \tag{75}$$

the surface fraction of i in the mixture is

$$\xi_i = q_i x_i \Big/ \sum_i q_i x_i \quad , \tag{76}$$

and the molecular surface fraction of surface of type s on molecule i is defined by

$$\alpha_{si} = q_{si}/q_i \text{ and } \sum_s \alpha_{si} = 1 \quad . \tag{77}$$

The parameter g_{st} is called the molar interchange Gibbs energy referring to contact of surfaces of type s and t. For the molar excess enthalpy we obtain

$$H^E = \frac{1}{2}\left(\sum_i q_i x_i\right)\sum_i\sum_j \xi_i \xi_j h_{ij} \quad , \tag{78}$$

$$h_{ij} = -\frac{1}{2}\sum_s\sum_t (\alpha_{si} - \alpha_{sj})(\alpha_{ti} - \alpha_{tj}) h_{st} \quad , \tag{79}$$

where the molar interchange enthalpy h_{st} is related to g_{st} by

$$h_{st} = -T^2 \frac{\partial(g_{st}/T)}{\partial T} , \qquad (8$$

and so forth. The interchange parameters have to be obtained from *systematic experiments* on mixtures and are subsequently tabulated[12)]. As concerns the heat capacities of interchange, the majority of the necessary experimental data have become available only because of significant improvement of calorimetric equipment during the mid-seventies[45,47,52] (see Fig. 5). We note that in genera prediction of $C_P^E = -T(\partial^2 G^E/\partial T^2)_{P,x}$ is a much more delicate matter than prediction of $H^E = [\partial(G^E/T)/\partial(1/T)]_{P,x}$, since with increasing order of derivatives of the excess Gibbs energy deficiencies of the underlying model are considerably magnified.

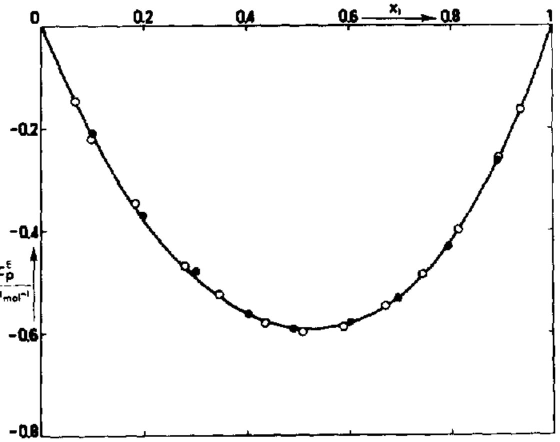

FIGURE 5. Comparison of the molar excess heat capacity at constant pressure C_P^E for [tetrachloromethane(x_1) + cyclohexane(x_2)] at 298.15 K. Experimental results: ○ , ref. 47; ● , ref. 45b.

[12)] An interesting application of the GBK theory (random-mixing approximation) to the calculation of solid-liquid equilibria by using interchange parameters obtained from experimental data on VLE, H^E and C_P^E is reported in ref. 74.

In this connection it is emphasized that conformational (or cooperative) effects, associated for instance with mixtures containing an n-alkane as one component, are *not* incorporated in any of the current versions of group contribution theories such as GBK, UNIFAC[75], ASOG[76] etc.13), but may have profound influence on H^E and C_p^E. Additional areas of current research activities include orientational effects due to complex polar groups, molecular shape (packing!) and intramolecular proximity effects; when strongly associating substances - such as alkanoic acids (see Fig. 6) - are involved, chemical association theories are indicated and have been rather successful. Representative articles on these topics are given in refs. 52, 53, 83-93, while critical discussions of group contribution methods are provided by refs. 72 and 94.

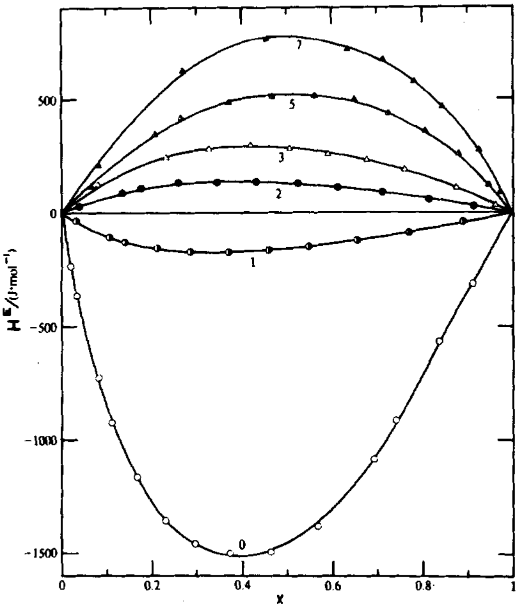

FIGURE 6. Molar excess enthalpies H^E of [1,4-dioxane(x) + $C_nH_{2n+1}COOH$] at 298.15 K. ○ , n = 0; ◑ , n = 1; ● , n = 2; △ , n = 3; ◭ , n = 5; ▲ , n = 7. From ref. 89c, p. 517.

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13) The UNIFAC (UNIQUAC functional-group activity coefficients) method and the ASOG (analytical solution of groups) method are both based on the "local composition" concept[77], which has recently been criticized severely[78-82].

4. DILUTE SOLUTIONS

In recent years there has been a resurgence of interest in dilute solutions general and in dilute aqueous solutions in particular, the experimental basis c which has been an impressive array of newly designed and readily available hig precision equipment - not the least calorimetric equipment. For excess enthalpi step-wise isothermal dilution calorimeters[95] or flow calorimeters based on the designs of either Monk and Wadsö[96] or Picker[97] have been rather successful, whi the introduction of the Picker calorimeter for heat capacity measurements (see above and ref. 98) has made feasible high-precision determination of partial mc heat capacities (or alternatively of apparent molar heat capacities at high dilution). Since the quantity actually measured with the Picker calorimeter is t heat capacity per unit volume, C_p/V, precise volumetric data for the mixtures must be available. Most of the measurements of the excess volumes are nowadays made with either continuous dilution dilatometers[99,100] or with digital densimeter[46,47,101] (for a recent review of experimental techniques and of publishe data see ref. 102). In conjunction with isentropic compressibilities obtained from ultrasonic speeds, reliable isothermal compressibilities and isochoric hea capacities (see eqs. 52-54) are now becoming available for an increasing numbe of dilute aqueous solutions[103,104]. A novel method for direct continuous measurement of the thermal expansivity is described in ref. 105. It uses a differential flow heat-capacity microcalorimeter (Picker design) to monitor in continuous mode the thermal expansion of a sample during a programmed temperatu scan.

The composition of a solution is often expressed *not* in terms of the mole fractions of the solutes but in terms of their molalities m. For a solute i (i= 2,3,...,k) dissolved in solvent 1, the molality is defined by

$$m_i = n_i/n_1M_1 \quad , \tag{8}$$

where n denotes the amount of substance, and M_1 is the molar mass of the solvent. The molality is related to the mole fraction by

$$m_i = x_i/(1-\sum_{i=2}^{k}x_i)M_1 \qquad \text{or} \qquad x_i = M_1m_i/(1+M_1\sum_{i=2}^{k}m_i) \quad . \tag{8}$$

Instead of partial molar quantities X_i some authors prefer to use apparent mola quantities of the solute. For solute 2 dissolved in solvent 1 the definition is

$$\Phi_{X,2} = (X - n_1X_1^\circ)/n_2 \tag{8}$$

where X is the corresponding extensive quantity, and X_1° denotes here the molar quantity of pure solvent. $\Phi_{X,2}$ is related to the corresponding partial molar quantity by

$$X_2 = \Phi_{X,2} + m_2 (\partial \Phi_{X,2}/\partial m_2)_{T,P} \quad . \tag{84}$$

Discussion of thermodynamic quantities concerning biochemical systems is most profitably based on results obtained for relatively simple model substances dissolved in liquid water. Such an approach has proved eminently useful in the discussion of hydrophobic interaction[106-110] and its contribution, for instance, to the reversible aggregation of molecules with long non-polar chains as in the case of phospholipids and to the conformational stability of proteins.

The partial molar heat capacity $C^{\infty}_{P,2}$ of the solute at infinite dilution is regarded as one of the most interesting thermodynamic quantities. For many substances dissolved in liquid water, values of $C^{\infty}_{P,2}$ have been obtained through extrapolation of calorimetrically obtained data over reasonably selected composition ranges (note that $C^{\infty}_{P,2} = \Phi^{\infty}_{C_P,2}$). However, for substances sparingly soluble in water, such as benzene and cyclohexane[111,112], oxygen[113], carbon monoxide[114] or methane and ethane[115], high-precision VLE measurements over a sufficiently large temperature range are often the only sources of partial molar heat capacities (see below and Fig. 7). $C^{\infty}_{P,2}$ data have been used by various authors to develop relatively simple estimation techniques based on concepts from group contribution theory[116-120]. Considering the complexity of the solutions they work surprisingly well.

While VLE studies at very low, though finite, mole fractions (e.g. for C_6H_6 dissolved in water[112] $x_2 \leqslant 3 \cdot 10^{-4}$) provide quantitative information on the Gibbs energy of interaction of *pairs* of molecules, calorimetric measurements of enthalpies of dilution $\Delta_{dil}H$ may be used to determine pairwise enthalpies of interaction[121]. Specifically

$$\Delta_{dil}H/n = h_2(m_i - m_f) + h_3(m_i^2 - m_f^2) + \cdots \quad , \tag{85}$$

where n is the total amount of solute initially at molality m_i and then diluted with water to give a final solution with molality m_f. The coefficient h_2 contains the desired information, that is to say for a single solute A

$$h_2 = h_{AA} \quad , \tag{86}$$

and for a mixture of solutes A and B the relation is

$$h_2 = h_{AA}\hat{x}_A^2 + 2h_{AB}\hat{x}_A\hat{x}_B + h_{BB}\hat{x}_B^2 \quad . \tag{87}$$

Here, $\hat{x}_A = n_A/(n_A + n_B)$ is the mole fraction of A in the solute mixture, and $m = m_A + m_B$ is the total molality. Further analysis of the pairwise (molecular) interaction enthalpies h_{AB} between two solute molecules A and B may be based on group contribution methods, for instance that of Savage and Wood[122]

$$h_{AB} = \sum_{i,j} n_{A,i}\, n_{B,j}\, H_{ij} \quad . \qquad \text{(88}$$

Here, $n_{A,i}$ and $n_{B,j}$ are the number of type i groups on A and of type j groups on B, and H_{ij} is the group interaction enthalpy.

Albeit somewhat outside the scope of this article, two other areas of intensi research activities should be mentioned. The first concerns solutions of surfactants, micelles and microemulsions[123-126]. Microemulsions[14)] have become increasingly important in the medical sciences as well as in chemical engineerin in particular since solubilization of oil by microemulsions appears to be a promising method in tertiary oil recovery processes. Calorimetrically determined partial molar heat capacities have recently been used for the characterization o model microemulsions[127] such as [water + sodium dodecyl sulfate(SDS) + n-butanol + toluene]. Enthalpy and heat capacity changes associated with micelle formation of SDS in water are reported in ref. 128.

The second topic concerns measurements of accurate thermodynamic quantities for aqueous salt solutions at elevated temperatures and pressures, including the critical region. Despite the formidable experimental problems, Wood and collaborators have succeeded in constructing a flow calorimeter for the rapid determination of enthalpies of dilution[129] up to 473 K. From the same laboratory come a differential flow heat-capacity calorimeter for operation at temperatures up t 600 K and pressures up to 20 MPa, which has been used to measure the heat capaci of aqueous sodium chloride[130] from 0.1 to 3.0 mol/kg. At low molalities and high temperatures, the apparent molar heat capacity of the salt is enormously negativ -2138 J/K·mol at 0.1 mol/kg, 600 K and 17.7 MPa. These results were discussed in terms of the Born equation for the electrostatic contribution to the Gibbs energy of hydration of salt composed of hard-sphere ions in a continuous dielect medium

$$\Delta G^{el} = -(N_A e^2/8\pi\varepsilon_0)(r_+^{-1} + r_-^{-1})(1 - \varepsilon_r^{-1}) \quad , \qquad \text{(89}$$

where e is the elementary charge, ε_0 is the permittivity of vacuum, ε_r is the relative permittivity, and r_+ and r_- are the radii of the cation and anion,

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[14)] Microemulsions are optically transparent multicomponent systems which contai water, surfactant, cosurfactant (often an aliphatic alcohol), a hydrocarbon often, salts.

respectively. Taking appropriate derivatives, the electrostatic contributions to the solution enthalpy and solution heat capacity may be obtained from eq. 89. A modification to include the compressibility of the solvent is introduced in ref. 131, while a corresponding-states theory for the heat capacities of aqueous salt solutions is proposed in ref. 132. This theory correctly predicts the very large *negative* values of the partial molar heat capacity of dilute solutions of electrolytes just below the critical point of water and also predicts very large but *positive* values just above the critical point, see also ref. 133.

We conclude this review with a brief discussion of solutions of gases in liquids at low to moderate pressures. Besides being of fundamental interest for the physical chemist (see above, in particular refs. 4, 5, 7, 106-110), reliable gas solubility data are often required in chemical process design, in environmental science (pollution control), and in biophysical and medical applications. Areas of recent interest are the solubility of hydrogen in hydrocarbon solvents, which is of importance in hydrofining of oil and coal[134]; removal of CO_2 and H_2S from sour natural gases by mixed-solvent absorption (gas sweetening)[135]; solubility of Freons in water[136]; solubility of gases in selected solvents (or solvent mixtures) and anesthetic potency[137]; solubility of oxygen in perfluorocarbons[138], which substances may be used as blood substitutes and as carriers in liquid breathing[139].

The thermodynamic analysis[114,115,140] is based on the rigorous criterion for vapor-liquid phase equilibrium in PVT-systems of uniform temperature and pressure, eq. 67. For the "gaseous" component 2 (not necessarily a supercritical fluid) dissolved in solvent 1, the standard-state fugacity is usually taken to be the experimentally accessible Henry coefficient $H_{2,1}$, that is to say

$$f_2^\circ(T,P) = H_{2,1}(T,P) = H_{2,1}(T,P_{s,1})\mathcal{P}_2 \quad , \tag{90}$$

$$\begin{aligned} \mathcal{P}_2 &= \exp\left\{\int_{P_{s,1}}^{P}\left[V_2^{\infty L}(T,P)/RT\right]dP\right\} \\ &\simeq \exp\left[V_2^{\infty L}(P-P_{s,1})/RT\right] \ . \end{aligned} \tag{91}$$

The standard-state fugacity for the solvent is the Poynting-corrected orthobaric fugacity of pure solvent 1

$$f_1^\circ(T,P) = f_1^\circ(T,P_{s,1})\mathcal{P}_1 = P_{s,1}\phi_1^\circ(T,P_{s,1})\mathcal{P}_1 \quad , \tag{92}$$

$$\mathcal{P}_1 = \exp\left\{\int_{P_{s,1}}^{P}\left[V_1^{\circ L}(T,P)/RT\right]dP\right\}$$

$$\simeq \exp\left[V_{s,1}^{oL}(P - P_{s,1})/RT\right] . \qquad (9$$

$V_2^{\infty L}$ denotes the partial molar volume of dissolved gas at infinite dilution[141], and $V_{s,1}^{oL}$ is the molar volume of pure liquid solvent. For the liquid-phase activi coefficients γ_i we now have the so-called asymmetric convention

$$\begin{aligned} \gamma_1 &\rightarrow 1 \quad \text{for} \quad x_1 \rightarrow 1 \\ \gamma_2 &\rightarrow 1 \quad \text{for} \quad x_2 \rightarrow 0 \ . \end{aligned} \qquad (9$$

At the saturation pressure of the solvent, $H_{2,1}(T,P_{s,1})$ is rigorously obtained through evaluation of the limiting values of *experimental* isothermal ratios of fugacity over mole fraction, that is

$$\begin{aligned} H_{2,1}(T,P_{s,1}) &= \lim_{\substack{x_2 \rightarrow 0 \\ P \rightarrow P_{s,1}}} (f_2^L/x_2) \\ &= \lim_{\substack{x_2 \rightarrow 0 \\ P \rightarrow P_{s,1}}} \left[y_2 \phi_2(T,P,y_2)P/x_2\right] \ . \end{aligned} \qquad (9$$

High-precision measurements of $H_{2,1}(T,P_{s,1})$ over sufficiently large ranges of temperature constitute, with very few exceptions[143-148], the only source of information on enthalpies of solution of sparingly soluble gases in liquids. Specifically

$$\begin{aligned} \Delta H_2^{\infty} &\equiv H_2^{\infty L} - H_2^{oV} \\ &= -\frac{RT^2}{H_{2,1}(T,P_{s,1})} \frac{dH_{2,1}(T,P_{s,1})}{dT} + TV_2^{\infty L} \frac{dP_{s,1}}{dT} \ , \end{aligned} \qquad (9$$

where $H_2^{\infty L}$ is the partial molar enthalpy of gas at infinite dilution in the liquid phase, and H_2^{oV} is the molar enthalpy of pure gas in the perfect-gas reference state. Particularly gratifying is the excellent accord between the recent flow-calorimetric results of Gill and Wadsö[148] for essentially ΔH_2^{∞} of (water + oxygen) at 298.15 K and the value derived by Benson et al.[113] from the temperature dependence of the Henry coefficient.

As concerns the heat capacity change upon solution of a gas in a liquid, tha is the difference between the partial molar heat capacity of gas $C_{P,2}^{\infty L}$ at infini dilution and the molar heat capacity of pure gas $C^{\circ V}_{P,2}$ in the perfect-gas reference state,

$$\Delta C^{\infty}_{P,2} \equiv C^{\infty L}_{P,2} - C^{\circ V}_{P,2} = \left(\frac{\partial \Delta H^{\infty}_{2}}{\partial T}\right)_{P} \quad , \tag{97}$$

direct calorimetric determinations are completely absent. The few results for $\Delta C^{\infty}_{P,2}$ obtained from the temperature dependence of ΔH^{∞}_{2} have still considerably larger uncertainties[146] than values obtained from high-precision solubility measurements. For instance, Fig. 7 shows recent results for $\Delta C^{\infty}_{P,2}$ of the three solutions (water + oxygen)[113], (water + carbon monoxide)[115] and (water + methane)[114] in the temperature range 273.15 K to 333.15 K. The experimental imprecision of the corresponding Henry coefficients is of the order of a few *hundredth of a percent.* Important recent measurements of the solubility of the rare gases in liquid water and heavy water over very large temperature ranges (up to about 600 K), though with experimental imprecisions of the Henry coefficients of ca. 1%, have been

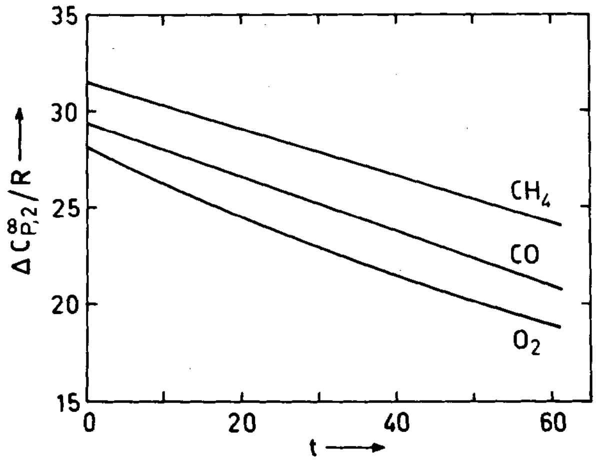

FIGURE 7. Temperature dependence of the heat capacity change on solution, $\Delta C^{\infty}_{P,2}/R = (C^{\infty L}_{P,2} - C^{\circ V}_{P,2})/R$, for (water + oxygen)[113], (water + carbon monoxide)[115], and (water + methane)[114]. $t = T/K - 273.15$.

reported in refs. 149 and 150. For an interesting gas chromatographic technique see ref. 151.

Following Ben-Naim[106,107], when discussing hydrophobic interaction (HI) between two solute particles we refer to the *indirect* part $\delta G^{HI}(r)$ of the Gib free energy change (that is the part which originates from the presence of the solvent) required to bring the solute particles from fixed positions at infinit separation to some close distance r (at constant temperature and pressure). The link with experimentally accessible quantities is established by noting that an indication of the strength of hydrophobic interaction is provided by the approximate relation

$$\delta G^{HI}(r=d) = \Delta\mu^{o}_{C_2H_6} - 2\Delta\mu^{o}_{CH_4} \quad , \tag{98}$$

where d = 0.1533 nm is the carbon-carbon distance in ethane.

$$\Delta\mu^{o} = -RT \ln L^{\infty} \quad , \tag{99a}$$

$$L^{\infty} = \lim_{c_2^L \to 0} (c_2^L / c_2^V)_{equil} \quad , \tag{99b}$$

is obtained from VLE measurements of methane and ethane in water[114]. L^{∞} is the limiting value ($c_2^L \to 0$) of the conventional Ostwald coefficient, and c_2^L and denote the amount-of-substance concentration of gas in the liquid and in the vapor phase, respectively. We note that[114,140]

$$L^{\infty} = \frac{Z_1^{oV}(T,P_{s,1})\,\phi_2^{\infty}(T,P_{s,1})}{H_{2,1}(T,P_{s,1})} \, \frac{RT}{V_1^{oL}(T,P_{s,1})} \quad , \tag{100}$$

where Z_1^{oV} is the compressibility factor of pure saturated solvent vapor, and ϕ_2^{∞} is the fugacity coefficient of gas at infinite dilution in the vapor phase The corresponding changes in entropy $\delta S^{HI}(d)$, enthalpy $\delta H^{HI}(d)$, and heat capacity $\delta C_P^{HI}(d)$ may be obtained[114] by appropriate differentiation of eq. 98. It is possible to inquire about the strength of hydrophobic interaction at othe separations, for instance at r = 0 (see refs. 106, 107 and 110), which quantity is related to the free energy of solution of a single hard sphere solute.

5. CONCLUDING REMARKS

Calorimetry is one of the oldest and best established experimental disciplines of physical chemistry. Although simple in principle, considerable effort and ingenuity has gone into designing the instruments of today's precision, accuracy and speed. Calorimetry has advanced to the point where exceedingly small changes of energy and very small amounts of substance can be investigated, while at the same time pressure and temperature ranges of apparatus have been impressively increased. Though theoretically highly important, calorimetric measurements in the critical region have been deliberately excluded from this article. Let it suffice to say that the difficulties of measuring thermodynamic quantities in the critical region (e.g. proper allowance for gravitational effects has to be made) make it hard to arrive at precise values of the critical exponents characterizing, for instance, the infinities in C_V:

$$C_V(V=V_c,T) \sim |T-T_c|^{-\alpha} \quad \text{for } T \to T_c \ . \qquad (101)$$

α_2^-, that is to say for a pathway along the critical isochore for $T < T_c$, appears to have the same value (≈ 0.1) as the critical exponent α_1^+ for a pathway along the critical isochore for $T > T_c$. For recent discussions of critical exponents see refs. 8, 16, 152 and 153.

In this review we have endeavored to cover the main areas of current calorimetric research. New fields of potential interest to physics, chemistry, chemical engineering, biophysics and medicine have been indicated by showing the close relations with recent advances in molecular thermodynamics. Evidently, precision calorimetry continuous to be a versatile and powerful tool for enhancing our understanding of fluids.

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