

Short Fundamental Equations of State for New Refrigerants

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ABSTRACT

For many widely used refrigerants, highly accurate multiparameter Equations of State (EOS) are available today, which are internationally agreed upon as standards for thermophysical properties of the corresponding fluids. In the field of halogenated hydrocarbons the working group “*Annex 18*” of the *International Energy Agency (IEA)* has established standards for the most relevant pure refrigerants. Beside this, it has inspired coordinated work on several other halogenated hydrocarbons and mixtures used in refrigeration and air conditioning. For the “natural” refrigerants carbon dioxide, ammonia and isobutane reference equations of state have been developed in Germany in the past 15 years; the *National Institute of Standards and Technology (NIST)* of the United States of America has almost finalized work on a new reference equation for propane.

Besides these fluids, there are still a number of refrigerants for which an internationally accepted standard does not exist. For this scope, empirical equations of state with simultaneously optimized structure offer new possibilities. With only 12 fitted coefficients equations of this kind [1–3] achieve a higher accuracy than, e.g., the well known Bender-type equations with 19 coefficients. At the same time they are numerically more stable than other empirical equations of state since the optimization process largely reduces intercorrelations among the coefficients. This fact allows for fitting the coefficients of the equation to fluids for which only few reliable experimental data are available, and for which an accurate equation of state could not be established before. Equations of state of this new type are available now for example for R23, R41, R116, R141b, R142b, R218, R227ea and isopentane [4]. Current work focuses on an improved description of strongly associating fluids such as ethers or alcohols.

Due to their numerical stability, simultaneously optimized equations of state can be fitted to very small, purposely measured data sets. In this way the development of accurate equations of state as a “work on commission” becomes a realistic option.

1. INTRODUCTION

In the second half of the 1980s the research on thermophysical properties of ‘new’, ‘ozone friendly’ refrigerants based on partly fluorinated hydrocarbons became one of the dominant activities in engineering thermodynamics. At the beginning of the 1990s the working group “*Annex 18*” was founded by *IEA* with active members in Europe, Japan and the USA. As a result of the activities of *Annex 18*, recommendations were made for thermophysical properties standards for a number of pure refrigerants. Models for mixtures were also discussed, but corresponding recommendations have not been issued.

Later on, on a proposal from *ASERCOM*, another working group coordinated by *ASHRAE* was formed. This working group prepared the Guideline *ISO 17584*. With regard to the halogenated hydrocarbons, this guideline substantially adopts the recommendations of *Annex 18*. However, in *ISO 17584* ‘natural refrigerants’ like ammonia and carbon dioxide are considered for the first time. For the mixtures R404A, R407C, R410A and R507 *ISO 17584* refers to the model published by Lemmon and Jacobsen [16]. Thermophysical property standards for hydrocarbons, which are widely used as refrigerants, are still lacking. For this purpose, a cooperation between *Ruhr-Universität Bochum* and *NIST* was established. As part of this cooperation EOS were developed for ethane (R150), normal butane (R600) and isobutane (R600a) by Bückner [17] and for propane (R290) by Lemmon [18].

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Thus, internationally accepted ‘standard’ EOS are available for the description of thermodynamic properties of the most widely used refrigerants; Table 1 summarizes these recommendations. The corresponding EOS are implemented in commercial software as, e.g., REFPROP [19], which offers user-friendly interfaces. Nonetheless there are many other refrigerants, used either as pure fluids or as mixtures components, for which no highly accurate ‘standard’ EOS is available. This situation will hardly change, because new fluids are proposed every year, and because many fluids are used only in niches, for which nobody wants to develop international standards.

Table 1: Standard EOS for thermophysical properties of refrigerants.

Halogenated Hydrocarbons (<i>ISO 17584</i>)		Refrigerant Mixtures (<i>ISO 17584</i>)	
R 32	Tillner-Roth, Yokozeki [5]	R 404A	Lemmon and Jacobsen [16]
R 123	Younglove and McLinden [6]	R 407C	Lemmon and Jacobsen [16]
R 125	Lemmon and Jacobsen [10]	R 410A	Lemmon and Jacobsen [16]
R 134A	Tillner-Roth and Baehr [8]	R 507A	Lemmon and Jacobsen [16]
R 143A	Lemmon and Jacobsen [9]		
R 12	Marx et al. [11]	Hydrocarbons	
R 22	Kamei et al. [12]	Ethane	Bücker [17]
R 152A	Outcalt and McLinden [13]	Propane	Lemmon [18]
CO ₂	Span and Wagner [15]	Isobutane	Bücker [17]
NH ₃	Baehr and Tillner-Roth [14]	n-Butane	Bücker [17]

In this work we present simultaneously optimized EOS that do not aim at substituting the internationally accepted standard EOS, but whose application is particularly promising for fluids for which standard EOS are not available. Simultaneously optimized EOS can quickly be set up, starting also from small data sets if necessary. Simultaneously optimized EOS satisfy the accuracy demands of typical technical applications, and they are able to provide reliable values for derived properties such as heat capacities even in regions with scarce data.

2. SETTING UP EQUATIONS OF STATE

In order to understand the peculiarities of simultaneously optimized EOS it is necessary to consider the way in which empirical multiparameter EOS are developed today. State of the art EOS are usually expressed in form of the reduced Helmholtz energy a as function of temperature T and density ρ ; this combination of variables corresponds to one of the ‘fundamental equations’ known in thermodynamics. All other thermodynamic properties can be calculated from a combination of derivatives of the Helmholtz energy with respect to temperature and density. Therefore a single equation allows for a consistent description of all thermodynamic quantities.

It is convenient to split the Helmholtz energy in an ideal-gas part a^0 and in a real, or residual, part a' . The residual part results from intermolecular interactions, which are neglected in the ideal-gas part. While the ideal-gas part can be quite easily determined based on heat capacity or speed of sound measurements in the gas phase, the residual part must be determined by a regression to experimental data for several thermodynamic properties; for details, see [20]. Nowadays, the ‘regression to experimental data’ consists of a linear optimization process and a nonlinear fit of the coefficients of the EOS. Figure 1 shows the form of an empirical equation for the description of the residual part of the Helmholtz energy. In such an equation the coefficients n_i can be fitted to experimental data by linear and non-linear algorithms. The exponents $p_{j,i}$ and the summation indexes I_j determine the structure of the equation. This structure is optimized (which means that the best combination of parameters such as exponents and number of terms is chosen) by evolutionary and/or deterministic algorithms, which are able to select the most appropriate combination of terms from all the terms contained in a general functional approach called ‘*bank of terms*’, for a specific fluid. The coefficients n_i are fitted to the selected experimental data using a non-linear algorithm after the structure of the EOS has been determined.

The introduction of advanced algorithms for the optimization of the EOS structure has led, from the end of the 80s, to a new generation of highly accurate EOS. Without optimization of the structure such accuracies would not have been attainable (see also [20]).

At the same time the optimization of the structure ensures that intercorrelations between terms of an EOS are drastically reduced. In this way the EOS needs less terms to achieve a given level of accuracy, gaining at the same time in numerical stability.

$$\alpha^r = \frac{a^r(T, \rho)}{RT} = \sum_{i=1}^{J_1} n_i \delta^{p_{1,i}} \tau^{p_{2,i}} + \sum_{i=l_1+1}^{J_2} n_i \delta^{p_{1,i}} \tau^{p_{2,i}} \exp(-\delta^{p_{3,i}}) + \sum_{i=l_2+1}^{J_3} n_i f_{crit}(\delta, \tau, p_i)$$

coefficients n_i are linearly / nonlinearly fitted

the structure is (usually) optimized

Figure 1: Mathematical form of an empirical equation for the description of the residual part of the Helmholtz Energy.

Now we can comprehend why the development of an EOS is a very time-consuming task. If a non-optimized structure is used, the terms of the EOS may be highly intercorrelated and an extensive set of experimental data is needed to ensure that the EOS provides meaningful results in a wide validity range. If the structure is optimized, fitting of the coefficients becomes less demanding since intercorrelations are reduced. However, in this case an extensive data set is needed for the optimization process, which is numerically very demanding. Thus, accurate multiparameter EOS are available only for a very limited number of fluids mostly because demands on the available data sets are very high.

3. SIMULTANEOUSLY OPTIMIZED EQUATIONS OF STATE

The simultaneous optimization method presented by Span et al. in 1998 [21] circumvents this problem. The basic concept of simultaneous optimization is to optimize an equation structure in such a way, that it is able to describe not only a single fluid with very high accuracy, but rather a whole family of fluids with high accuracy. If experimental data for different fluids belonging to a family are used in the optimization process, it is supposed that the equation can represent other fluids of the same family as well, even though data for these fluids were not included in the regression. In this way, extensive data sets are needed only for some typical fluids chosen among a broader group of fluids. For the remaining fluids far fewer data are sufficient, in order to fit the coefficients of an EOS with optimized functional form, where intercorrelations between the different terms are very limited.

Figure 2 illustrates the principle of the simultaneous optimization algorithm. In the first step a regression matrix is set up for every single fluid; this matrix is based on an evaluated set of experimental data and on a pre-selection of suitable algebraic terms, the so called “bank of terms”.

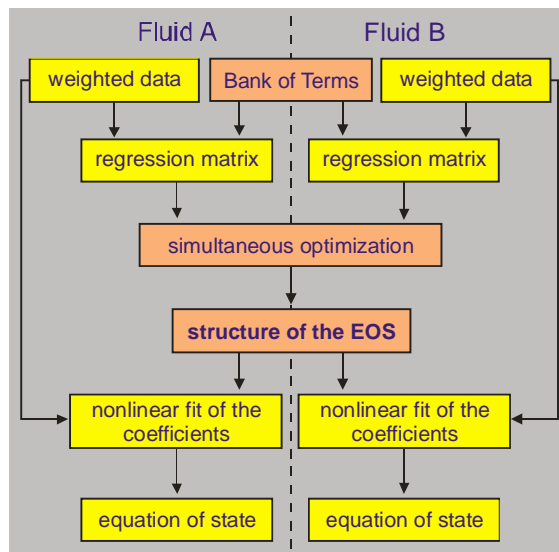


Figure 2: Block diagram of the simultaneous optimization method.

The *bank of terms* has to be the same for all fluids (for details see [21]). On the basis of the regression matrixes (one for each fluid), the optimization process selects the equation structure that describes the experimental data sets of all fluids best. In this method, 10 to 15 fluids are typically considered, although only 2 fluids are represented in Figure 2. After a suitable structure has been established, its coefficients are non-linearly fitted to selected experimental data for each fluid. In this way we have a common structure for the whole group of fluids, and fluid-specific coefficients.

Span and Wagner [1] used this method to develop a new class of empirical EOS. Aim of the work was not to develop reference quality EOS, which would be able to represent all experimental data within their respective experimental uncertainty, but rather to reach an accuracy sufficient for advanced technical applications, combined with high numerical stability. While reference EOS typically contain 18 to 40 terms, the new ‘short’ EOS are able to satisfy the accuracy demands needed for technical applications with only 12 terms. As a consequence of these features, it is possible to extend this kind of EOS to fluids with scarce data, for which traditional ‘long’ EOS couldn’t even be developed. To date, simultaneously optimized functional forms have been developed for non-polar fluids [2] and for typical polar fluids [3].

An extension of the method to strongly associating fluids is foreseen. It has been verified that the form for polar substances cannot satisfactorily describe such substances as, e.g., water or alcohols [3]. The deviating thermodynamic behavior of these fluids is explained by the phenomenon of association. Association is observed particularly if in a molecule a hydrogen atom is in the proximity of a strongly electronegative atom like oxygen, or if it is directly connected to it. It is not yet clear whether such fluids can be described by the abovementioned approach if they are considered a third group of fluids, or if a more refined concept, with the inclusion of physical terms, has to be used. In the field of statistical thermodynamics Wertheim has developed theories, which are able to describe the effect of association if they are incorporated into an equation of state [22,23]. Such physical terms were used by Chapman et al. [24] to develop the so called ‘S.A.F.T.’ equation of state, whereby S.A.F.T stands for ‘Statistically Associating Fluid Theory’. These terms, in the form presented in the S.A.F.T. theory, might in principle be combined with an optimized structure approach. This could allow for a thermodynamic description of strongly polar and associating fluids with a limited number of terms. Some families of associating fluids, like alkanols and ethers, are increasingly applied in refrigeration technologies.

Both the functional form for non-polar and the functional form for polar substances has been extensively tested and applied to wide groups of fluids: Lemmon and Span [4,5] have proposed simultaneously optimized EOS for a number of technically relevant industrial fluids, for which no accurate EOS were available before, and whose data sets are too limited to go for a fluid specific optimization. These EOS and the EOS published by Span and Wagner [2,3] are, e.g., implemented in the current revision of REFPROP [19]. Table 2 summarizes the refrigerants and fluids used in refrigeration technologies otherwise, for which a simultaneously optimized EOS is available.

Table 2: Fluids relevant for applications in refrigeration technologies, for which simultaneously optimized EOS are available.

Equation Type	Fluids
Non-polar [2, 4]	Ethane, propane, n-butane, isobutane, isopentane
Polar [3, 4]	Ammonia, carbon dioxide, R11, R12, R22, R32, R113, R123, R125, R134A, R-141B, R-142B R143A, R152A, R23, R41, R116, R141b, R142b, R218, R227EA
Associating*	Akanols (methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, 2-butanol, 1-pentanol, 2-pentanol), ethers (diehylether and dipropylether)

* Work in progress

The simultaneously optimized functional form for polar fluids developed by Span and Wagner [3] yields good results especially for the description of halogenated refrigerants, while the functional form for non-polar fluids is more suitable for the description of alkanes used as refrigerants or as blowing agents [2].

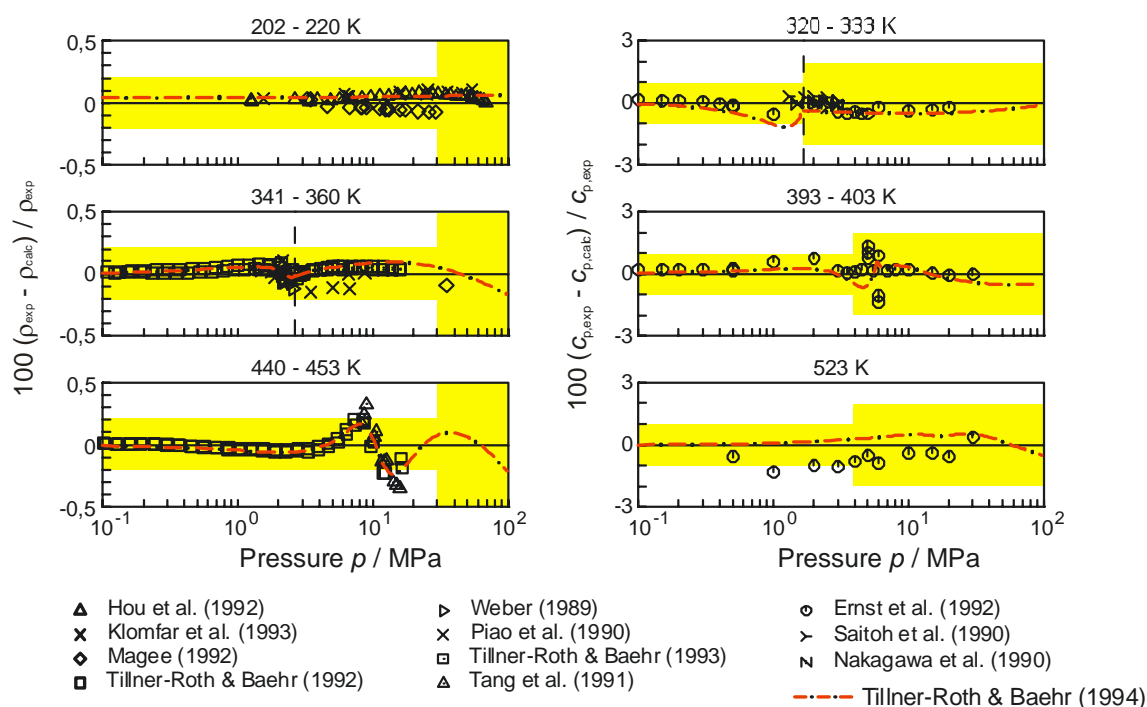


Figure 3: Percentage deviations between selected experimental data for the density and isobaric heat capacity of R134a and values calculated from the EOS by Span and Wagner [3]. Values calculated from the reference EOS by Tillner-Roth and Baehr [8] are represented as a dotted line.

Figure 3 shows a comparison between accurate experimental data for the density and the isobaric heat capacity of R134a and values calculated from the simultaneously optimized EOS developed by Span and Wagner [3]. The shaded background illustrates the accuracy demands for ‘advanced technical’ EOS defined by Span and Wagner [1]. The dotted line represents values calculated from the reference EOS by Tillner-Roth and Baehr [8]. The simultaneously optimized EOS satisfies the demands on accuracy; the experimental data are represented within the claimed uncertainty, the points lay within the shaded area. In a wide range, the two EOS produce similar results. The reference EOS for R134a shows better performances in some regions, for example on the isotherm 440 – 453 K for density. However, the scope of the work by Span and Wagner was not to replace existing reference EOS for fluids, for which extensive sets of accurate data are available. The new class of EOS was particularly developed for fluids with scarce data sets, for which no reference EOS is available.

4. FITTING SHORT EOS TO A VERY LIMITED DATA SET

An analysis of experimental data sets for various fluids shows that problems in establishing accurate multiparameter equations of state usually do not result from the total number of available data points. Where literature data are used as input, the problems mostly arise from the fact, that the data are evenly distributed neither over the relevant range of temperatures and pressures nor over the relevant properties. Vapor pressures and liquid densities at saturation and / or atmospheric pressure are usually measured rather well, while data at high (supercritical) pressures and temperatures and data for caloric properties are either scarce or very inaccurate [20]. The intention of this section is to show that numerically stable multiparameter EOS, such as the new simultaneously optimized EOS, can successfully be fitted to a very small number of accurate data, if these data are well distributed in temperature and pressure.

Table 3 gives an overview of the data available for R134a. This refrigerant belongs to the best measured fluids ever with a total of 4844 published data points. A deeper analysis of the data set showed that 3524 points satisfy the accuracy demands defined for advanced technical applications. These data points have been used by Span and Wagner [3] during the development of the simultaneously optimized EOS for R134a (in Table 3: “Selected Data Set”).

In order to simulate a smaller, but purposely measured set of sufficiently accurate data, the number of selected data has been drastically reduced (in Table 3: “Reduced Data Set”) and has been restricted to density, vapor pressure and speed of sound data. This reduced data set consisting of a total of only 49 data points (!) was used to nonlinearly fit the twelve coefficients of the EOS, which resulted from simultaneous optimization for typical polar fluids [1,3].

Table 3: Overview of Experimental Data Sets for R134a.

Data Type	Available Data Set	Selected Data Set	Reduced Data Set
$\rho(p, T)$	2611	1897	30
$p_s(T)$	505	100	9
$\rho'(T)$	182	47	---
$\rho''(T)$	55	5	---
$w(p, T)$	746	746	10
$c_v(\rho, T)$	150	150	---
$c_{p/\sigma}(p, T)$	400	395	---
$\Delta h(p, T)$	18	18	---
$\mu(p, T)$	108	102	---
$B(T), C(T)$	69	64	---
$\Sigma =$	4844	3524	49

Figures 4 and 5 show that the EOS fitted to the reduced data set reproduces all kinds of data within the accuracy demands defined for advanced technical EOS. For density and speed of sound, Figure 4 shows deviations between values calculated from the refitted EOS, from the simultaneously optimized EOS fitted to all selected data (Span and Wagner (2003), [3]) and from the internationally agreed upon reference EOS (Tillner-Roth and Baehr (1994), [8]).

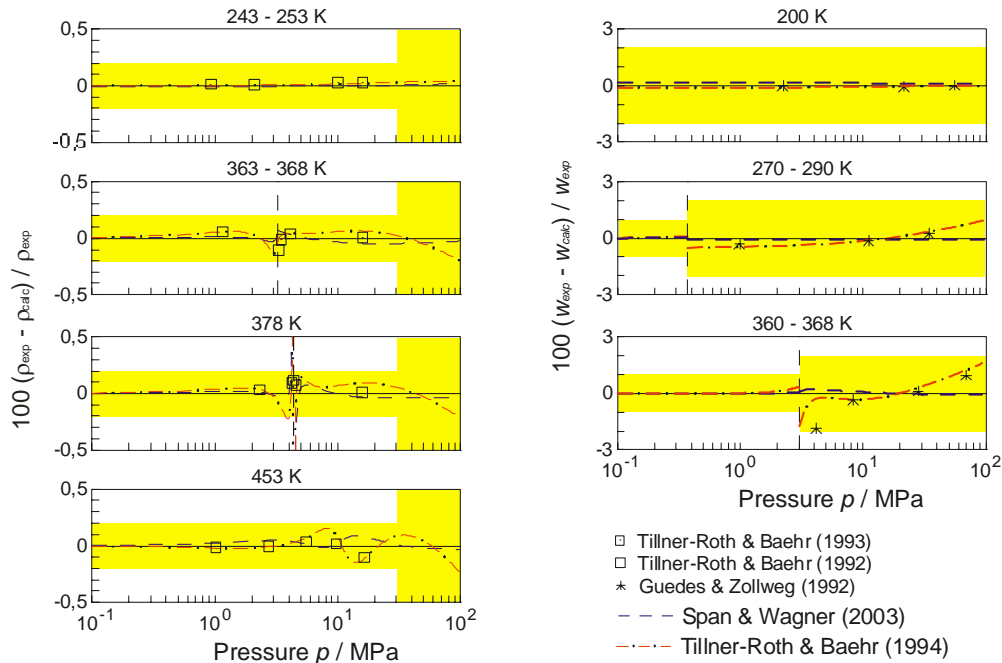


Figure 4: Percentage deviations between values for the density and the speed of sound calculated from the simultaneously optimized EOS fitted to the reduced dataset and experimental data selected for this reduced data set. Values calculated from the EOS by Span and Wagner [3] fitted to the complete set of selected data and from the reference EOS by Tillner-Roth and Baehr [8] are represented by the dash dotted lines.

The plotted data points correspond to data used in the reduced data set. The deviations between values calculated from the simultaneously optimized EOS fitted to the complete set of selected data and the EOS fitted to the reduced data set are negligible except for the critical region, where the uncertainty of technical EOS increases anyway. Figure 5 shows deviations between calculated and measured isobaric and isochoric heat capacities. These “derived” quantities were not included in the fitting process, but nonetheless they are satisfactorily represented by the simultaneously optimized EOS fitted to the reduced data set.

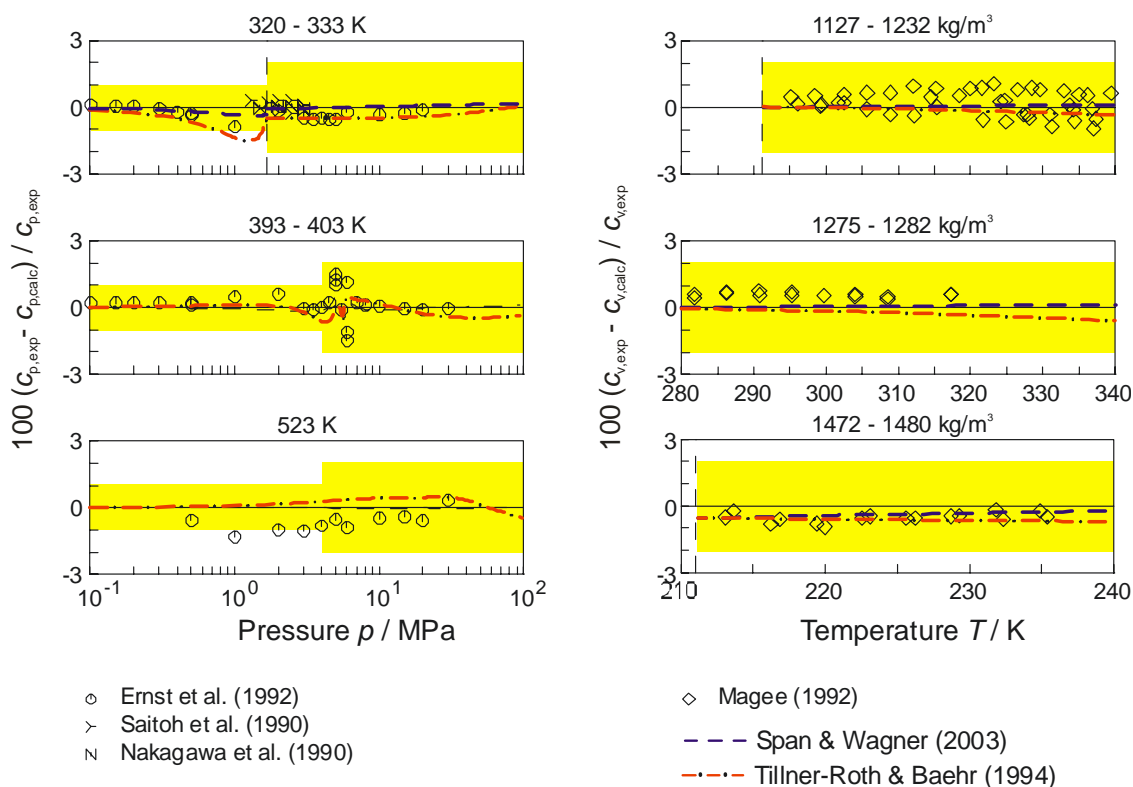


Figure 5: Percentage deviations between values for the isobaric and isochoric heat capacity calculated from the simultaneously optimized EOS fitted to the reduced data set and selected experimental data not used in this fit. Values calculated from the EOS by Span and Wagner [3] fitted to the complete set of selected data and from the reference EOS by Tillner-Roth and Baehr [8] are represented by the dash dotted lines.

5. SUMMARY AND OUTLOOK

The example in the previous section shows the strength of the new class of simultaneously optimized EOS, which are both accurate and numerically stable. It has been shown that simultaneously optimized EOS can be fitted to extremely small data sets without significant loss of accuracy. Thanks to this feature, there is the possibility of measuring a limited data set (with limited efforts) for a specific fluid, aiming directly at developing an accurate EOS, if this fluid belongs to a family for which a simultaneously optimized form has already been developed. This approach offers interesting perspectives in the refrigeration sector: from the moment a new refrigerant is “discovered”, till the moment a thermodynamic property model with sufficient accuracy is developed, it must not take years anymore. If, on the other side, a new family of fluids must be studied, one can gather experimental data from literature or from data banks for a certain number of fluids of the family, and then develop through simultaneous optimization a functional form able to describe all fluids of the family. This second option aims at the needs of the chemical industry, with its large number of fluids of interest.

The experimental technique that is necessary for this goal is basically available. For density measurements in a broad range of temperatures and pressures, single-sinker densimeters with magnetic suspension couplings are well established [25]. Spherical resonators are state of the art for speed of sound measurements in the gas phase,

whilst the pulse-echo method is preferably used at high densities [26]. At University of Paderborn a thermophysical properties laboratory is being established, which will be devoted to the measurements necessary to develop simultaneously optimized EOS. This laboratory will include a new apparatus designed for simultaneous measurement of density and speed of sound, facilities for the gravimetric preparation of mixtures and gas-chromatographs for the analysis of mixtures. Figure 6 shows a sketch of the device foreseen for the simultaneous measurement of densities and speeds of sound from vapor to liquid states.

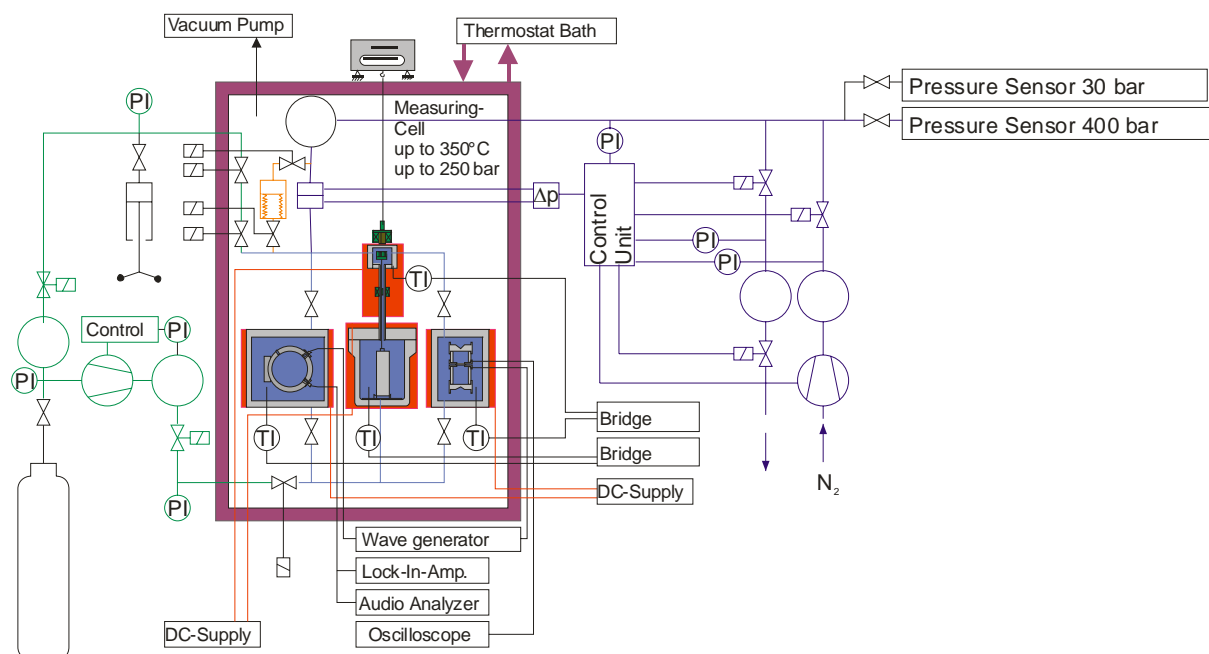


Figure 6: Device for the simultaneous measurement of densities and speeds of sound.

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