

## The fascinating world of pure and mixed nonelectrolytes\*

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*Abstract:* In the first part of this work, the focus is on the molar heat capacity  $C_V$  at constant volume of fairly simple liquids. This quantity contains valuable information on the type of motion executed by the constituent molecules. Using the residual property formalism, the (hindered) rotational behavior of quasi-rigid molecules in the dense liquid phase will be discussed. To this end, the change of  $C_V$  determined for states along the saturation curve has to be resolved into the separated changes with temperature and volume, respectively. In the second part, the focus is on binary liquid mixtures containing one strongly polar component. Polar interactions constitute an important example of orientational forces between molecules, and substantial deviations of the properties of polar fluids from those of comparable nonpolar fluids are to be expected and indeed observed. At sufficiently low temperatures, these directional forces lead to significantly increased local structure. Extension of these ideas to liquid mixtures allows a semi-quantitative discussion of W-shaped excess molar heat capacities  $C_p^E$  at constant pressure and M-shaped excess molar enthalpies  $H^E$ .

*Without experimentalists, theorists tend to drift,  
without theorists, experimentalists tend to falter.*

T. D. Lee (Nobel Prize 1957, with C. N. Yang), *CERN Courier*,  
January/February 1987, p. 12.

*Keywords:* Chemical thermodynamics; liquids; mixtures; heat capacities; excess enthalpies.

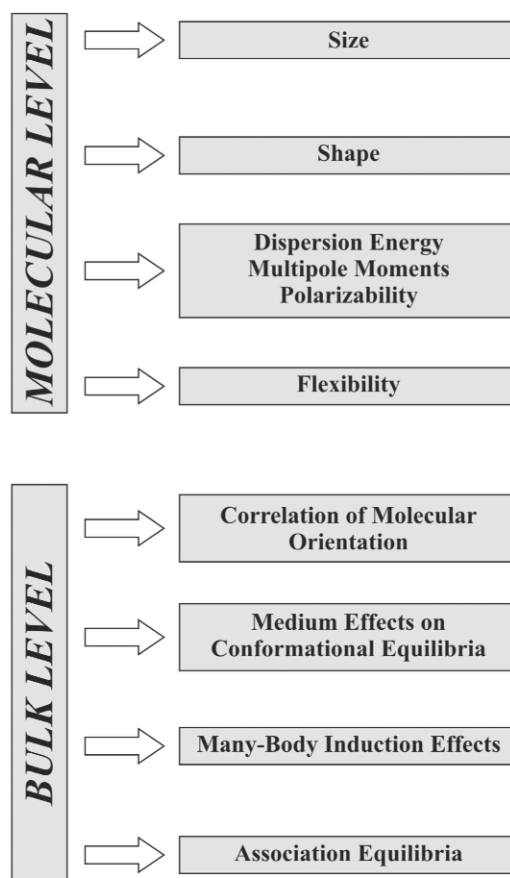
### INTRODUCTION

Chemical thermodynamics is a highly formalized scientific discipline of enormous generality: By providing a mathematical framework of equations (and a few inequalities), it yields exact interrelations between thermodynamic equilibrium properties of bulk phases. This aspect itself is of the highest value for the practicing physicist, chemist, or chemical engineer. In combination with specific, preferably molecular-based models of material behavior, chemical thermodynamics contributes substantially toward a better understanding of molecular interactions and hence of macroscopic systems [1]. Figure 1 summarizes schematically the most important aspects to be considered in the description of pure liquids and solutions/mixtures on the molecular level as well as on the bulk level [2,3].

A plenary lecture at an ICCT conference affords the lecturer an opportunity to review one or two reasonably large areas, to present his or her contributions, and to reflect on them from the perspective

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**Fig. 1** Some important aspects to be considered in the discussion of pure liquids and liquid mixtures/solutions (molecular level and bulk level).

of many years of research. The subject I selected for the 18<sup>th</sup> ICCT in Beijing, China is liquid non-electrolytes, either pure or mixed. While the title of this lecture was selected so as to provide an umbrella large enough to cover every aspect of the indicated field, I will focus on just two topics with the bias reflecting some of my current research interests:

- Heat capacities and related quantities of fairly simple molecular liquids, such as tetrachloromethane, predominantly at (or near) orthobaric conditions.
- Chemical thermodynamics of binary liquid mixtures containing one strongly polar component (atmospheric pressure).

Both topics are more complex and less understood than might be supposed.

## HEAT CAPACITIES AND RELATED QUANTITIES

Undoubtedly, heat capacities are highly important thermophysical quantities not only from a practical point of view, but also from a theoretical one. They have long provided important information on molecular motion in the ideal-solid state as well as the ideal-gas state. However, while the theory of dilute gases at equilibrium (second virial coefficient domain) is essentially complete, this is not the case for dense gases and liquids.

From experimentally determined accurate heat capacities of liquids, relatively simple approximate models have been used to extract information on the type of motion executed by molecules in the liquid state. In general, they are based on the separability of contributions due to translation, rotation, vibration, and so forth. Though none of them is completely satisfactory, they have provided eminently useful insights and thereby furthered theoretical advances. Following the early work of Eucken [4,5], Bernal [6], Eyring [7], Staveley [8,9], Moelwyn-Hughes [10], Kohler [11,12], Bondi [13], and their collaborators, one may resolve the total molar heat capacity  $C_V$  at constant volume of simple, nonassociated liquids into the following contributions [14]:

$$C_V = C_{\text{tr}} + C_{\text{rot}} + C_{\text{int}} + C_{\text{or}} \quad (1)$$

Since there is no risk of ambiguity, for convenience all molar quantities will appear without a subscript *m*. The translational contribution  $C_{\text{tr}}$  arises from the motion of the centers of gravity of the molecules under the influence of all molecules in the system (translational movement within their respective free volumes). It is of the order  $3R/2 + R$ ,  $R$  (the gas constant) being roughly the excess over the translational molar heat capacity of the ideal gas.  $C_{\text{rot}}$  represents the contribution from rotation or libration of the molecules as a whole. For nonlinear molecules, it may be appreciably higher than its ideal-gas-phase value of  $3R/2$  (free rotation). The contribution from internal degrees of freedom,  $C_{\text{int}}$ , can be subdivided into a part  $C_{\text{vib}}$  resulting from vibrations which are *not* appreciably influenced by density changes (that is, by changes from the liquid to the ideal-gas state), and another part  $C_{\text{conf}}$  resulting from internal rotations (conformational equilibria) which depend on changes in the surroundings of the molecule and hence on density [11–13,15–18]. Lastly, for polar substances there is a further contribution  $C_{\text{or}}$  from the change of the dipole–dipole orientational energy with temperature, which may become quite important [12,15–17]. Here, the focus will be on fluids composed of quasi-rigid and not too anisotropic nonpolar molecules of which tetrachloromethane or benzene are generic representatives. We note that eq. 1 conforms to the usual assumptions introduced for calculating the semiclassical canonical partition function [1].

Preferably, all these contributions to  $C_V$  are discussed in terms of residual quantities as elaborated by Wilhelm et al. [14]. Such quantities are the most direct measure of the contributions due to intermolecular interactions at any given state condition [19]. The residual molar heat capacity  $C_V^r$  at constant volume is defined by

$$C_V^r = C_V(T, V, x) - C_V^{\text{ig}}(T, V, x) \quad (2)$$

where the superscript *ig* refers to the ideal-gas state at the same temperature  $T$ , same molar volume  $V$ , and same composition (mole fraction  $x$ ). For fluids composed of quasi-rigid molecules, one may assume (see above)

$$C_{\text{int}}^r = C_{\text{int}} - C_{\text{int}}^{\text{ig}} = 0 \quad (3)$$

Usually, this is an excellent approximation, whence for quasi-rigid nonpolar molecules eq. 2 may be recast into

$$C_V^r = C_{\text{tr}}^r + C_{\text{rot}}^r \quad (4)$$

where  $C_{\text{tr}}^r = C_{\text{tr}} - 3R/2$ , and  $C_{\text{rot}}^r = C_{\text{rot}} - 3R/2$  (for nonlinear molecules) represents the excess over the gas-phase value due to *hindered* rotation in the liquid of the molecules as a whole. Using corresponding states arguments,  $C_{\text{tr}}^r$  may be approximated by  $C_V^r$  of argon [20] (where  $C_{\text{rot}}^r = 0$ ) at the same reduced temperature  $T_r = T/T_c$ , where  $T_c$  is the critical temperature, whence

$$C_{\text{rot}}^r = C_V^r - C_V^r(\text{Ar}) \quad (5)$$

Equation 5 offers a convenient way for obtaining semiquantitative estimates of residual rotational heat capacities.

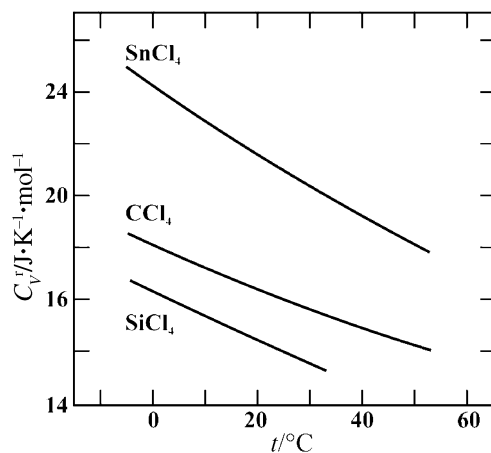
Direct measurement of  $C_V$  of a liquid at temperatures well below  $T_c$  is difficult because the thermal pressure coefficient  $(\partial p/\partial T)_V$  is large. Thus, the heat capacity at constant volume is usually determined indirectly by means of

$$\kappa \equiv C_p/C_V = 1 + TM\alpha_p^2 u^2/C_p \quad (6)$$

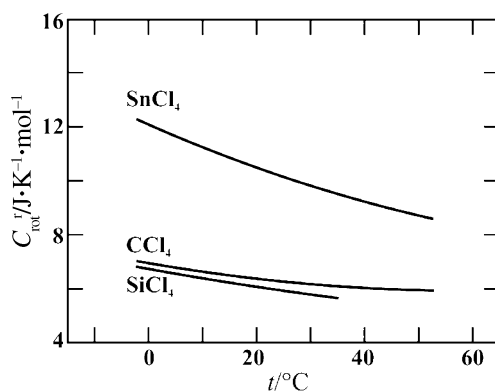
where  $C_p$  is the calorimetrically determined molar heat capacity at constant pressure  $p$ ,  $M$  is the molar mass,  $\alpha_p = V^{-1}(\partial V/\partial T)_p$  is the isobaric expansivity, and  $u$  is the ultrasonic speed at frequencies sufficiently below the dispersion region. Since also  $\kappa = \beta_T/\beta_S$ , where  $\beta_S = -V^{-1}(\partial V/\partial p)_S = V/(Mu^2)$  denotes the isentropic compressibility and  $\beta_T = -V^{-1}(\partial V/\partial p)_T$  the isothermal compressibility, the latter quantity may also be obtained indirectly:

$$\beta_T = \kappa V/(Mu^2) \quad (7)$$

Figure 2 shows the residual molar heat capacity  $C_V^r$  of the quasi-sphericals tetrachloromethane, tetrachlorosilane, and tin tetrachloride. We selected these liquids [14] to corroborate and quantify Sackmann's geometry-based cogwheel model [21] in which the interlocking of the tetrahalide molecules hinders free rotation. Figure 3 shows the residual molar rotational heat capacity  $C_{rot}^r$  of  $\text{CCl}_4$ ,  $\text{SiCl}_4$ , and  $\text{SnCl}_4$  for orthobaric conditions between 273.15 and 323.15 K. Whereas the results for  $\text{CCl}_4$  and  $\text{SiCl}_4$  are quite similar, with  $C_{rot}^r \approx 3R/4$  at 298.15 K,  $C_{rot}^r$  for liquid  $\text{SnCl}_4$  is distinctly larger, i.e., about  $5R/4$ : this clearly indicates significantly more hindered overall molecular rotation in this liquid.

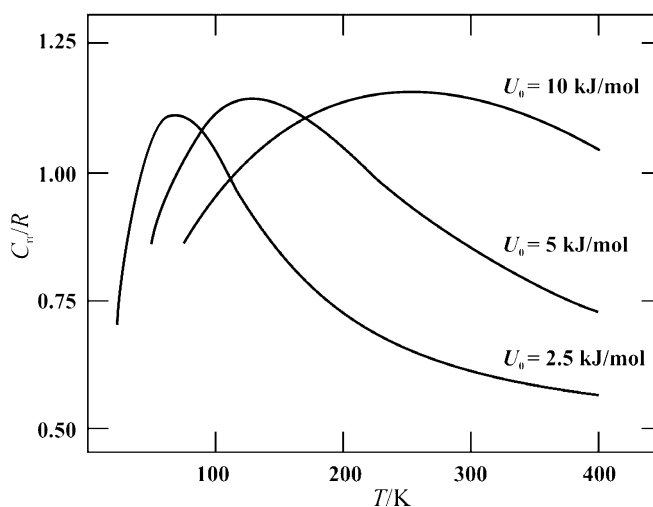


**Fig. 2** Residual molar heat capacity  $C_V^r$  at constant volume as a function of temperature  $t/^\circ\text{C} = T/\text{K} - 273.15$  of tetrachloromethane ( $\text{CCl}_4$ ), tetrachlorosilane ( $\text{SiCl}_4$ ), and tin tetrachloride ( $\text{SnCl}_4$ ) for orthobaric conditions:  $V_\sigma = V(T, p_\sigma)$  [14].

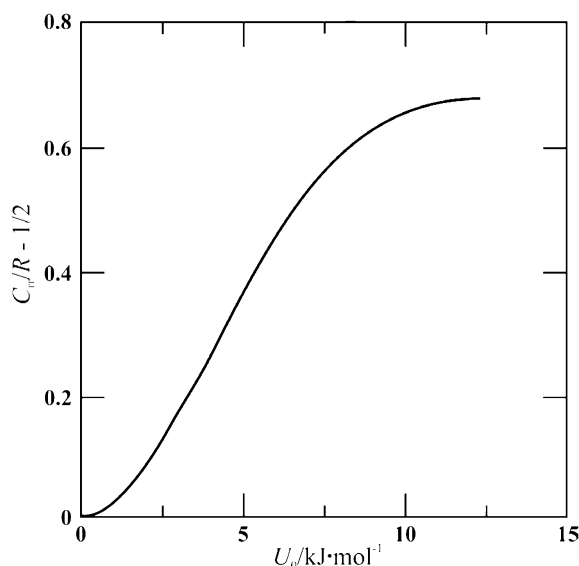


**Fig. 3** Residual molar rotational heat capacity  $C_{\text{rot}}^{\text{r}}$  as a function of temperature  $t/^{\circ}\text{C} = T/\text{K} - 273.15$  of tetrachloromethane ( $\text{CCl}_4$ ), tetrachlorosilane ( $\text{SiCl}_4$ ), and tin tetrachloride ( $\text{SnCl}_4$ ) for orthobaric conditions:  $V_{\sigma} = V(T, p_{\sigma})$  [14].

Adopting the Pitzer model for restricted rotation [14,22], the resulting contribution  $C_{\text{rr}}$  (for one degree of freedom) to the total heat capacity  $C_V$  of  $\text{CCl}_4$  is shown in Fig. 4 as a function of temperature and barrier height  $U_0$  restricting free rotation. We note that the maximum value for three degrees of freedom is about  $7R/2$ , which is *larger* than the classical value. Similar curves are obtained for  $\text{SiCl}_4$  and  $\text{SnCl}_4$ . In principle, the quantity  $(\partial C_{\text{rot}}^{\text{r}}/\partial T)_V$  plays a discriminatory role in that its sign indicates whether the substance is to be positioned on the high-temperature decline past the maximum of the  $C_{\text{rr}}$  curve (negative sign) or before (positive sign). It may be obtained by appropriate differentiation of eq. 5, provided  $(\partial C_V^{\text{r}}/\partial T)_V$  {and  $[\partial C_V^{\text{r}}(\text{Ar})/\partial T]_V$ } is known. The available data [14] suggest that at 298.15 K all the tetrahalides are already on the high-temperature decline, though the associated uncertainties are appreciable. Figure 5 shows the residual rotational heat capacity for one degree of freedom,  $C_{\text{rot}}^{\text{r}}/3 = C_{\text{rr}} - R/2$ , as a function of barrier height. It was calculated from the Pitzer model for the tetrahalides at 298.15 K. From our experiments (see Fig. 3), we obtain for  $\text{SnCl}_4$  at 298.15 K  $C_{\text{rot}}^{\text{r}}/3R \approx 0.4$ , which corresponds to about  $U_0 = 5.5$  kJ/mol. For the other two tetrahalides, molecular rotation is much less hin-



**Fig. 4** Molar heat capacity  $C_{\text{rr}}$  divided by  $R$  for *one* degree of freedom as a function of temperature  $T$  and barrier height  $U_0$  restricting free rotation in liquid tetrachloromethane ( $\text{CCl}_4$ ). The curves were calculated with a Pitzer-type model [14,22].



**Fig. 5** Residual molar rotational heat capacity divided by  $R$  for one degree of freedom,  $C_{\text{rot}}^r/3R = C_{\text{rot}}^r/R - 1/2$ , as a function of barrier height  $U_0$  restricting free rotation in the liquid tetrahalides  $\text{CCl}_4$ ,  $\text{SiCl}_4$ , and  $\text{SnCl}_4$  at 298.15 K.  $C_{\text{rot}}^r$  was calculated with a Pitzer-type model [14,22].

dered with  $C_{\text{rot}}^r/3R \approx 0.25$ , which corresponds to a barrier height of about 4.0 kJ/mol. These results corroborate the Sackmann model, which predicts increased interlocking in liquid  $\text{SnCl}_4$  as compared to liquid  $\text{CCl}_4$  or  $\text{SiCl}_4$ .

Most probably, tetrachloromethane is the molecular liquid most extensively studied by X-ray and neutron scattering (see, e.g., refs. [23–27]). These studies indicate an interlocking structure, as do computer simulations [28,29]. In liquids, the nuclear spin relaxation rate via quadrupolar interaction is related to the rotational correlation time. From its temperature dependence in  $\text{CCl}_4$ , O'Reilly and Schacher [30] derived an activation energy of  $(5.4 \pm 0.4)$  kJ/mol. Relaxation times of  $^{119}\text{Sn}$  in liquid  $\text{SnCl}_4$  have been measured as a function of temperature by Sharp [31], yielding a distinctly higher activation energy of 7.8 kJ/mol, in satisfactory accord with our findings. For an analogous analysis of heat capacity data on aromatics see refs. [16,32].

A major limitation of the discussion of heat capacities as outlined above originates from the required resolution of the change of  $C_V$  (and related quantities) obtained for states  $(T, p_\sigma)$  along the saturation curve (subscript  $\sigma$ ) into the respective variations with temperature and volume. This is by itself a most interesting problem deserving more attention than usually given [14,19,33,34]. It is important to realize that due to the close packing of molecules in a liquid, even a rather small change of the average volume available for their motion may have a considerable impact on the molecular dynamics: volume effects may become more important in influencing molecular motion in the liquid state than temperature changes. For the heat capacity at constant volume

$$(\partial C_V / \partial T)_\sigma = (\partial C_V / \partial T)_V + (\partial C_V / \partial V)_T \alpha_p V \quad (8)$$

Thus, in order to evaluate  $(\partial C_V / \partial T)_V$ , the second term of the rhs of eq. 8 must be known. In principle, this quantity is accessible via precise  $(p, V, T)$  measurements, since

$$(\partial C_V / \partial V)_T = T(\partial^2 p / \partial T^2)_V \quad (9)$$

Unfortunately, measurements of this second derivative are quite rare, but available data (see, e.g., refs. [35,36]) confirm that it is small and negative for organic liquids, that is,  $C_V$  decreases with increasing volume. Alternatively, with the help of a Maxwell equation, one may use [12,14]

$$(\partial C_V / \partial V)_T = T\beta_T^{-1}[(\partial \alpha_p / \partial T)_p - 2(\alpha_p / \beta_T)(\partial \beta_T / \partial T)_p - (\alpha_p / \beta_T)^2(\partial \beta_T / \partial p)_T] \quad (10)$$

where the last term on the rhs is approximated by means of a modified Tait equation [10,12,14,37], that is,

$$(\partial \beta_T / \partial p)_T = -n\beta_T^2 \quad (11)$$

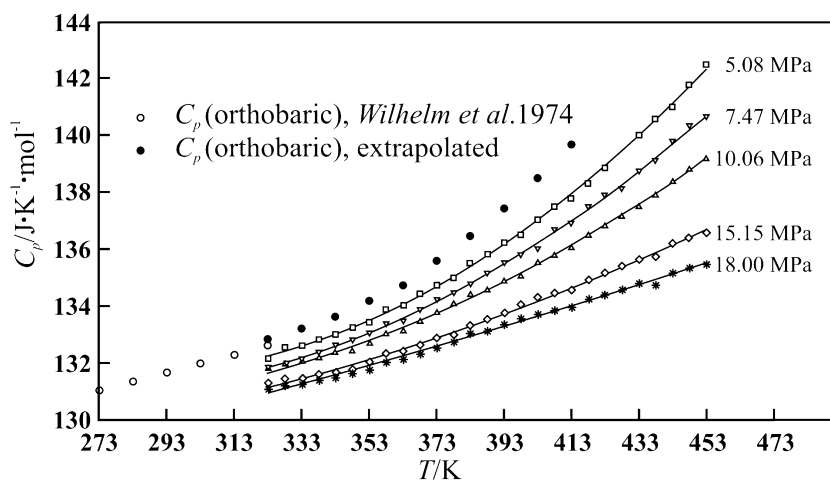
The modified Tait equation holds remarkably well up to pressures of several hundred bars, and for many liquid nonelectrolytes  $n \approx 10$ , with only a weak temperature dependence.

Comparison of literature data shows quite similar values for  $(\partial C_V / \partial V)_T$ . For instance, for liquid tetrachloromethane at 298.15 K this quantity amounts to about  $-0.48 \text{ J}\cdot\text{K}^{-1}\cdot\text{cm}^{-3}$  [14], while for liquid toluene at 303.15 K we obtained  $-0.57 \text{ J}\cdot\text{K}^{-1}\cdot\text{cm}^{-3}$  [38]. These results indicate a *substantial* contribution of  $(\partial C_V / \partial V)_T \alpha_p V$  to the change of  $C_V$  along the saturation curve as well as to the corresponding change of  $C_V^r$ , since

$$\left(\partial C_V^r / \partial T\right)_\sigma = \left(\partial C_V^r / \partial T\right)_V + (\partial C_V / \partial V)_T \alpha_p V \quad (12)$$

For a number of additional interesting aspects, the reader is referred to the original literature.

One final remark concerns experiment. In 1974, we measured  $C_p$  of liquid tetrachloromethane at saturation pressure  $p_\sigma$  between 273.15 and 323.15 K [14] with a classical adiabatic calorimeter of the Arnold type [39]. The derived molar heat capacity at constant volume at 323.15 K amounted to  $C_V = 91.8_2 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ . In 2004,  $C_p$  of tetrachloromethane was measured with a modified C80 calorimeter between 323.15 and 453.15 K, and for several pressures up to 18.0 MPa (Fig. 6). The derived  $C_V$  at 323.15 K and saturation conditions amounts to  $91.5_9 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$  [40]. Such an agreement within  $\pm 0.12\%$  is indeed highly satisfactory, and reflects both instrument quality and state-of-the-art data treatment.



**Fig. 6** Molar heat capacity  $C_p$  at constant pressure of tetrachloromethane ( $\text{CCl}_4$ ) between 273.15 and 453.15 K at pressures up to 18.00 MPa. The open and filled circles represent results for orthobaric conditions [14,40].

## BINARY LIQUID MIXTURES CONTAINING ONE STRONGLY POLAR COMPONENT

Mixtures of practical interest for the chemist or chemical engineer are usually quite complex mixtures, that is to say, the intermolecular potential energy functions characterizing the components differ strongly, thereby frequently causing pronounced nonideal thermodynamic behavior. Heuristically, a discussion may be conducted in terms of differences in molecular size, shape anisotropy, dispersion energy, polarity, polarizability, flexibility, and so forth (see Fig. 1). In fact, in many liquid mixtures, dipolar (and quadrupolar) interactions contribute significantly to the thermodynamic properties and may involve cooperative phenomena. The principal obstacles for treating complex fluid mixtures are:

- Uncertainty about the appropriate intermolecular potential energy functions of the components, and insufficient knowledge about the potential energy function characterizing unlike interaction (combining rules [41–43]).
- Difficulties encountered when two or more of the above-mentioned molecular aspects, say shape anisotropy and a permanent electric dipole moment, are present simultaneously [44].
- Meager knowledge of many-body effects, e.g., correlation of molecular orientation [45–48], medium effects on conformational equilibria [12,15,18,48,49], and many-body induction effects [50].

Additional aspects may include molecular association via hydrogen bonds [33,51,52] or charge transfer, and if aqueous solutions are involved, hydrophobic effects [53,54].

A polar substance is usually characterized by its permanent molecular electric dipole moment  $\mu$ . However, this quantity by itself is not particularly helpful in guiding the discussion of the impact of polarity on thermodynamic properties of pure liquids and liquid mixtures. For the purpose of characterizing the *effective* polarity of a molecule, one may define a reduced dipole moment [3,19] according to

$$\mu_r = \left[ \mu^2 N_A / (4\pi\epsilon_0 V_c k_B T_c) \right]^{1/2} \quad (13)$$

where  $N_A$  is the Avogadro constant,  $\epsilon_0$  is the permittivity of vacuum,  $V_c$  is the critical molar volume, and  $k_B$  is the Boltzmann constant. Note, however, that even this quantity does not reflect adequately the increase in effective polarity, which results from an unsymmetrical disposition of the polar group within the molecule, i.e., from dipole moments exposed on the molecular periphery.

Here, I will only consider binary systems of type (a polar component + a hydrocarbon). With aliphatic or alicyclic hydrocarbons, the focus is on dipolar orientational effects and increasing nonrandomness in solution when the temperature is lowered: W-shaped excess molar heat capacities  $C_p^E$  at constant pressure will be discussed [3,48,55–61]. With aromatic hydrocarbons, the focus is on the so-called *aromatic effect* [15,62,63], which may lead to M-shaped excess molar enthalpies  $H^E$  [63–65].

Directional intermolecular forces contribute significantly to the thermodynamic properties of pure liquids and liquid mixtures. A versatile approximate statistical–mechanical method for estimating and discussing such effects was presented some time ago by Pople [66]. At high densities and low temperatures, these directional interactions lead to local structure, that is, to ordering in the pure liquid. Assuming a lattice model, the extra Helmholtz energy due to the contribution of dipole–dipole interactions is given by

$$F_{\text{or}}/RT = -a \left[ \mu^2 N_A / (4\pi\epsilon_0 V k_B T) \right]^2 = -a \left[ \mu_r^2 / (V_r T_r) \right]^2 \quad (14)$$

where  $V_r = V/V_c$  is the reduced molar volume, and  $a$  depends on the lattice selected (for a face-centered cubic lattice, including also interactions beyond the first coordination sphere,  $a = 1.2045$ ). This contribution is, of course, superimposed on that due to shape anisotropy.

The dipolar interaction parameter [48]



$$y = \mu_r^2 / (V_r T_r) \quad (15)$$

may serve as a semiempirical solvent polarity parameter; it is well correlated with the normalized Dimroth–Reichardt spectroscopic solvent parameter  $E_T^N$  [67]. The orientational contribution to the Helmholtz energy is always negative and varies with  $y^2$ , that is, with  $\mu^4/(VT)^2$ . From eq. 14, the dipole–dipole orientational contributions to the molar entropy,  $S_{or}$ , internal energy,  $U_{or}$ , and heat capacity at constant volume,  $C_{V,or}$ , are easily obtained:

$$F_{or} = TS_{or} = \frac{1}{2}U_{or} = -\frac{1}{2}TC_{V,or} \quad (16)$$

In summary, the presence of dipolar order in a liquid lowers the Helmholtz energy as well as the internal energy and the entropy, and increasingly so at low temperatures. The orientational contribution to the heat capacity is positive. Extension to liquid mixtures is fairly straightforward.

For mixtures, Kalali et al. [58] have used an approach similar in spirit involving the corresponding set of thermodynamic quantities in  $(T,p,x)$ -space, that is, excess molar Gibbs energy  $G^E$ , excess molar enthalpy  $H^E$ , excess molar entropy  $S^E$ , and excess molar heat capacity  $C_p^E$  at constant pressure, which are directly accessible through experiment. Using a simple model [68] and including contributions from shape anisotropy, they showed that the net destruction of order resulting from mixing a polar liquid with a nonpolar liquid leads to positive contributions to  $G^E$ ,  $H^E$ , and  $S^E$ , and to a negative contribution to  $C_p^E$  (see also refs. [46,47]), which may be expressed as

$$C_p^E = -2(H^E - G^E)/T \quad (17)$$

This relation appears to hold well for nonpolar or weakly polar mixtures [69]. However, for mixtures of a strongly polar liquid with a nonpolar liquid, say an alkane, the experimental  $C_p^E$  is usually less negative than demanded by eq. 17. This indicates that some dipole–dipole orientations have considerably greater stability (one may regard this as weak association) than accounted for by the angle-averaging procedure involved. As was pointed out some time ago [3], as long as the temperature is sufficiently high so as to make  $y \ll 1$ , orientational effects are essentially swamped by thermal randomization.

One way of treating these nonrandomness effects is through application of Guggenheim's quasi-chemical theory [68], as suggested by Saint-Victor and Patterson [57]. Denoting the molar cooperative free energy by

$$W = A + B/T, \quad (18)$$

the excess molar heat capacity  $C_p^E$  may be separated to an excellent approximation into a random (r) and a nonrandom (nr) contribution [3,48,57]:

$$\begin{aligned} C_p^E/R &= C_p^E(r)/R + C_p^E(nr)/R \\ &= -x_1x_2Tk_B^{-1} \left( d^2W / dT^2 \right) + \\ &\quad \left( x_1x_2 \right)^2 \left[ \left\{ W - T(dW/dT) \right\}^2 2\eta^2 \left( zk_B^2T^2 \right)^{-1} + Tk_B^{-1} \left( d^2W / dT^2 \right) (\eta^2 - 1) \right] \end{aligned} \quad (19)$$

where  $\eta = \exp(W/zk_B T)$ , with  $z$  being the coordination number.

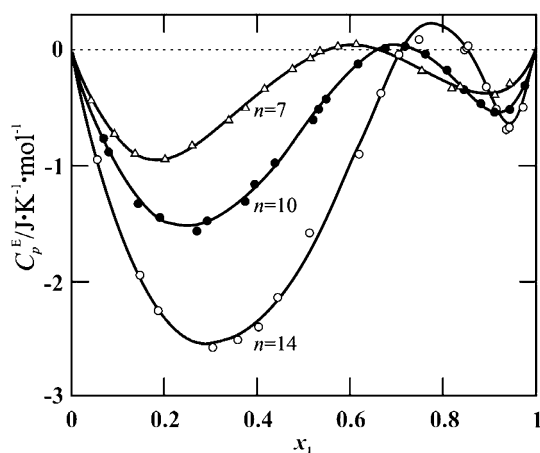
The random term  $C_p^E(r)$  is negative with a parabolic composition dependence, as expected for mixtures where dipole–dipole order is being destroyed in the mixing process. On the other hand, the nonrandom term  $C_p^E(nr)$  is positive and has *zero slope* against mole fraction at the ends of the composition range. For a more rigorous treatment, see Cobos [70].

These two contributions account qualitatively for the appearance of W-shaped curves  $C_p^E$  vs.  $x$ . We first reported such a composition dependence in 1982 at the 37<sup>th</sup> Annual Calorimetry Conference

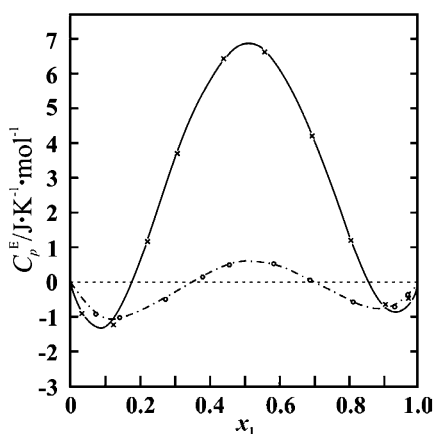
in Snowbird, Utah (see Fig. 7 [55]), and it is now recognized as being of wide occurrence in mixtures of type (a strongly polar substance + an alkane). With decreasing temperature, the maximum caused by  $C_p^E$  (nr) increases and the W-shape becomes more pronounced as shown in Fig. 8, which presents  $C_p^E$  of  $\{x_1 \text{ bis(2-dichloroethyl)ether (chlorex)} + x_2 \text{ 2,2,4-trimethylpentane}\}$  determined by Kalali et al. [58] at 293.15 and 313.15 K. However, it is important to note that many of the mixtures showing W-shaped  $C_p^E$  curves are rather close to phase separation with an upper critical solution temperature (UCST),  $T_{UC}$ . When a UCST is approached from the homogeneous region at constant pressure and constant critical composition  $x_c$ , the heat capacity along this path diverges weakly [19] according to

$$C_p^E(x_c) = C_p^E(x_c, \text{noncritical}) + A_c t^{-\alpha} \quad (20)$$

where  $A_c$  is the critical amplitude,  $t \equiv (T - T_{UC})/T_{UC}$ , and  $\alpha = 0.11$  is the critical exponent. Extended scaling [71,72] may be included [58]. Evidently, the quasicheical approximation underestimates the nonrandom contribution to  $C_p^E$  and becomes qualitatively incorrect for  $T \rightarrow T_{UC}$ .

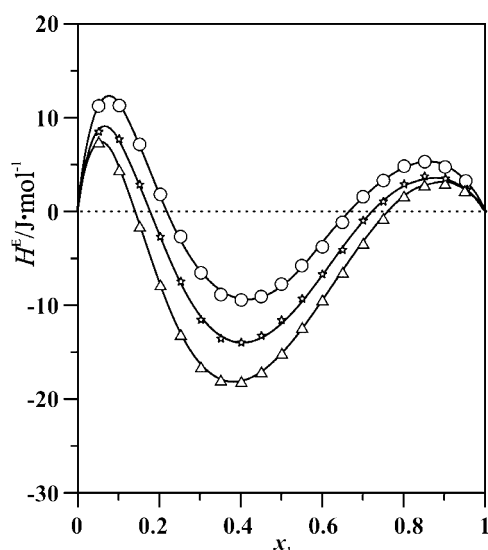


**Fig. 7** Excess molar heat capacities  $C_p^E$  at constant pressure of  $\{x_1 \text{ 1,4-C}_4\text{H}_8\text{O}_2 + x_2 \text{ C}_n\text{H}_{2n+2}\}$  at 298.15 K. The circles and triangles are experimental points obtained for the series of mixtures of 1,4-dioxane with  $n$ -heptane ( $n = 7$ ),  $n$ -decane ( $n = 10$ ), and  $n$ -tetradecane ( $n = 14$ ). From ref. [55].



**Fig. 8** Excess molar heat capacities  $C_p^E$  at constant pressure of  $\{x_1 \text{ bis(2-dichloroethyl)ether (chlorex)} + x_2 \text{ 2,2,4-trimethylpentane (isooctane)}\}$  at 293.15 K (crosses) and 313.15 K (circles). For this system, the upper critical solution temperature was determined to be  $T_{UC} = 290.47$  K at  $x_{1,c} = 0.492$  [58].

In mixtures with *flexible* polar compounds, complications arise which have their origin in the existence of rotamers with greatly differing dipole moments as found, for instance, in alkylalkanoates [48] and 1,2-dihaloethanes [12,15,18]. In fact, the most thoroughly investigated binary liquid systems with prototype conformational equilibria between an essentially nonpolar rotamer and strongly polar rotamers (*trans/gauche* equilibria) are the mixtures of 1,2-dichloroethane and 1,2-dibromoethane, respectively, with either alicyclic or aromatic compounds. For the mixtures with cyclohexane, the results [15] are in qualitative accord with predictions based on Onsager's reaction field theory [73]. However, for the mixtures with benzene, significant deviations are observed, though the relative permittivity of cyclohexane ( $\epsilon_r = 2.0$  at 298.15 K) is almost the same as that of benzene ( $\epsilon_r = 2.3$ ). For instance, when considering mixtures with 1,2-dibromoethane ( $\epsilon_r = 4.8$ ), the relative mole fraction of polar *gauche* rotamers decreases—as expected—when cyclohexane is added, but increases slightly on addition of benzene [15]. Thus, besides the relative permittivity, the *local* polarizability of the surrounding molecules must also be considered. This aspect is particularly important in mixtures of aromatics with strongly polar molecules where the dipole moment is located near the molecular periphery. The ensuing special induction effect, known as the *aromatic effect* [15,62,63], manifests itself by an additional attractive energy and is thought to be connected with the strong inhomogeneous field of the nonideal dipole inducing a peripheral dipole moment in the  $\pi$ -system. For instance, at 298.15 K and  $x_1 = 0.5$ ,  $H^E$  of  $\{x_1$  ethylethanoate +  $x_2$  n-hexane $\}$  is 1279 J/mol, whereas  $H^E$  of  $\{x_1$  ethylethanoate +  $x_2$  benzene $\}$  is only 84 J/mol, i.e., almost 1200 J/mol less. Similarly, while  $H^E(x_1 = 0.5)$  of  $\{x_1$  benzonitrile +  $x_2$  cyclohexane $\}$  is about 1391 J/mol [64], the excess enthalpy is much smaller for mixtures of benzonitrile with benzene [ $H^E(x_1 = 0.5) = 32$  J/mol] or toluene [ $H^E(x_1 = 0.5) = -12$  J/mol] [64,65]. In fact, for the latter two systems, the curves  $H^E$  against  $x_1$  are quite unusual in that they belong to the very few examples reported in the literature [63–65,74–76] showing *three extrema* (M-shape). For  $\{x_1$  benzonitrile +  $x_2$  toluene $\}$  two maxima at about  $x_1 = 0.07$  and  $0.87$ , respectively, and one minimum at about  $x_1 = 0.40$  are observed (Fig. 9).  $H^E$  of  $\{x_1$  benzonitrile +  $x_2$  benzene $\}$  is positive throughout, and at 298.15 K the M-shape is much less pronounced, the minimum being extremely shallow.



**Fig. 9** Excess molar enthalpies  $H^E$  of  $\{x_1\text{C}_6\text{H}_5\text{CN} + x_2\text{C}_6\text{H}_5\text{CH}_3\}$  as a function of mole fraction  $x_1$  at three temperatures. Experimental results:  $T = 293.15$  (triangles);  $T = 298.15$  K (stars);  $T = 303.15$  K (circles). The dipole moment of benzonitrile is  $13.94 \cdot 10^{-30}$  C·m, the dipole moment of toluene is  $1.20 \cdot 10^{-30}$  C·m [65].

Invoking 1:1 complex formation [65] between benzonitrile and toluene, a simple lattice model advanced by McGlashan and colleagues [74] is sufficient to account for the salient features of Fig. 9, that is for the M-shaped curves  $H^E$  and the corresponding  $C_p^E$  curves (it even predicts qualitatively correctly the decrease of  $C_p^E$  with increasing temperature). In this model, the excess molar enthalpy is given by

$$H^E = \xi \left[ \Delta_f H_{AB}^\circ - \left\{ (W - TdW/dT)/2 \right\} \right] + x_1 x_2 (W - TdW/dT) \quad (21)$$

where the molar enthalpy of formation  $\Delta_f H_{AB}^\circ$  of the (hypothetical) pure liquid 1:1 complex is assumed to be negative and, for want of a better assumption, is regarded as temperature-independent. It is related to the equilibrium constant for complex formation  $K_{AB}$  by  $d \ln K_{AB} / dT = \Delta_f H_{AB}^\circ / RT^2$ .  $W$  is of the form suggested by eq. 18, and  $\xi$  is determined for given  $x_1$ ,  $K_{AB}$ , and  $W$  from the equilibrium condition [65]. It cannot, of course, account for the asymmetry of the experimental results about  $x_1 = 0.5$ . For a detailed investigation of this system, including nuclear magnetic resonance and Raman light-scattering studies as well as computer simulations (using an OPLS model [77] with Lennard–Jones centers and partial charges), see Egger [78].

## CONCLUDING REMARKS

In this review, I have briefly surveyed molar heat capacities  $C_V$  of fairly simple, nonpolar molecular liquids (without conformational equilibria), as well as results pertaining to liquid mixtures containing a strongly polar component. Such a discussion has been made possible only through continuing advances in instrumentation, leading to ever-increasing precision, accuracy, and speed of measurements over wide ranges of temperature and pressure. Solution nonideality is frequently regarded by many physicists, chemists, and chemical engineers, as a complicating, albeit relatively uninteresting, feature. Yet as I hope to have shown, it is the source of important, qualitatively new aspects in liquid-state physical chemistry, thereby allowing me answer my rhetorical question posed at the Beijing conference (“*Is there life after the parabola?*”) affirmatively.

Finally, a few words about future trends in chemical thermodynamics of pure liquids and liquid mixtures are indicated. Automation of instruments will continue, and so will miniaturization. In addition, the ranges of temperature and pressure have to be expanded continuously to further theoretical advances, and to meet the needs of industry. Without a doubt, liquid-state thermodynamics will continue to be a modern and highly active field of science comprising experimental technique, theory, computer simulation, and application.

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