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**Multiparameter Equations of State – Recent Trends and  
Future Challenges**

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*Fluid Phase Equilibria*

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## **Abstract**

During the 1970's, accurate empirical multiparameter equations of state became available which were used as a reliable source of thermodynamic property data both in scientific and engineering applications. The advantages and disadvantages of these equations were discussed in detail at that time and most scientists working in thermodynamics are well aware of the corresponding arguments. However, the development of such equations has continued over the course of the last 20 years and state-of-the-art multiparameter equations of state disprove many of the common teachings which are mostly based on experiences with older formulations. The intention of this article is to update the common knowledge on characteristic features of empirical multiparameter equations of state, to increase the confidence of potential users, and possibly to attract other scientists to theoretical and experimental work which is relevant for the future development of these kinds of thermodynamic property models. To do so, the most important features of current multiparameter equations of state and of the algorithms which are used to develop such formulations are briefly explained. Future challenges are outlined both with regard to the development of multiparameter equations of state and with regard to the underlying experimental basis. Relevant references are given for further studies.

*Keywords:* Equation of state; empirical; general overview; mixture; multiparameter; pure

## 1. Introduction

During the 1970's, accurate empirical multiparameter equations of state became available which were used as a reliable source of thermodynamic property data both in scientific and engineering applications. The advantages and disadvantages of these equations were discussed in detail at that time and most scientists working in thermodynamics are well aware of the corresponding arguments. However, the development of such equations continued over the course of the last 20 years and state-of-the-art multiparameter equations of state disprove many of the common teachings which are mostly based on experiences with older formulations.

For pure substances, one has to distinguish between empirical *reference equations of state* and *technical equations of state*. State-of-the-art formulations are available in both categories but since they are designed for different tasks, their features are quite different. For mixtures, the introduction of Helmholtz energy based *multi-fluid mixture models* enabled a highly accurate description of thermodynamic properties for the first time. Finally, the availability of suitable *software tools* increased the impact of accurate empirical property models in practical applications. While the reference equations of state of the 1970's and 1980's were used mostly in the form of property charts and tables, today, the most accurate and most complex reference equations are used directly in a broad variety of scientific and technical applications.

In this article, the current status of the development of empirical multiparameter equations of state is described focusing on the subjects which were highlighted above. Section 7 subsequently deals with future challenges which result from the achieved status and from scientific and technical demands on accurate thermodynamic property models. However, the body of the article begins with a brief discussion of the numerical methods used to establish multiparameter equations of state since methodical advancements had a direct impact on the performance of multiparameter equations of state. In part, the following chapters would be difficult to understand without these foundations. The discussion of the different topics necessarily is very brief in this article. Wherever possible, references are given for further studies. For more detailed compilations see Refs. [1,2].

## 2. Numerical Methods

Currently, empirical equations of state are usually formulated in terms of the reduced Helmholtz energy. The reduced Helmholtz energy is split up into one part which describes the behavior of the hypothetical ideal gas at given values of temperature and density and a second part which describes the residual behavior of the real fluid. Thus, the reduced Helmholtz energy becomes

$$\frac{a(T, \rho)}{RT} = \frac{a^o(T, \rho) + a^r(T, \rho)}{RT} = \alpha^o(\tau, \delta) + \alpha^r(\tau, \delta), \quad (1)$$

with the inverse reduced temperature  $\tau = T_r/T$  and the reduced density  $\delta = \rho/\rho_r$ . The reducing parameters usually correspond to the critical parameters of the described substance. Correlations for the ideal gas part of the reduced Helmholtz energy,  $\alpha^o(\tau, \delta)$ , can be derived from either spectroscopic data or from experimental results for the isobaric heat capacity of the ideal gas,  $c_p^o(T)$ . The corresponding techniques are well known; for details see Ref. [2]. The difficult step is the development of a formulation for the residual part of the reduced Helmholtz energy,  $\alpha^r(\tau, \delta)$ . Empirical formulations for the reduced Helmholtz energy are usually written as a sum of so called *polynomial terms* and *exponential terms*, namely as

$$\alpha^r(\tau, \delta) = \sum_{i=1}^{I_{\text{Pol}}} n_i \tau^{t_i} \delta^{d_i} + \sum_{i=I_{\text{Pol}}+1}^{I_{\text{Pol}}+I_{\text{Exp}}} n_i \tau^{t_i} \delta^{d_i} \exp(-\delta^{p_i}). \quad (2)$$

Highly accurate equations of state may contain additional terms for improving the representation of properties in the critical region, but this is not important for describing the numerical techniques.

The values of the coefficients  $n_i$  in Eq. (2) are determined by fitting them to experimental data; the corresponding techniques have been basically known for a long time, see Refs. [3,4]. In the 1960's and 1970's, these algorithms were adapted to the needs of empirical equations of state. Hust and McCarty [5] used the method of Lagrangian multipliers to exactly constrain empirical equations of state to preselected critical parameters. Bender [6] and Wagner [7] considered the Maxwell criterion to establish equations of state which were able to accurately describe phase equilibria and caloric properties in the liquid phase and McCarty [8] used the relation

$$g'(T) = g''(T) \quad (3)$$

to improve the description of caloric properties in the liquid phase – multiparameter equations of state which were fitted not only to  $p\rho T$  data but simultaneously to data of different properties became available. As a consequence, a proper weighting of the experimental data used became mandatory [9]. Finally, Ahrendts and Baehr presented theoretically sound algorithms for nonlinear fitting of the coefficients  $n_i$  [9] and for the simultaneous use of data for multiple properties [10]. This multi-property fitting was later sophisticated but there were not any really new techniques developed after the work of Ahrendts and Baehr was completed in 1979. Today, the coefficients  $n_i$  of state-of-the-art equations of state are determined by nonlinear multi-property fits which consider hundreds or even thousands of weighted data for a broad variety of thermodynamic properties.

Aside from the coefficients  $n_i$ , Eq. (2) contains several other parameters, namely the number of terms  $I_{\text{Pol}}$  and  $I_{\text{Exp}}$  and the exponents  $d_i$ ,  $t_i$ , and  $p_i$ . Further parameters become

involved if special critical region terms are used. All of these parameters cannot be determined by common fitting algorithms and are referred to as the *functional form* of the equation of state. In the 1960's and 1970's, the functional form of equations of state was developed based on a trial and error procedure and on the experience of the correlator. If a suitable functional form was established, it was often used for different substances. In 1974, Wagner [11] presented a mathematical algorithm for an objective optimization of the functional form of equations of state. In 1982, the first algorithm containing evolutionary elements [12] followed. Around 1985, a new generation of equations of state with optimized functional forms became available, see, e.g., Refs. [13,14].

During the optimization process, terms which do not properly improve the quality of the equation of state are either canceled or replaced by more effective terms and intercorrelated pairs of terms are replaced by single terms which yield a similar contribution to  $\alpha^r$ . In this way, the same quality can be achieved with less terms and the numerical stability of the functional form is increased since intercorrelations between the terms are reduced. The introduction of optimized functional forms resulted not only in equations of state with previously unknown accuracy but also in equations with improved extrapolation behavior and high reliability in regions which are difficult to describe. The development of increasingly sophisticated optimization algorithms has continued; for details on this development, see Ref. [2]. Together with improved experimental techniques, the new optimization algorithms resulted in the highly accurate reference equations of the 1990's, see Section 3. For such equations, the use of quasi nonlinear optimization algorithms which rely on a combination of evolutionary and deterministic elements [15] is state-of-the-art and the development of such algorithms will go on, see Sec. 7.1.

However, the use of optimized functional forms had a serious disadvantage as well. Optimized functional forms are substance specific; they lose most of their advantages when being transferred to other substances. Furthermore, optimization algorithms are numerically very flexible and can be successfully applied only to substances for which large and accurate data sets are available. Thus, the development of accurate equations for well measured substances was methodically separated from the work on technical equations of state for broader groups of less well measured substances in the 1980's. At least partly, this split was overcome again in 1998 with the introduction of an optimization algorithm which simultaneously considers data for different substances [16], see Chap. 4.

### 3. Reference Equations of State

The basic idea behind the concept of reference equations of state is that a single equation should be able to describe all experimental thermodynamic property data available for a certain fluid within their experimental uncertainty. In this way, the equation of state itself can be used as a reference for all thermodynamic properties. Irregardless of whether properties of the corresponding fluid are needed for process calculations or for the

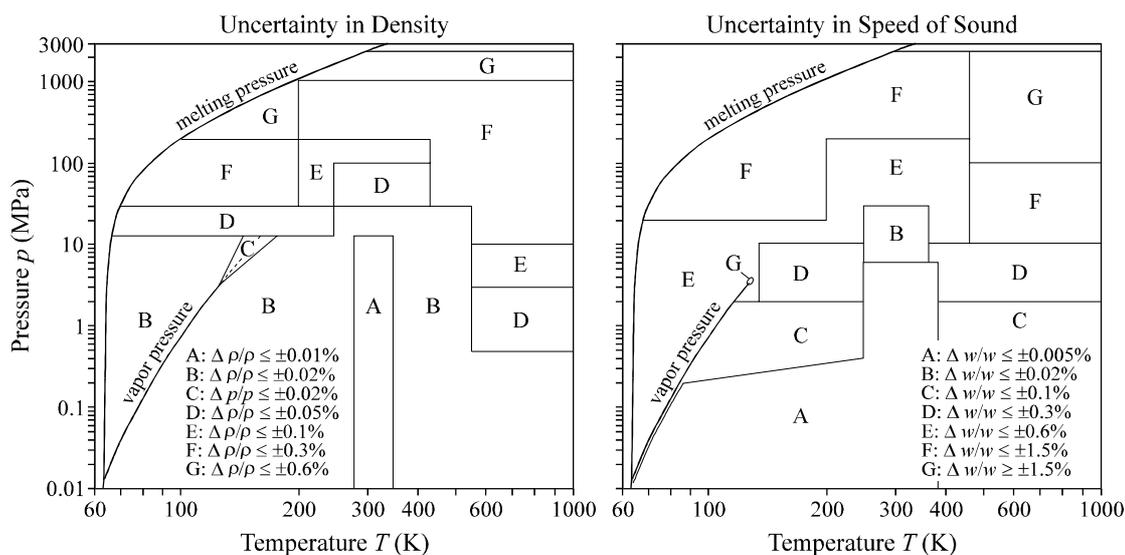


Fig. 1. Uncertainties of densities and speeds of sound calculated from the current reference equation of state for nitrogen [24].

calibration of accurate scientific instruments, there is no need to directly refer to experimental data any longer. Whenever the thermodynamic surface of a fluid is redefined by a significant set of substantially more accurate experimental data, the need for a new reference equation should be considered – there is nothing like a “final reference equation” for a certain fluid. This may seem questionable from a technical point of view but it is unavoidable to satisfy all scientific demands on reference equations of state.

One of the first successful reference equations of state was the well known MBWR equation by Jacobsen and Stewart [17] published in 1973. In the 1980’s, reference equations with optimized functional forms resulted in significantly increased accuracies, see, e.g., Refs. [13,14]. In the 1990’s, data based on new experimental techniques such as density measurements with single- and two-sinker densimeters [18] and speed of sound measurements with spherical resonators [19,20] became available for a number of reference fluids. Sophisticated optimization algorithms [15,21] and the introduction of special terms for an improved representation of properties in the critical region [22,23] were used to keep up with these experimental advancements and resulted in a new generation of *highly accurate reference equations of state* [22–27]. With respect to the accuracy of calculated properties, to their extrapolation behavior, and to their reliability in regions with scarce data situation, these equations define the state-of-the-art for the development of reference equations and disprove a number of common teachings.

As a typical example, Fig. 1 shows uncertainties claimed for densities and speeds of sound calculated from the recent reference equation of state for nitrogen [24]. In the technically and scientifically most important regions, densities can be calculated with an uncertainty of  $\Delta\rho/\rho \leq \pm 0.01\% - \pm 0.02\%$ . In the range where data from measurements

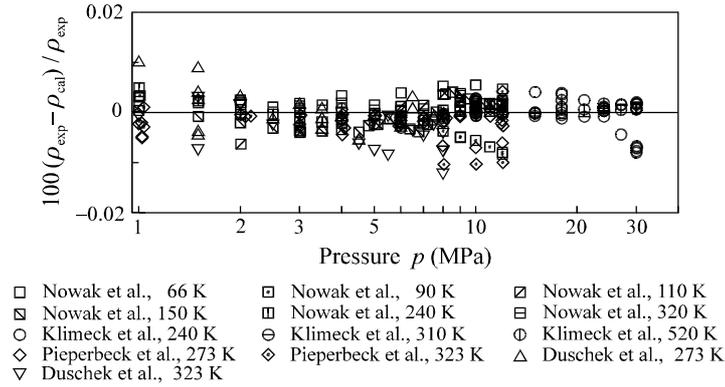


Fig. 2. Percentage deviations between experimental data for the density of nitrogen by Nowak et al. [28], Klimeck et al. [29], Pieperbeck et al. [30], and Duschek et al. [31] and values calculated from the current reference equation of state for nitrogen [24].

with spherical resonators are available, speeds of sound in the gas phase can be calculated with an uncertainty of  $\Delta w/w \leq \pm 0.005\% - \pm 0.02\%$ . However, outside of this region, the uncertainty of calculated speeds of sound is substantially higher than the uncertainty of calculated densities. To prove that these assessments are still conservative, Fig. 2 shows deviations between calculated densities and highly accurate experimental results for the density of nitrogen which cover a range almost from the triple point temperature to  $T \approx 4.1 \cdot T_c$  at pressures up to 30 MPa. With very few exceptions, all of these data are represented within  $\Delta\rho/\rho \leq \pm 0.01\%$ . For most states, the uncertainty claimed for the equation of state is twice as high.

One of the common teachings on shortcomings of empirical multiparameter equations of state is that they cannot represent properties in the critical region. As can be seen from Fig. 1,  $p\rho T$  data in the critical region are actually represented within  $\Delta p/p \leq \pm 0.02\%$  and thus within the uncertainty of the most accurate experimental results. The same is true for thermal properties on the phase boundary. The properties which are most difficult to describe are the isochoric heat capacity and the speed of sound in the critical region. Figure 3 shows plots of the isochoric heat capacity on the critical isochore of carbon dioxide calculated with three different types of empirical multiparameter equations of state. An oxygen type [13] equation of state which uses only polynomial and exponential terms refitted to the data available for carbon dioxide fails to describe the steep increase of the isochoric heat capacity in the range  $1 \leq T/T_c \leq \approx 1.01$ . A methane type [22] equation which additionally uses so called *modified Gaussian bell shaped terms* fails only in the range  $1 \leq T/T_c \leq \approx 1.002$ . An equation which additionally uses *nonanalytic terms* [23] represents all data within their experimental uncertainty and yields an infinite value for the isochoric heat capacity at the critical point, just as scaled equations of state do. State-of-the-art reference equations of state are able to satisfy all kinds of data needs in the critical region, see also Sec. 7.2.

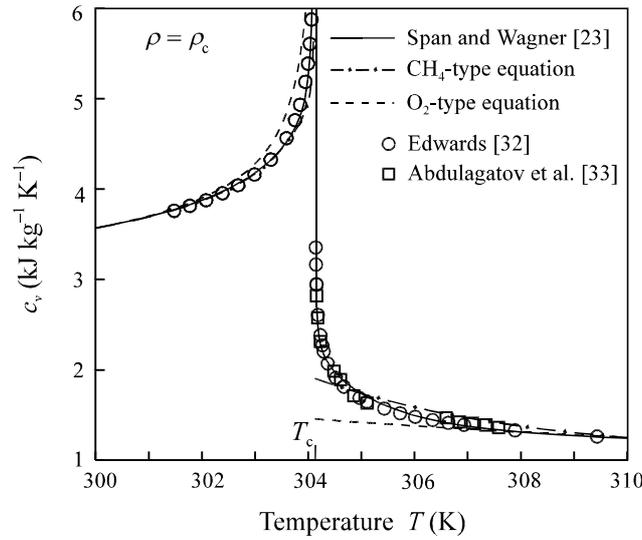


Fig. 3. Values of the isochoric heat capacity on the critical isochore of carbon dioxide calculated from three different multiparameter equations of state and determined experimentally.

Another common teaching on multiparameter equations of state is that they cannot be extrapolated beyond the range where they were fitted to experimental data. However, the use of optimized functional forms increased the numerical stability of multiparameter equations and special criteria were formulated to guarantee reasonable behavior up to extreme pressures and temperatures [34]. Based on these developments, recent reference equations of state can be extrapolated up to the limits of chemical stability of the described

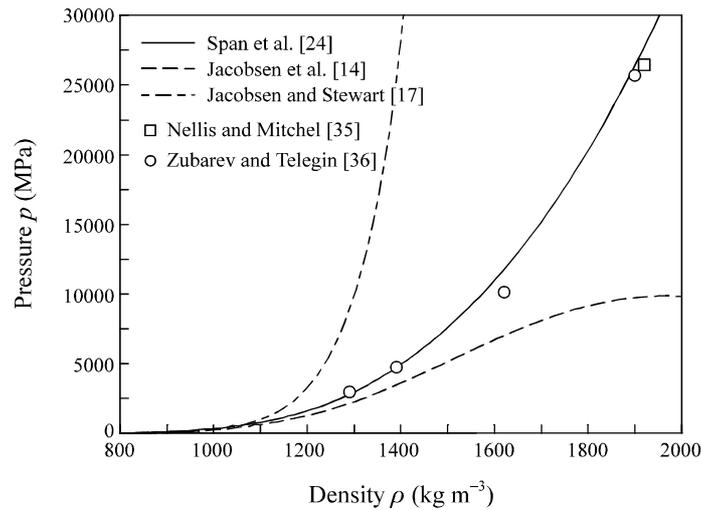


Fig. 4. Plots of the Hugoniot curve of nitrogen calculated from three multiparameter equations of state compared with experimentally determined values.

substance. At very high pressures and temperatures, they yield results which are as good as those of special high temperature and pressure formulations, but they connect accurately to states where reliable experimental data are available. As an example of this advancement, Fig. 4 shows plots of Hugoniot curves calculated from multiparameter equations for nitrogen which belong to three generations of reference equations.

The highly accurate equations of state developed in the 1990's can be used as references for thermodynamic properties without any restriction both in scientific and in technical applications. However, they have one serious disadvantage – corresponding formulations are available for just six pure fluids (methane [22], carbon dioxide [23], nitrogen [24], argon [25], ethylene [26], and water [27]). *Technical reference equations of state* were developed in the 1980's and 1990's for a broader group of mostly technically relevant fluids for which less extensive and less accurate sets of experimental data are available. The most ambitious project in this area was the task group *Annex 18* of the heat pump project of the International Energy Agency (IEA). From 1989 to 1998, internationally agreed upon standards for the thermodynamic properties of five alternative refrigerants were developed within the scientific framework of this task group [37–41]. In general, the performance of technical reference equations of state is less uniform than the performance of the highly accurate reference equations discussed above, but the cooperation within Annex 18 resulted in a set of accurate and reliable formulations. Aspects such as reasonable extrapolation behavior and reasonable behavior of all properties in regions which are difficult to describe were considered when selecting the equations established as property standards. As an example for the performance of one of the best of these equations, Fig. 5 shows deviations between accurate experimental results for the density of R134a (1,1,1,2-tetrafluoroethane) and values calculated from the equation of state by Tillner-Roth and Baehr [37]. The work on technical reference equations of state substantially increased the number of fluids for which accurate thermodynamic property data are available and it helped to establish accurate

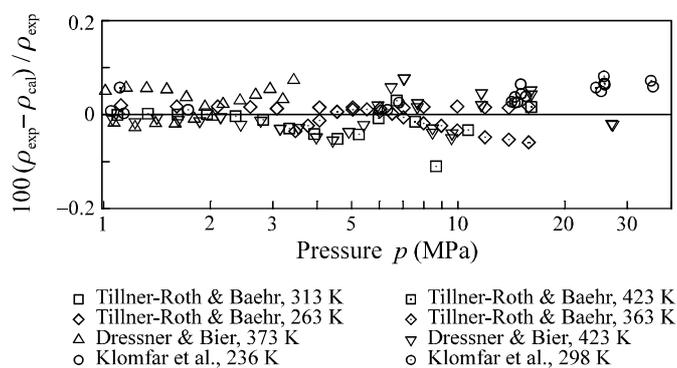


Fig. 5. Percentage deviations between experimental data for the density of HFC 134a by Tillner-Roth and Baehr [42,43], Dressner and Bier [44], and Klomfar et al. [45] and values calculated from the equation of Tillner-Roth and Baehr [37].

multiparameter equations of state in practical applications, see Chap. 6. A selection of recommended reference equations of state is given in Table 1.

Table 1  
A selection of recommended reference equations of state

Fluid	Reference	Explicit in <sup>a</sup> (no. of coeff.)	Range of validity	
			$T/K$	$p_{\max}/\text{MPa}$
Ammonia	Baehr, Tillner-Roth [46]	Helmholtz (21)	195–700	1000
Argon	Tegeler et al. [25]	Helmholtz (41)	83–700	1000
Carbon dioxide	Span, Wagner [23]	Helmholtz (42)	216–1100	800
Chlorine <sup>b,c</sup>	Angus et al. [47]	Pressure (18)	180–900	25
Cyclohexane <sup>c</sup>	Penoncello et al. [48]	Helmholtz (26)	279–700	80
Ethane	Friend et al. [49]	Helmholtz (32)	90–500	60
Ethylene	Smukala et al. [26]	Helmholtz (35)	104–450	300
Helium	McCarty, Arp [50]	Pressure (32)	2–1500	100
Isobutane <sup>c</sup>	Younglove, Ely [51]	Pressure (32)	113–600	35
Methane <sup>b</sup>	Setzmann, Wagner [22]	Helmholtz (40)	90–625	1000
Methanol <sup>b</sup>	de Reuck, Craven [52]	Helmholtz (44)	175–570	800
n-Butane <sup>c</sup>	Younglove, Ely [51]	Pressure (32)	134–500	70
Neon	Katti et al. [53]	Helmholtz (29)	24–700	700
Nitrogen	Span et al. [24]	Helmholtz (36)	63–1000	2200
Oxygen <sup>b</sup>	Schmidt, Wagner [13]	Helmholtz (32)	161–800	350
Propane	Younglove, Ely [51]	Pressure (32)	85–600	100
Propene <sup>b,c</sup>	Angus et al. [54]	Pressure (21)	87–575	1000
R11	Marx et al. [55]	Helmholtz (21)	163–525	200
R12	Marx et al. [55]	Helmholtz (22)	116–525	200
R22	Wagner et al. [56]	Helmholtz (22)	116–525	200
R32 <sup>d</sup>	Tillner-Roth, Yokozeki [39]	Helmholtz (19)	136–435	70
R113	Marx et al. [55]	Helmholtz (18)	237–525	200
R123 <sup>d</sup>	Younglove, McLinden [38]	Pressure (32)	166–500	40
R124	de Vries et al. [57]	Helmholtz (20)	100–400	40
R125 <sup>c,d</sup>	Piao, Noguchi [40]	Pressure (18)	173–475	68
R134a <sup>d</sup>	Tillner-Roth, Baehr [37]	Helmholtz (21)	170–455	70
R143a <sup>d</sup>	Lemmon, Jacobsen [41]	Helmholtz (20)	161–500	60
R152a	Outcalt, McLinden [58]	Pressure (32)	162–453	35
Water <sup>e</sup>	Wagner, Pruß [27]	Helmholtz (56)	273–1273	1000
Xenon <sup>c</sup>	Šifner, Klomfar [59]	Pressure (63)	161–800	350
Air <sup>f</sup>	Lemmon et al. [60]	Helmholtz (19)	60–2000	2000

<sup>a</sup> “Helmholtz” refers to equations explicit in the reduced Helmholtz energy, “Pressure” to equations explicit in terms of pressure or compression factor

<sup>b</sup> recommended as standard by the IUPAC

<sup>c</sup> equation lags behind common expectations regarding the accuracy of reference equations

<sup>d</sup> recommended as standard by Annex 18 of the IEA

<sup>e</sup> recommended as standard by the IAPWS

<sup>f</sup> air can be treated as pseudo pure fluid for calculations in the homogeneous phases

#### 4. Technical Equations of State

Reference equations of state are directly used in a multitude of technical applications today; they are not only “scientific equations of state.” However, in the 1980’s the introduction of substance specific optimized functional forms restricted the work on reference equations to well measured fluids while equations of state without optimized functional forms were often fitted to less well measured substances as well, see Refs. [61,62]. Thus, quite often, obsolete equations of state are still in use in technical applications where data for a broad variety of fluids are required since these fluids could never be covered by current reference equations of state with optimized functional forms.

In general, “technical equations of state” without an optimized functional form have at least one of the following disadvantages. Equations with a rather small number of coefficients, such as the well known equation by Starling [61], hardly satisfy the demands on accuracy which result from advanced technical applications. Problems are observed, especially for caloric properties, at liquid and liquid-like supercritical states; for a detailed discussion see Ref. [2]. When being fitted to small data sets, the functional forms of the equations are numerically not stable enough to guarantee reasonable results for derived properties or for regions outside the range where the equation was fitted to data. This problem becomes obvious especially for equations with a rather large number of coefficients, such as the well known equation by Bender [6]. Figure 6 illustrates this problem using a refitted Bender-type equation of state as an example. In the range where the equation was fitted mostly to reliable data for thermal properties, the isotherms in the

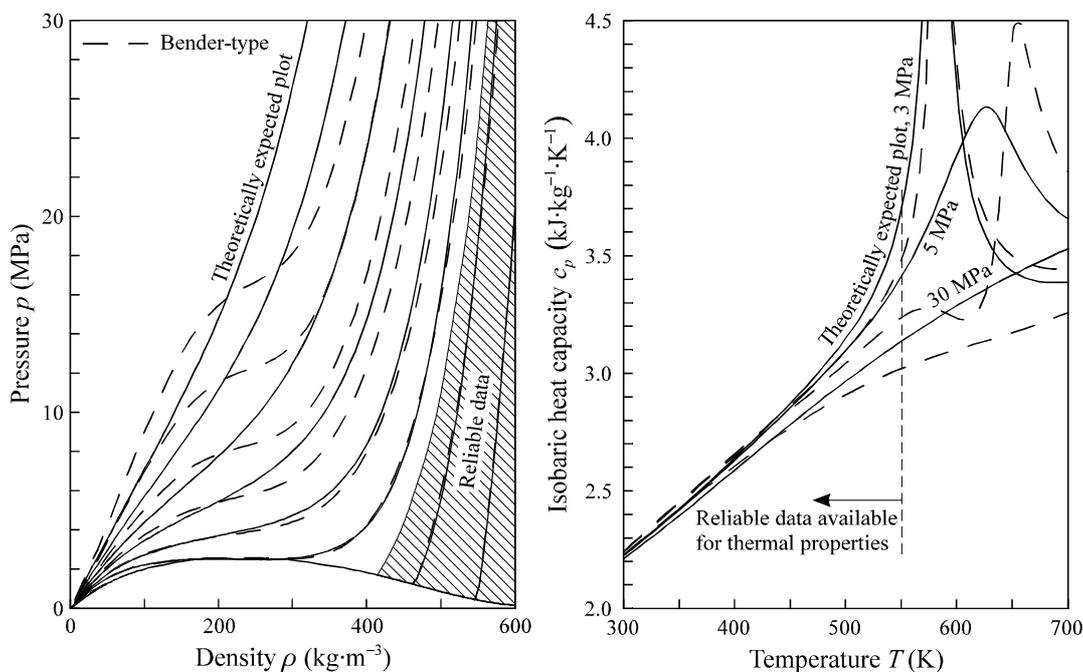


Fig. 6. Isotherms in a  $p, \rho$ -diagram and isobars in a  $c_p, T$ -diagram for n-octane which were calculated from a Bender-type equation refitted to the data set available for n-octane today.

$p, \rho$ -diagram seem to indicate reasonable behavior but outside this range, unreasonable results become obvious. The  $c_p, T$ -diagram shows that large errors occur for derived caloric properties also at states within the range where the equation was fitted to data.

To transfer the methodical advancements achieved for reference equations of state to technical equations of state, Span et al. [16] developed a *simultaneous optimization* algorithm. This algorithm optimizes functional forms considering data sets for different substances simultaneously. On average, the resulting functional form yields the best results for all considered fluids. If the considered fluids are typical for a certain group of fluids, the simultaneously optimized functional form can be used for other fluids out of the same group without significant disadvantages. In this way, it is possible to make use of the advantages of optimized functional forms for substances with restricted data sets.

Based on this algorithm, Span and Wagner [63] developed functional forms for typical non- and weakly polar fluids and for typical polar fluids which are designed to satisfy advanced technical demands on the accuracy of thermodynamic properties. With just 12 terms, these equations are on average more accurate than Bender-type equations with 19 terms, but they are numerically much more stable. This fact results in significant advantages when fitted to small data sets – the “theoretically expected plots” in Fig. 6 were calculated from an equation based on the simultaneously optimized functional form for non- and weakly polar fluids. In a first set of articles, such state-of-the-art technical equations of state will be published for 15 non- and weakly polar fluids [64] and for 13 typical polar fluids [65], see also Ref. [2]. Further equations are being developed.

For substances with very restricted data sets, the use of *generalized empirical equations of state* is common in technical applications. Completely predictive generalized models express the coefficients of an empirical equation of state as a function of one or two substance specific factors which usually depend on reduced vapor pressures, see, e.g., Ref. [66]. The most common parameter is the well known acentric factor  $\omega$ . For different reasons, the accuracy of such completely predictive models is very restricted. Higher

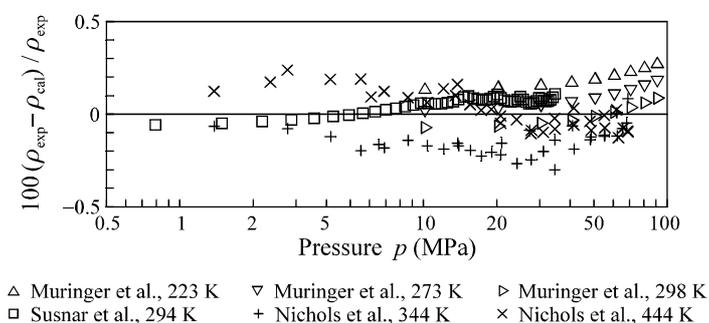


Fig. 7. Percentage deviations between experimental data for the density of n-heptane by Muringer et al. [68], Susnar et al. [69], and Nichols et al. [70] and values calculated from the generalized equation of state by Span and Wagner [71].

accuracies can be achieved with models which use the reducing parameters and the parameter used to generalize the coefficients as adjustable parameters, see, e.g., Ref. [67]. In combination with simultaneously optimized functional forms, such models are both numerically very stable and surprisingly accurate, at least for nonpolar fluids. As an example, Fig. 7 shows deviations between accurate  $p\rho T$  data for n-heptane and values calculated from the generalized three parameter equation by Span and Wagner [71], see also Ref. [2].

## 5. The Application of Multiparameter Equations of State in Mixture Models

Multiparameter equations of state have always been used for mixtures as well. Purely empirical approaches relied on mixing rules defined for single coefficients or for groups of terms [61,72]. Compared to these very simple approaches, extended corresponding states models lead to an improved description of less ideal mixtures [73–76]. However, in such mixture models the performance of multiparameter equations of state never came close to their performance for pure fluids.

This situation changed, when *Helmholtz energy models* were introduced for mixtures in the 1990's. Such models have been developed by Tillner-Roth [77] and by Lemmon [78] independently of each other during overlapping periods of time. A comprehensive survey which points out similarities and differences of the two approaches has recently been published by Lemmon and Tillner-Roth [79].

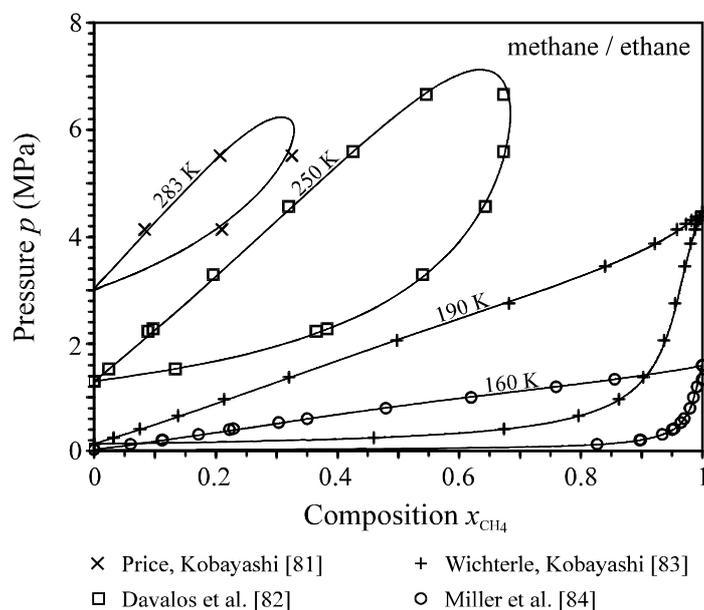


Fig. 8. Representation of vapor-liquid equilibria for the system methane/ethane by a Helmholtz energy model using only accurate pure component equations of state and adjusted reducing functions.

In Helmholtz energy models for mixtures, the reduced Helmholtz energy  $\alpha$  of a mixture with  $I$  components is written as

$$\frac{a(T, \rho, \mathbf{x})}{RT} = \alpha^{\circ}(T, \rho, \mathbf{x}) + \sum_{i=1}^I x_i \alpha_i^r(\tau, \delta) + \Delta\alpha^r(\tau, \delta, \mathbf{x}) \quad (4)$$

with the inverse reduced temperature  $\tau = T_r(\mathbf{x})/T$  and the reduced density  $\delta = \rho/\rho_r(\mathbf{x})$ . The term  $\alpha^{\circ}(T, \rho, \mathbf{x})$  corresponds to the reduced Helmholtz energy of a hypothetical ideal gas mixture at given values for  $T, \rho$ , and  $\mathbf{x}$  which can easily be calculated if correlations for the Helmholtz energy of the involved components,  $\alpha_i^{\circ}(T, \rho)$ , are given.

The second term in Eq. (4) formally looks like an ideal mixture of real fluids. However, the equations of state for the pure components which are needed to calculate  $\alpha_i^r(\tau, \delta)$  are evaluated not for given values of  $T$  and  $\rho$  but for reduced properties  $\tau$  and  $\delta$  of the mixture. These reduced properties are determined with composition dependent *reducing functions*  $T_r(\mathbf{x})$  and  $\rho_r(\mathbf{x})$ . Thus, the second term in Eq. (4) corresponds to an extended corresponding states approach rather than to an ideal mixture of pure fluids. The relations which have been discussed for the reducing functions range from simple linear mixing rules without adjustable parameters to quadratic mixing rules with suitable combination rules and up to four adjustable binary interaction parameters, see Refs. [79,80].

Based only on accurate equations of state for the pure components and on adjustable reducing functions, Helmholtz energy models are able to describe VLE data for common mixtures within the accuracy of the available data. This is shown in Fig. 8 using the binary system methane/ethane as an example. Data in the homogeneous phases are described reasonably well, but not as well as for pure substances. To come close to the accuracy known for pure substances or to describe phase equilibria of strongly nonideal mixtures [85], an additional *departure function*,  $\Delta\alpha^r(\tau, \delta, \mathbf{x})$ , is required.

With regard to the departure function, Tillner-Roth and Lemmon used different approaches. The work of Tillner-Roth focused mainly on well measured refrigerant mixtures [77,86]. For a highly accurate description of such systems he introduced binary specific departure functions of the general form

$$\Delta\alpha_{ij}^r(\tau, \delta, x_i, x_j) = x_i x_j \sum_{k=1}^K n_k \delta^{d_k} \tau^{t_k} \exp(-\gamma_k \delta^{p_k}), \quad (5)$$

where both the coefficients  $n_k$  and the parameters  $d_k, t_k, g_k$ , and  $p_k$  are binary specific. The number of terms in such formulations is typically of the order of 5, reaching up to 14 with a more complicated composition dependence for strongly nonideal systems like ammonia/water [85]. Based on binary departure functions, the departure function for a multicomponent mixture can be written as

$$\Delta\alpha^r(\tau, \delta, \mathbf{x}) = \sum_{i=1}^{I-1} \sum_{j=i+1}^I \Delta\alpha_{ij}^r(\tau, \delta, x_i, x_j). \quad (6)$$

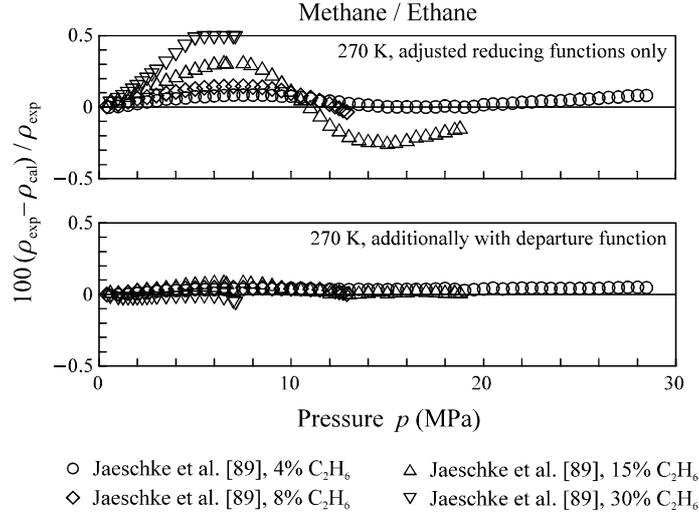


Fig. 9. Percentage deviations between experimental data for the density of mixtures of methane and ethane and values calculated from a Helmholtz energy model using only accurate pure component equations of state and adjusted reducing functions and from a Helmholtz energy model using a binary specific departure function [88].

The work of Lemmon focused mainly on the description of both well known and less well measured binary mixtures and on multicomponent mixtures [78,87]. To be able to describe such mixtures he introduced a *generalized departure function*

$$\Delta\alpha_{ij}^r(\tau, \delta, x_i, x_j) = x_i x_j F_{ij} \sum_{k=1}^{10} n_k \delta^{d_k} \tau^{t_k} \exp(-\gamma_k \delta^{p_k}), \quad (7)$$

where only the coefficient  $F_{ij}$  is binary specific. The coefficients  $n_k$  and the parameters  $d_k$ ,  $t_k$ ,  $\gamma_k$ , and  $p_k$  were determined for a suitable set of binary mixtures once and are assumed to be valid for other mixtures as well. In this way, less well measured binary systems and multicomponent mixtures can be described accurately as well.

Figure 9 gives an example for the accuracy which can be achieved at homogeneous states using a binary specific departure function. Today, the work on Helmholtz energy models for mixtures focuses mainly on the description of natural gases and related systems. Corresponding projects exist both in Europe [88] and in the USA [90]. Hybrid formulations which use binary specific departure functions like Eq. (5) for the well measured binary systems of the main components, generalized departure functions like Eq. (7) for less well measured binary systems, and only adjusted departure functions for the binary systems of minor components are the most promising candidates for future natural gas property models.

## 6. Software Tools

Ten to twenty years ago, results from reference equations of state were mostly used in the form of printed property charts and tables. Applications of reference equations of state based on available *source code libraries* were infrequent and the corresponding programs were mostly developed by a few specialists. However, over the course of the last decade, the direct application of reference equations of state has become common both in scientific applications and in technical applications. This trend was pushed by the development of powerful desktop computers and by the availability of suitable software products. Today, comfortable *interactive programs* enable even untrained users to evaluate the most complex reference equations of state. The availability of *Dynamic Link Libraries (DLL's)* enables an easy use of multiparameter equations of state in user defined applications, for example in Microsoft Excel<sup>®</sup> spread sheets, and has a tremendous impact on the acceptance of such equations. For example, most of the groups working on the development of mobile carbon dioxide based air conditioning systems in Europe use dynamic link libraries based on the current reference equation for carbon dioxide [23] which is one of the most accurate but also most complex multiparameter equations of state available today. User developed programs which are based directly on source code libraries became less frequent but they are still the first choice if computation time becomes a relevant factor in applications with a very large number of thermodynamic property calculations. Furthermore, source code libraries are essential for transferring thermodynamic property calculations to different platforms such as UNIX systems or future versions of PC operating systems.

However, the availability of software tools is no excuse for the development of unnecessarily complex equations of state. There will always be technical and scientific applications where users have to develop their own software. Current examples for such applications are the programming of microprocessors integrated in flow computers or the development of fast iterative algorithms for on-line process calculations in a restricted range of states. In general, such tasks become extremely complicated if equations of state do not use a single set of measurable variables such as temperature and density or temperature and pressure – sophisticated transformations of variables should be avoided wherever possible.

## 7. Future Challenges

As previously discussed, the accurate description of thermodynamic properties with multiparameter equations of state is a scientific discipline which has developed continuously during the last 30 years and will continue to do so. Scientific challenges exist on very different levels – nobody is able to predict which problems will become urgent over the course of the next 30 years. However, there are a number of obvious scientific challenges regarding the development of equations itself as well as methodical, theoretical

and experimental aspects. Some of these topics will be discussed briefly in the following sections.

### *7.1 Improvement of Numerical Methods*

As discussed in Chap. 2, the development of numerical methods has focused on optimization algorithms throughout the last two decades. Very recently, Lemmon and Jacobsen [91] developed a procedure where a direct nonlinear fit of the exponents  $d_i$ ,  $t_i$ , and  $p_i$  in Eq. (2) is used to further improve functional forms previously optimized with a stepwise regression algorithm [11]. In a kind of “manual backward regression”; the number of terms in an equation of state can be reduced in this way without losing quality. Consequently, intercorrelations should be reduced further and the numerical stability of the resulting equation should be improved. To incorporate an automated form of this manual algorithm into state-of-the-art, quasi nonlinear optimization algorithms with evolutionary elements could be a promising step into the next generation of optimization algorithms.

With regard to the consideration of constraints, problems arise from the fact that current optimization algorithms always rely on linear fits in assessing the quality of functional forms. Even the quasi nonlinear algorithms by Tegeler et al. [15] use linear criteria in preselection steps. In linear fits, constraints which can be written as equalities (such as  $p(T_c, \rho_c) = p_c$ ) can be considered using Lagrangian multipliers [5] but inequalities (such as  $(\partial p(T, \rho) / \partial \rho)_T > 0$ ) cannot be considered as constraints. This is a severe restriction, e.g., for the development of functional forms with a more reasonable behavior in the two-phase region, see Sec. 7.3. In nonlinear fits, such inequalities can be considered at least approximately. Thus, with completely nonlinear optimization algorithms, we could consider constraints on the behavior of the thermodynamic property surface which are qualitatively known from thermodynamics but which cannot be written as equalities.

### *7.2 Limiting Behavior at the Critical Point*

State-of-the-art reference equations of state are able to describe all properties in the critical region of a pure fluid within the uncertainty of the most accurate experimental data. Thus, they satisfy the data needs they are designed for. When looking at the limiting behavior infinitely close to the critical point, they do not meet expectations which result from the renormalization group theory when treating pure fluids as three dimensional Ising like systems without an influence of outer fields. Recent work on special critical region terms has focused on an improved approximation of this limiting behavior [92]. However, the highly accurate experimental results of Kurzeja and Wagner [93–96] who have measured thermal properties very close to the critical points of sulfur hexafluoride and carbon dioxide indicate that pure fluids under gravitational conditions do not behave like three dimensional Ising like systems without an influence of an outer field. The discussion of these results and of their implications both with regard to physical models and to multiparameter equations of state is still in a very early state but it will have a considerable impact on the development of highly accurate reference equations.

### *7.3 Properties in the Liquid-Vapor Two Phase Region*

Current multiparameter equations of state extrapolate smoothly into the metastable parts of the liquid-vapor two phase region. However, even for well measured substances, experimental data which are needed to verify their accuracy are scarce, especially for the metastable vapor, and little is known about the plot of the thermodynamic surface in the unstable part of the two phase region. It is well known that empirical multiparameter equations tend to yield unreasonable results like multiple Maxwell loops in this region [97,2]; they are not valid in the unstable part of the two phase region. However, this has never been a severe problem for pure fluids. Numerically stable algorithms which allow for a calculation of accurate phase equilibrium data from such equations are available.

For multiparameter equations of state which are used in mixture models, the situation is different. For the systems for which accurate mixture models are being developed today, phase equilibria can still be calculated reliably, but algorithms which are used to calculate more complex phase equilibria are usually sensitive to these kinds of shortcomings. In order to be able to proceed to the description of more complex phase equilibria, it would be desirable to have technical equations of state which show a more reasonable description of the unstable part of the two phase region. Elhassan et al. [97] showed that the most important criterion is that the Helmholtz energy of the stable two phase system has to be smaller than the Helmholtz energy of the unstable system at given values of temperature and density. Equations of state could be constrained to this inequality during nonlinear fits, but not during the linear steps of the optimization algorithms. Substantial advancements with regard to the description of the unstable part of the two phase region seem to be linked closely to the development of completely nonlinear optimization algorithms. For more details see Ref. [2].

### *7.4 Application to Pure Fluids*

To date, highly accurate reference equations of state are available for 6 fluids, technical reference equations of state of very different quality are available for about 30 other fluids, and technical equations of state are available for another 30 fluids. Compared to the large number of fluids which are relevant in technical and scientific applications, it is obvious that accurate equations of state are needed for further substances. However, the actual needs are very different for the different groups of equations.

Highly accurate reference equations of state are required for additional fluids to increase the number of reference fluids available for the verification of theoretical models, experimental set-ups, or for calibration needs. New equations are currently being developed for ethane, propane, and sulfur hexafluoride. For calibration purposes, an accurate description of two or three fluids which at ambient conditions have liquid densities between propane and water would be helpful. As references for theoretical projects, it would be useful to have highly accurate equations for some simple associating fluids like methanol and ethanol which are technically important as well.

With regard to technical reference equations of state, the need for equations for previously undescribed substances is small. The main task is to replace obsolete equations for a number of technically and scientifically important fluids like chlorine, propene, benzene, and toluene by more accurate and more reliable state-of-the-art equations of state.

Really large numbers of fluids become relevant when talking about technical equations of state. To satisfy the primary needs of chemical engineers, accurate thermodynamic property models would be required for at least 1000 pure fluids and their mixtures. Based on relatively small data sets, simultaneously optimized functional forms (see Chap. 4) enable the development of state-of-the-art equations of state for broad groups of fluids. However, little is known about the limitations of this kind of equation of state. Functional forms for more than the two groups of fluids which have been described will become necessary, although it is not clear how many different forms will be required and whether the simultaneous optimization approach has to be supplemented by different models for certain groups of fluids. Systematic work in this field is essential to satisfy advanced technical data needs especially for applications in the area of chemical and petrochemical engineering, for related subjects in mechanical engineering like the development of compressors, and to establish the pure component basis for new mixture approaches.

### *7.5 Application to Mixtures*

The use of accurate equations of state in Helmholtz energy mixture models is a very new approach and a number of fundamental theoretical questions are still open. For well measured binary and ternary refrigerant mixtures, this approach has been used successfully and models for natural gas like multicomponent systems have reached a very promising status. The extension of such models to mixtures beyond the range of compositions which is typical for pipelining applications will come within the next few years. From gas processing applications, the development will go on to petrochemical applications and to applications in the chemical industry. To describe the multitude of mixtures which will become relevant throughout this development, the range of options for the set-up of such models (models with binary specific departure functions, generalized departure functions, and adjusted reducing functions only) has to be supplemented by generalized reducing functions. Steps like the development of group contribution methods have to be repeated on the basis of Helmholtz energy mixture models. However, real improvements can only be expected if the development is done step by step – there is little use in developing group contribution methods while there are still open questions regarding limitations in the description of well measured systems.

### *7.6 Experimental Challenges*

Advancements in the field of multiparameter equations of state strongly depend on the availability of sufficiently accurate experimental data. Only a few laboratories in the world maintain experimental equipment which is accurate enough to establish the experimental basis for the development of reference equations of state. Limitations of these experimental set-ups can be visualized qualitatively using Fig. 1 as an example. For

selected reference fluids, highly accurate data for densities are available up to temperatures of 520 K and up to pressures of about 30 MPa. Beyond this range, the quality of the available data drops drastically. State-of-the-art apparatuses for measurements at higher temperatures and pressures would be very desirable. Highly accurate data for caloric properties are available mostly for gaseous and gas-like supercritical states from speed of sound measurements in spherical resonators. Experimental techniques of comparable accuracy are needed for speeds of sound at liquid and liquid-like states and for other caloric properties in general.

For the development of technical equations of state, relatively few data of high but not necessarily the highest quality are required for a multitude of fluids, see also Ref. [63]. Experimental equipment for this task needs to cover a broad range of states, needs to be robust, and needs to allow for fast measurements. Since many of the relevant fluids are not available in high purities, the purification of samples or at least an accurate determination of their composition which may enable suitable corrections become key issues.

Most of the mixture properties currently available consist of phase equilibrium data. Accurate data for properties at homogeneous states are rare and the quality of the available VLE data is mostly poor. The rather large uncertainty of measured compositions prevents accuracies as they are known from experimental results for vapor pressures of pure fluids, and the scatter of most of the available VLE data is about one order of magnitude larger as would be expected from combining realistic estimates for state-of-the-art uncertainties of all measured properties. To establish significantly more accurate mixture models, data sets are required which cover not only pressure, temperature and composition of the equilibrium phases but also the corresponding densities and thermal and caloric properties at homogeneous states and which are measured with current experimental set-ups.

### *7.7 Development of Software*

In general, suitable software for the application of existing multiparameter equations of state is available today. However, multiparameter equations are not adequately considered in most commercially available thermodynamic property and process simulation packages; major exceptions are software products in the field of refrigeration and air conditioning and for steam turbine applications.

For technical equations of state, algorithms are being developed which will enable quasi automatic fits to data sets extracted from databases. Based on data for only a few properties, the resulting equations of state could be used to predict data for all kinds of thermodynamic properties. Such algorithms would enable a new quality of data preparation when incorporated into data analysis tools of databases. For rather well measured substances, multiparameter equations of state with simultaneously optimized functional forms seem to be promising candidates; generalized equations of state with only 3 to 4 adjustable parameters could be used for less well measured substances.

## 8. Conclusion

The accurate description of thermodynamic properties of fluids with multiparameter equations of state is a scientific discipline which has developed continuously during the last 30 years and which will continue to do so. The unsolved problems in this field offer a multitude of scientific challenges with regard to the actual development of equations of state and mixture models, with regard to the used theoretical approaches and numerical methods, and with regard to purposive experimental work. Fast success can only be expected in exemplary applications which are of little practical use in most cases. Thus, more than the work of just a few groups in the world is required to achieve satisfactory solutions in a limited amount of time.

### List of Symbols

$a$	Specific or molar Helmholtz energy
$c$	Heat capacity
$F$	Binary specific parameter
$g$	Specific or molar Gibbs energy
$I$	Number of components in a mixture
$I, K$	Upper limits of summations
$n$	Coefficient
$p$	Pressure
$R$	Specific or molar gas constant
$T$	Thermodynamic temperature
$w$	Speed of sound
$x$	Molar concentration of a certain components
$\mathbf{x}$	Vector of molar composition

#### *Greek Letters*

$\alpha$	Reduced Helmholtz energy
$\delta$	Reduced density
$\Delta$	Difference
$\gamma$	Parameter
$\rho$	Density
$\tau$	Inverse reduced temperature
$\partial$	Partial derivative

#### *Subscripts*

$c$	Critical
Exp	Exponential
$i, j, k$	Serial numbers
$p$	At constant pressure
Pol	Polynomial
r	Reducing

$T$  At constant temperature

*Superscripts*

o Ideal gas

r Residual

$d, p, t$  Exponents

' Saturated liquid

" Saturated vapor

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