

## From the Beginning to this Day - My First Naive Ideas and the Research Results Achieved -

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In the period from 1975 to 2006, the Chair of Thermodynamics at the Ruhr-University Bochum was working in the field of the calculation and experimental determination of thermodynamic properties of pure fluid substances and mixtures. The research projects have covered the fields of equations of state, very accurate density measurements with new types of densimeters, and the critical region of pure fluids. This article gives a survey of these research activities emphasizing the close interaction between the development of equations of state and very accurate density measurements ( $p\rho T$  data). Moreover, a statement on the critical exponents is given, and the development of a new equation of state for natural gases and other mixtures is described.

### Introduction

According to the Gibbs Award Lecture this article reports on the main steps of our research activities over the last 30 years. The following topics are covered:

- Equations of state for pure fluid substances
- New type of a densimeter for very accurate density measurements
- Statement on the critical exponents of pure fluids
- The new equation of state for natural gases and other mixtures.

### Equations of State for Pure Fluid Substances

Until about 1980, the functional structure of multi-parameter equations of state was chosen by trial and error based on corresponding long-term experiences. As a consequence, the single terms (density and temperature functions) were correlated with each other which led to too long and not very accurate equations that could not be extrapolated beyond the range they were fitted to experimental data. Based on this knowledge, in 1975, I dreamed of the following goal: *We should develop equations of state to be about 10 times more accurate than the best equations of that time!*

### Structure optimization of equations of state

From about that time on, multi-parameter equations of state have not been developed any longer as thermal equations, e.g. pressure  $p$  as a function of density  $\rho$  and temperature  $T$ ,  $p(\rho, T)$ . The new type of equations of state have been fundamental equations explicit in the Helmholtz energy  $a$  as a function of density  $\rho$  and temperature  $T$ . Such an equation is usually expressed in dimensionless form,  $\alpha = a/(RT)$ , and is divided into two parts, an ideal-gas part  $\alpha^0$  and a residual part  $\alpha^r$  that accounts for intermolecular forces. The equation can be written as

$$\frac{a(\rho, T)}{RT} = \alpha(\delta, \tau) = \alpha^0(\delta, \tau) + \alpha^r(\delta, \tau) \quad (1)$$

with  $\delta = \rho/\rho_c$  and  $\tau = T_c/T$ ,

where  $\delta$  is the reduced density and  $\tau$  is the inverse reduced temperature with  $\rho_c$  as the critical density and  $T_c$  as the critical temperature;  $R$  is the specific gas constant of the substance considered. The actual equation of state corresponds to the residual part  $\alpha^r$  as the difference between the real-fluid behaviour and the ideal-gas part  $\alpha^0$ . The form of an

equation for  $\alpha^0$  is rather well known and is not considered here.

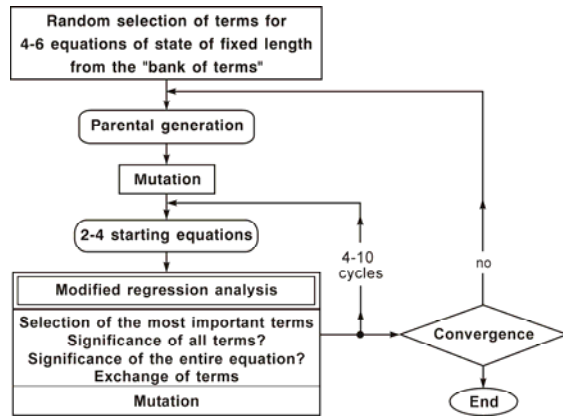
The idea to overcome the unsatisfactory situation of the equations at that time and to take a step in the direction of my wish (dream) formulated above was to optimize the functional structure of such multi-parameter equations of state. Thus, we developed a procedure for optimizing the functional structure of an equation for the residual part  $\alpha^r$ . This structure-optimization procedure consists of two steps:

- (1) Formulation of a comprehensive set of mathematical functions of the reduced density and the inverse reduced temperature which is used as a “bank of terms”.
- (2) From this bank of terms, the structure-optimization procedure determines the best combination of a certain number of terms.

Equation (2) shows an example for such a bank of terms for the residual part  $\alpha^r$ :

$$\alpha^r = \sum_{i=1}^4 \sum_{j=0}^{16} n_{ij} \delta^i \tau^{j/4} + \sum_{k=1}^6 \exp(-\delta^k) \sum_{i=1}^{10} \sum_{j=2}^{20} n_{ij} \delta^i \tau^{j/4} + \sum_{i=1}^{48} n_i \delta^{d_i} \tau^{t_i} \exp[-\eta_i (\delta - \varepsilon_i)^2 - \beta_i (\tau - \gamma_i)^2] \quad (2)$$

The equation consists of three parts, namely pure polynomials in  $\delta$  and  $\tau$ , such polynomials combined with exponential functions in  $\delta$ , and so-called Gaussian bell-shaped terms for the critical region. Such banks of terms can contain more than thousand terms of different functions of  $\delta$  and  $\tau$ .



**Figure 1:** Simplified scheme of the structure-optimization procedure.

Figure 1 shows a simplified scheme of the structure-optimization procedure. This procedure

OPTIM combines random-search steps and simplified steps from the biological evolution with our “old” stepwise regression analysis; for more details see [1, 2].

### **Experimental precondition for highly accurate equations of state**

It is well known that equations of state that are fitted to experimental data cannot be more accurate than the data themselves. Thus, the goal to develop equations of state that should be about 10 times more accurate than the best previous equations means that at least the main property, namely the density ( $p\rho T$  data), had to be about 10 times more accurate than the best  $p\rho T$  data available up to that time.

After developing new types of densimeters, we were indeed able to measure  $p\rho T$  data with experimental uncertainties of about 5–10 times smaller than it was possible at that time; for details see next section. Thus, after the development of the structure-optimization procedure, also the experimental precondition of establishing very accurate multi-parameter equations of state was met.

### **Developed equations of state**

As an example for an equation of state developed in this way, Eq. (3) shows the form of the residual part  $\alpha^r$  of the equation of state for methane [3,4]:

$$\alpha^r = \sum_{i=1}^{13} n_i \delta^{d_i} \tau^{t_i} + \sum_{i=14}^{36} n_i \delta^{d_i} \tau^{t_i} e^{-\delta^{k_i}} + \sum_{i=37}^{40} n_i \delta^{d_i} \tau^{t_i} e^{-a_i(\delta - \varepsilon_i)^2 - b_i(\tau - \gamma_i)^2} \quad (3)$$

In the structure-optimization process the equation was fitted to experimental  $p\rho T$  data including the phase-equilibrium condition (Maxwell criterion) and data of the properties second virial coefficient, speed of sound, isochoric and isobaric heat capacities and differences in enthalpy. Such a procedure is called “multi-property fitting”. The range of validity of Eq. (3) covers a temperature range from the melting line to 625 K and pressures up to 1000 MPa.

In the same way, i.e. by using the structure-optimization procedure described above and based on very accurate  $p\rho T$  measurements taken with the new densimeters (see next section), equations of state in reference quality have been developed for the substances listed in Fig. 2.

Development finished		Development recently finished	
Oxygen	IUPAC-Standard	Ethane	
Methane	IUPAC-Standard	n-Butane	
Carbon dioxide		Isobutane	
Water	IAPWS-Standard	Sulphur hexafluoride	
Water	IAPWS-Standard	Natural gases and other multicomponent mixtures	
Argon		<b>Being developed</b>	
Nitrogen		Propane (NIST)	
Ethene		Propene (NIST)	

**Figure 2:** Substances for which highly accurate reference equations of state have been developed. The equations for propane and propene are being developed at the National Institute of Standards and Technology (NIST), Boulder, USA, in cooperation with our group.

Except for the “second” equation for water, all these equations of state are fundamental equations explicit in the dimensionless Helmholtz energy. The equations for the pure substances (except for the equations for water) contain typically 30–40 fitted coefficients. All the equations cover wide ranges of temperature and pressure and can be reasonably extrapolated far beyond the range where they were fitted to experimental data. The references for the articles on the equations listed in Fig. 2 can be found on the website <http://www.rub.de/thermo>. Most of the articles have been published in J. Phys. Chem. Ref. Data.

### Equations of state for water

When looking at Fig. 2, it can be seen that there are two equations of state for water that were adopted as IAPWS standards.

#### Scientific standard IAPWS-95

This equation was developed by Wagner and Pruß [2]. In 1995, the equation was adopted by IAPWS under the name “The IAPWS Formulation 1995 for the Thermodynamic Properties of Ordinary Water Substance for General and Scientific Use” [5] referred to as IAPWS-95 for short. This equation of state is very accurate over the entire range of validity covering temperatures from the melting line to 1273 K at pressures up to 1000 MPa. The equation behaves reasonably when extrapolated up to about 5000 K and pressures up to 100 GPa.

#### Industrial standard IAPWS-IF97

This set of equations was developed in a close international cooperation [6]. In 1997, these equations were adopted by IAPWS under the name “The IAPWS Industrial Formulation 1997 for the Thermodynamic Properties of Water and Steam” [7] referred to as IAPWS-IF97 for short. This set of

equations was developed based on data for several properties that were calculated from IAPWS-95. In this way, the industrial formulation IAPWS-IF97 is coupled with the scientific standard IAPWS-95. The main body of IAPWS-IF97 is formed by so-called basic equations for regions 1–5 of the formulation. The special structure of the basic equations of IAPWS-IF97 allows a very fast calculation of all the thermodynamic properties for  $(p, T)$  as input values. This feature is very important for many industrial applications, in particular for power-cycle calculations. These basic equations are supplemented by a comprehensive set of so-called backward equations. By combining the basic and backward equations, even properties for input values of the combinations  $(p, h)$ ,  $(p, s)$  and  $(h, s)$  can be calculated extremely quickly; for more details see [8].

### A New Type of a Densimeter for Very Accurate Density Measurements

From the previous section we know that highly accurate  $ppT$  measurements are needed for the development of highly accurate equations of state. These experimental data should cover wide ranges of temperature and pressure. However, the most accurate  $ppT$  data that were available in the late 1970s had a total experimental uncertainty of about 0.1% in density. After reviewing the existing density-measuring techniques (e.g. constant-volume densimeters, hydrostatic balances, vibrating bodies), it became clear that all of these densimeters were not able to deliver  $ppT$  data with total uncertainties in density of less than 0.1%.

Against this background we decided to develop a new type of a densimeter that should allow density measurements with a *total* uncertainty in density (i.e. including uncertainties in temperature and pressure) of at most a few 0.01%. Such a densimeter should cover wide ranges of temperature and pressure, and this over the entire fluid state, i.e. from gases at low densities to compressed liquids at high densities.

To meet these requirements, we developed two new types of a hydrostatic balance densimeter, namely a two-sinker densimeter [9,10] and a novel single-sinker densimeter [11, 12].

Here, only the principle of the two-sinker densimeter is described. A short statement on the measuring range and the accuracy of the single-sinker densimeter is given at the end of this section. Details about both densimeter types are given in the comprehensive article of Wagner and Kleinrahm [13].

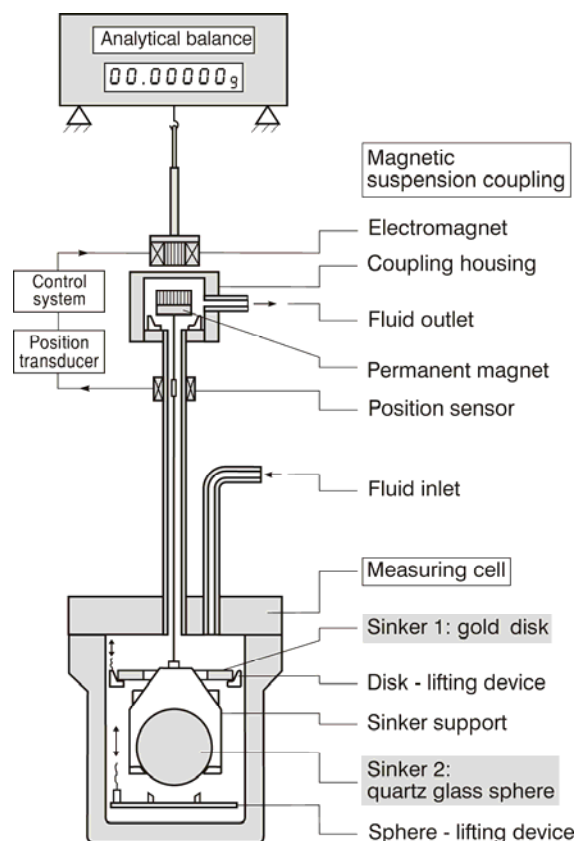
### Principle of the two-sinker densimeter

The method used for density measurements is based on the Archimedes' buoyancy principle applied in a novel way as a differential method. The principle of this two-sinker method is illustrated in Fig. 3. Instead of the usual single sinker, two specially matched sinkers are used; one of the sinkers is a gold covered quartz-glass sphere and the other is a disk of solid gold. Both sinkers have the same mass, the same surface area, and the same surface material, but a difference in volume of about 22 cm<sup>3</sup>. For density measurements the sinkers can be put alternately on a sinker support, or lifted from it by means of a sinker-changing device. This sinker support is connected to a commercial analytical balance (resolution 10 µg) by a thin wire via a magnetic suspension coupling so that the "apparent mass difference"  $\Delta m_{DS}^*$  of the sinkers, surrounded by the sample fluid, can be accurately measured. The difference  $\Delta m_{DS}^*$  is caused by the different buoyancy on the two sinkers due to their different volumes. Thus, the density  $\rho$  of the sample fluid in the measuring cell can be determined by the simple equation

$$\rho = \frac{\Delta m_{DS}^*}{V_S - V_D}, \quad (4)$$

where  $V_S$  and  $V_D$  are the volumes of the sphere and the disk, respectively. The volumes of the two sinkers are calibrated with water at ambient conditions with an uncertainty of 0.003%; the dependence of the volume of quartz glass and gold on temperature and pressure can be calculated very accurately.

Owing to the rigorous application of the Archimedes' principle in a *differential* mode, it was possible for the first time that all disturbing side effects which usually reduce the accuracy of such density measurements are automatically compensated, namely buoyant forces on the sinker suspension, surface-tension forces between the sample liquid and the suspension wire, and a great part of the uncertainty of the weighing device. Even the adsorption of gas on the sinker surfaces is approximately compensated because both sinkers have the same surface area and the same surface material.



**Figure 3:** Principle of the two-sinker densimeter.

A key component of the weighing system is the magnetic suspension coupling. By means of this coupling, the suspension force is contactlessly transmitted from the pressurized measuring cell to the balance at ambient conditions. This advanced type of a magnetic suspension coupling was developed by Lösch [14] and Lösch et al. [15, 16]. Details about the design of this coupling and its mode of operation are also given in [13].

Further details about the design of this densimeter with statements on the temperature control, the measurement of temperature and pressure, and its mode of operation is given in [13].

### Ranges of operation, accuracies and substances measured

The two-sinker densimeter was specially designed for accurate  $p\rho T$  measurements of pure fluids both in the homogeneous gas and liquid region, including the critical region as well as on the entire vapour-liquid coexistence curve from the triple-point temperature to the critical temperature. The densimeter covers a density range from 1 kg m<sup>-3</sup> to 2000 kg m<sup>-3</sup> at temperatures from 60 K to 340 K and pressures up to 12 MPa. Together with the uncertainty in the temperature and pressure measurement (0.003 K and 0.004% or 30 Pa, respectively), the *total* uncertainty in the density

measurement of pure fluids is 0.01% to 0.02% in most regions of the  $p\rho T$  surface.

Our single-sinker densimeter [11, 12], which is not described in this paper, was designed for higher temperatures and pressures. It covers a density range from  $2 \text{ kg m}^{-3}$  to  $2000 \text{ kg m}^{-3}$  at temperatures from 233 K to 523 K and pressures up to 30 MPa. Together with the uncertainty in the temperature and pressure measurement, the *total* uncertainty in the density measurement of pure fluids is about 0.02% except for low gas densities (below about  $20 \text{ kg m}^{-3}$ ).

Over the years, with both densimeters,  $p\rho T$  data of the following substances have been comprehensively measured over the entire operation range of the densimeters:

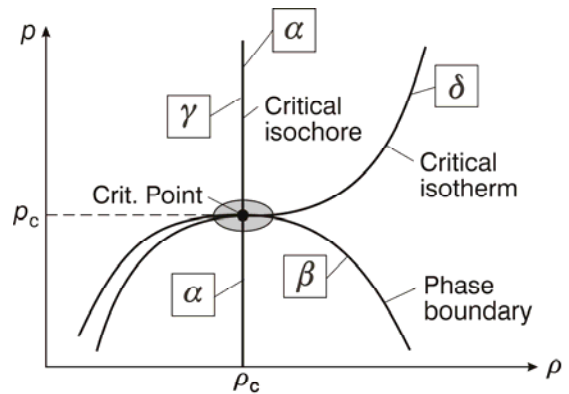
Methane, carbon dioxide, argon, nitrogen, ethene, ethane, n-butane, isobutane, propane, propene and sulphur hexafluoride. References for the corresponding articles can be found in my publication list on the website <http://www.rub.de/thermo> and for articles before 2003 also in [13].

### Statement on the Critical Exponents of Pure Fluids

The critical point of a pure fluid lies centrally in the  $p\rho T$  surface where it is no longer possible to distinguish between the gas and liquid phase. In the critical region, the thermodynamic properties of a fluid change drastically which in turn effects a strong curvature of the surface around the critical point; directly at the critical point some properties even take on the extreme values “infinite” and “zero”, respectively. The critical region is not unimportant with regard to technical application (e.g. it plays a role in supercritical extractions and the transport of ethene through pipelines), but from a physical point of view it is of outstanding interest.

Except for the caloric properties isochoric heat capacity and speed of sound in the small region of a few 0.1 K around the critical point, modern multi-parameter equations of state are able to represent the most accurate experimental  $p\rho T$  data up to the immediate vicinity of the critical point. Examples are the equations of state for ethene [17], and in particular, for sulphur hexafluoride [18]; these equations belong to the class of equations of state described in the first section. Although these equations of state can describe the critical region very well, there are significant differences in the values of the so-called critical exponents determined from these equations and from the theoretically founded renormalization group theory.

In our research project “critical region”, we have very thoroughly investigated this discrepancy.



Property	Exponent	Definition
Isochoric heat capacity	$\alpha$	$c_v \sim  T - T_c ^{-\alpha}$
Saturation densities	$\beta$	$(\rho' - \rho'') \sim (T_c - T)^\beta$
Isothermal compressibility	$\gamma$	$K_T \sim  T - T_c ^{-\gamma}$
Pressure	$\delta$	$ \rho - \rho_c  \sim  p - p_c ^\delta$

**Figure 4:** Definition of the critical exponents.

The upper part of Fig. 4 shows a pressure-temperature diagram with specific paths of state, namely the phase boundary, the critical isochore and the critical isotherm, along which the four critical exponents  $\alpha$ ,  $\beta$ ,  $\gamma$  and  $\delta$  are defined. In the lower part of Fig. 4, it can be seen how the four critical exponents are defined, namely  $\alpha$  via the isochoric heat capacity,  $\beta$  via the saturation densities,  $\gamma$  via the isothermal compressibility and  $\delta$  via the pressure on the critical isochore. However, it should be noted that the definition of the critical exponents via these simple power laws is only valid for the *limiting* approach to the critical point – a very important restriction.

Table 1 shows the values for the critical exponents derived once from the so-called renormalization group theory for magnets developed by Wilson [19, 20] and the other one from the classical mean-field theory; equations of state yield practically the classical values. For deriving the renormalization group theory combined with the so-called universality hypothesis, Wilson received the Nobel prize for physics in 1982.

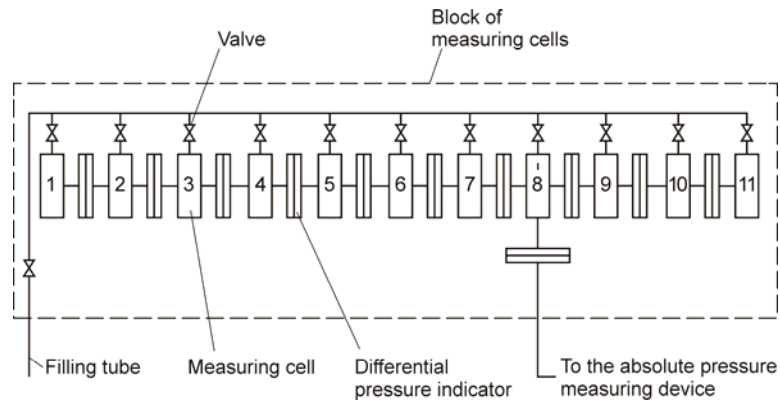
**Table 1:** Values of the critical exponents derived from the renormalization group theory and the classical theory.

Exponent	Renormalization group theory	Classical values
$\alpha$	0.11	0
$\beta$	0.326	0.5
$\gamma$	1.24	1
$\delta$	4.82	3

It can be seen that there is a significant difference between the values of the critical exponents according to the renormalization group theory and the classical values.

The well-known assessment of this discrepancy is that the classical values do not meet the real fluid behaviour near the critical point. However, the other question is whether the renormalization-group theory derived for magnets is also valid for pure *fluid* substances?

In order to try to clarify this discrepancy we designed a so-called  $ppT$  multi-cell method; for details see Kurzeja [21] and Wagner et al. [22]. The schematic design of the multi-cell method is illustrated in Fig. 5.



**Figure 5:** Schematic design of the  $ppT$  multi-cell method.

The reason for creating the special principle of the isochoric  $ppT$  multi-cell method was to achieve an extremely high internal consistency of the  $ppT$  measuring points with regard to temperature and pressure and, in addition to this, a minimization of the time needed for taking the measurements.

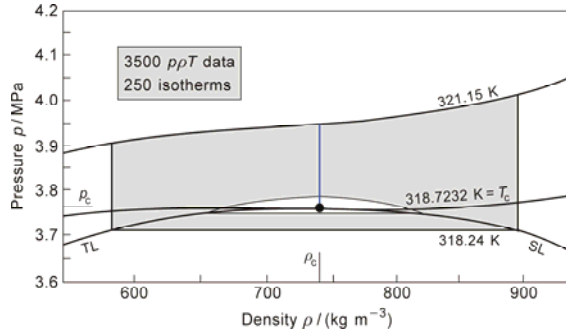
As shown in Fig. 5, the block of measuring cells consists of 11 cells with differential pressure indicators between the cells and cut-off valves directly integrated into the cells. The cells are filled with the fluid to be investigated (here  $SF_6$  and  $CO_2$ )

in such a way that the density of the fluid in the cells decreases from the 1st to the 11th cell. When filling the cells symmetrically with regard to the critical density  $\rho_c$ , the 6th cell is filled with the fluid at about  $\rho_c$ ; in this cell the temperature is also measured. The absolute pressure is only measured in the cell no. 8 which is connected with a fully automated piston manometer via an additional differential pressure indicator.

In order to make sure a reliable interpretation of the experimental results, an extremely high accuracy and, more important, internal consistency had to be achieved regarding temperature, differential pressure, absolute pressure and density. For example, the temperature stability was better than  $\pm 10 \mu K$  and the temperature gradient over the entire block of measuring cells was less than  $35 \mu K$ . For the  $ppT$  data, the absolute uncertainty in the differential pressure between two cells was  $\pm 10 Pa$ . For a reliable calculation of the critical exponents, however, the internal consistency of the  $ppT$  data is of utmost importance; thus, the scattering in the measured differential pressures was  $\pm 0.2 Pa$ . To meet the several temperature requirements as given above, the block of the measuring cells was placed in a very special four-stage thermostat [22].

The  $p$ - $\rho$  diagram in Fig. 6 shows the range for

which the measurements were carried out. Within the grey area 3500  $ppT$  data points along 250 isotherms were measured over a temperature range of about 2.4 K. The  $ppT$  data in the grey range served for the development of the wide-range equation of state for  $SF_6$  [18]. For determining the critical exponents, only the  $ppT$  data in the white range corresponding to the very near-critical range were used.



**Figure 6:** Range of the  $ppT$  measurements in the critical region of  $SF_6$ .

Table 2 summarizes the values for the critical exponents for  $SF_6$  and  $CO_2$  from our  $ppT$  measurements. The values of the exponents obtained from the classical theory, the renormalization group theory and from experiments of other authors are given for comparison. The surprising fact is that our results agree within the experimental uncertainties with the classical values!

**Table 2:** Results for the critical exponents for  $SF_6$  and  $CO_2$

Exponent	Classical theory	Renorm.group theory	Previous experiments	Results of our measurements	
				$SF_6$	$CO_2$
$\alpha$	0	0.11	0.08 - 0.15	$\approx 0$	$\approx 0$
$\beta$	0.5	0.326	0.32 - 0.36	$0.44 \pm 0.06$	$0.47 \pm 0.06$
$\gamma$	1	1.24	1.12 - 1.28	$0.99 \pm 0.05$	$0.98 \pm 0.05$
$\delta$	3	4.8	4.3 - 5.1	$3.0 \pm 0.2$	$3.0 \pm 0.5$

We think that the reason for these surprising results are as follows:

The values of the renormalization group theory were derived for magnets, i.e. for a solid. However, the thermodynamic properties of solids are not influenced by the gravitational field on earth, whereas our measurements with a fluid substance are influenced by such an outer field. It is well known that in the immediate vicinity of the critical point the gravity effects a significant density stratification in the fluid, through which the thermodynamic properties are clearly influenced. This conclusion is supported by the fact that from our measurements outside the gravity-influenced range, we get values for the critical exponents that are in agreement with those from the renormalization group theory. However, since the critical exponents are defined in the *limiting* approach to the critical point, the significant difference remains valid. Thus, our conclusion is not that the results from the renormalization group theory are not correct, but just that, on earth, the

results for magnets cannot be transferred to pure fluid substances – this is not the same universality class.

The reason for the agreement of the previous experiments with the renormalization group values is not so surprising because these measurements were taken relatively “far” from the critical point, where the density stratifications due to the gravity influence disappear. The temperature range in which the critical exponents are not any longer gravity influenced is only about 90 mK for  $SF_6$  and 55 mK for  $CO_2$  around the critical point [23]. However, note that the critical exponents are defined directly at the critical point.

If our conclusions are right, then our wide-range equations of state do not yield basically “wrong” values for the critical exponents.

### The Equation of State GERG-2004 for Natural Gases and Other Mixtures

The accurate knowledge of the thermodynamic properties of natural gases and other mixtures of natural-gas components is of indispensable importance for the basic engineering and performance of technical processes. This requires property calculations for a wide range of mixture compositions and operating conditions in the homogeneous gas, liquid, and supercritical regions, and also for vapour-liquid equilibrium (VLE) states. These data can advantageously be calculated from equations of state. Examples for technical applications of natural gas, where commonly equations of state are used, are the natural-gas production, its transportation through pipelines, the storage of natural gas in underground cavities, the liquefaction of natural gas to get liquefied natural gas (LNG) and its transportation by LNG tankers.

Currently, there is not any equation of state for natural gases that are appropriate for all of the exemplified applications and that satisfy the demands concerning the accuracy in the description of thermodynamic properties over the entire fluid region that is of technical importance. This statement includes the AGA8-DC92 equation of state [24], which is only valid for a part of the gas phase, as well as the different cubic equations and correlation equations for a small part of the liquid region.

Therefore, several years ago we decided to develop a new wide-range equation of state for natural gases. The research project aimed at developing an equation of state that is suitable for all technical applications using natural gases and other mixtures consisting of natural-gas

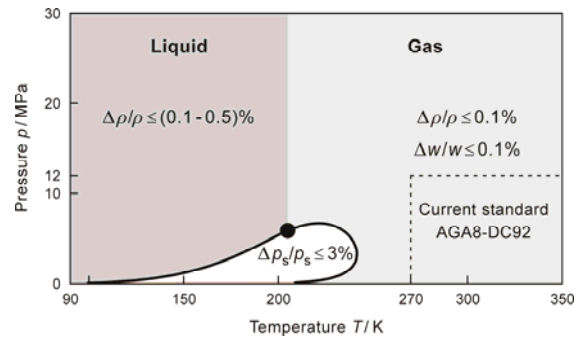
components. The work was supported by the DVGW (German Technical and Scientific Association on Gas and Water) and European natural gas companies (E.ON Ruhrgas, Germany; Enagás, Spain; Gasunie, The Netherlands; Gaz de France, France; Snam Rete Gas, Italy; and Statoil, Norway), which are members of GERG (Groupe Européen de Recherches Gazières). The main purpose of this European research project was to develop a thermodynamic property model that is appropriate as an international reference equation for all natural-gas applications where thermodynamic properties are required.

The equation of state was developed by Kunz [25] with the focus not to design an equation just for natural gases with a limited range of composition, but also for other multi-component mixtures covering the full concentration range of the single components. After the comprehensive process of development, the new equation of state was evaluated by GERG and was then adopted as GERG standard under the name GERG-2004 equation of state or just GERG-2004 for short. Therefore, the new equation is called GERG-2004 in the following.

This equation of state is comprehensively described by Kunz et al. in the GERG Technical Monograph 15 [26]; this monograph can be downloaded from the website of GERG <http://www.gerg.info/publications/tm.htm>. Here, only the most important features of GERG-2004 are summarized.

### Requirements on GERG-2004

The requirements on the equation are summarized in the  $p$ - $T$  diagram shown in Fig. 7. Thus, GERG-2004 should cover the gas phase, the liquid phase and the two-phase region gas-liquid over a temperature range from 90 K to 350 K and pressures up to 30 MPa. The allowed uncertainties in the calculation of density, speed of sound and vapour pressure are also given in this figure. It can be seen that the currently internationally accepted standard equation of state, the AGA8-DC92, is only valid in the homogeneous gas region in a limited range of temperature and pressure and (not visible in Fig. 7) only in a limited composition range for most of the natural-gas components.



**Figure 7:** Basic requirements on the new equation of state.

The pure components that are covered by the equation are listed in Fig. 8. In the left column the main components of natural gases are listed, the middle column comprises higher hydrocarbons and the right column contains further substances that are also important for describing a wide variety of natural gases by an equation of state. When starting the development, only 18 of the 21 pure substances had to be considered. The three substances n-nonane, n-decane and hydrogen sulphide had not been included in the equation that was adopted as GERG-2004 in 2004. Because of the technical importance of these three substances in connection with current processes with natural gases, we have further developed the equation in the last two years by incorporating the three components mentioned above.

Methane	n-Butane	Hydrogen
Nitrogen	Isobutane	Carbon monoxide
Carbon dioxide	n-Pentane	Hydrogen sulfide
Ethane	Isopentane	Water
Propane	n-Hexane	Oxygen
	n-Heptane	Argon
	n-Octane	Helium
	n-Nonane	
	n-Decane	

**Figure 8:** Components covered by the equation of state.

### Form of the equation of state

As well as for the equations of state for pure substances (see the first section), also GERG-2004 is a fundamental equation of the Helmholtz energy  $a$  that is made dimensionless by relating  $a$  to the universal gas constant and temperature,  $\alpha = a / (RT)$ . Then, the dimensionless Helmholtz energy  $\alpha$  is expressed by a so-called multi-fluid approximation that was firstly used by Lemmon and Tillner-Roth [27] for mixtures with a relatively small number of components. The equation according to the multi-fluid approximation reads:



$$\begin{aligned}
\alpha(\delta, \tau, \bar{x}) = & \alpha^0(\rho, T, \bar{x}) \\
& + \sum_{i=1}^N x_i \alpha_{0i}^r(\delta, \tau) \\
& + \sum_{j=i+1}^N \sum_{i=1}^{N-1} \Delta \alpha_{ij}^r(\delta, \tau, \bar{x}) \quad (5)
\end{aligned}$$

The equation consists of three parts: The function  $\alpha^0$  is the contribution of the ideal-gas mixture, the sum with  $\alpha_{0i}^r$  corresponds to the contribution of the equations of state of the pure components  $i$ , the double sum with  $\Delta \alpha_{ij}^r$  is the so-called departure function of the binary mixtures of the two pure components  $i$  and  $j$ . The reduced density  $\delta$  and the inverse reduced temperature  $\tau$  are determined from the density  $\rho$  and temperature  $T$  by relating them to the so-called reducing functions  $\rho_r$  and  $T_r$ . Thus, the dimensionless quantities  $\delta$  and  $\tau$  are defined by:

$$\delta = \rho / \rho_r(\bar{x}) \quad \tau = T_r(\bar{x}) / T \quad (6)$$

The composition of the mixture is given by the vector of the molar concentration  $\bar{x}$ , and  $N$  is the total number of components.

The reducing functions for the density  $\rho_r(\bar{x})$  and for the temperature  $T_r(\bar{x})$  depend on the critical density  $\rho_{c,i}$  and the critical temperature  $T_{c,i}$  of the pure components  $i$ , and on the composition  $\bar{x}$  of the respective binary mixture. The equations have the form:

$$T_r(x) = \sum_{i=1}^N \sum_{j=1}^N x_i x_j \beta_{T,ij} k_{T,ij} \frac{x_i + x_j}{\beta_{T,ij}^2 x_i + x_j} (T_{c,i} \cdot T_{c,j})^{0.5} \quad (7)$$

$$\frac{1}{\rho_r(\bar{x})} = \sum_{i=1}^N \sum_{j=1}^N x_i x_j \beta_{v,ij} k_{v,ij} \frac{x_i + x_j}{\beta_{v,ij}^2 x_i + x_j} \frac{1}{8} \left( \frac{1}{\rho_{c,i}^{1/3}} + \frac{1}{\rho_{c,j}^{1/3}} \right)^3 \quad (8)$$

Each of the reducing functions contains two parameters,  $k_{v,ij}$  and  $\beta_{v,ij}$ , and,  $k_{T,ij}$  and  $\beta_{T,ij}$ , that are fitted to experimental data. If the experimental data are not sufficiently accurate enough or if there are no data at all, these four parameters are set to 1, i.e. Eqs. (7) and (8) correspond to simple quadratic mixing rules without any fitting.

The basic form of the departure functions  $\Delta \alpha_{ij}^r$  for a binary mixture of the two pure components  $i$  and  $j$  reads:

$$\Delta \alpha_{ij}^r(\delta, \tau, \bar{x}) = x_i x_j F_{ij} \sum_{m_{ij}=1}^{M_{ij}} n_{m_{ij}} \tau^{t_{m_{ij}}} \delta^{d_{m_{ij}}} \exp[-\eta_{m_{ij}}(\delta - \varepsilon_{m_{ij}})^2 - \beta_{m_{ij}}(\delta - \gamma_{m_{ij}})] \quad (9)$$

Equation (9) corresponds to the so-called *binary-specific* departure function, if the coefficients  $n_{m,ij}$  are fitted to experimental data of the specific binary mixture of the pure components  $i$  and  $j$ ; in this case it is  $F_{ij} = 1$ .

Equation (9) is used in the form of a so-called *generalized* departure function for an entire group of binary mixtures that behave similarly and their data sets are not accurate enough or too small. In this case, the coefficients  $n_m$  (the subscripts  $ij$  are dropped) are fitted to the experimental data of this entire group. Only the coefficient  $F_{ij}$  is fitted to the data of the respective binary mixture of the components  $i$  and  $j$ .

The structure of the reducing functions and the way of summarizing the departure functions (only pairs of two indices) shows that GERG-2004 was developed only on the basis of experimental data for *binary* mixtures. Data for multi-component mixtures were used for comparisons only. However, the number of binary mixtures that can be formed from 21 pure components is not just small, namely 210 binary mixtures for which more than 90 000 data had to be handled.

#### **Range of validity, uncertainty and general quality of GERG-2004**

The entire range of validity covers the following temperatures and pressures:

$$\text{Normal range: } 90 \text{ K} \leq T \leq 450 \text{ K} \quad p \leq 35 \text{ MPa}$$

$$\text{Extended range: } 60 \text{ K} \leq T \leq 700 \text{ K} \quad p \leq 70 \text{ MPa}$$

Moreover, the equation can be reasonably extrapolated beyond the extended range, and each component can cover the entire composition range (0–100)%.

GERG-2004 represents the experimental data within their uncertainties. Therefore, the uncertainty values, roughly summarized in the following, correspond to about the uncertainties of the most accurate experimental data:

In the *liquid region*, the uncertainty in density and enthalpy differences are less than (0.1–0.5)%, and in heat capacities less than (1–2)%. In the *gas region*, the uncertainties in density and speed of sound are less than 0.1%, in enthalpy differences less than (0.2–0.5)% and in heat capacities less than (1–2)%. In the *two-phase region*, the total uncertainty in vapour pressure is (1–3)% corresponding to the uncertainties of the experimental VLE data.

GERG-2004 satisfies the important demands concerning the description of liquid-phase properties and vapour-liquid equilibrium states. Major improvements are achieved for saturated-

liquid densities of LNG-like multi-component mixtures compared to ordinary cubic equations of state. GERG-2004 well represents accurate experimental saturated-liquid densities.

The equation of state represents the most accurate experimental binary and multi-component data for the gas phase and gas-like supercritical densities, speeds of sound, and enthalpy differences mostly to within their low experimental uncertainties. GERG-2004 achieves an accuracy never obtained before by an equation of state for mixtures. Compared to the AGA8-DC92 equation of state, GERG-2004 achieves important and fundamental improvements in the description of gas-phase and gas-like supercritical densities of natural-gas mixtures containing, for example, high fractions of nitrogen, carbon dioxide, or ethane, or substantial amounts of the combination of ethane, propane and heavier hydrocarbons. The new equation of state allows for the accurate description of natural gas-hydrogen mixtures, low-calorific natural gases, and other mixtures of uncommon composition. Moreover, GERG-2004 is much more accurate for rich natural gases and in the description of all caloric properties, and also satisfies the demands concerning the description of liquid-phase properties and vapour-liquid equilibrium states.

The wide range of validity enables the use of GERG-2004 in both standard and advanced technical applications for natural gases and related mixtures. This includes, e.g. pipeline transport, natural-gas storage, improved and integrated processes with liquefied natural gas, the design of separation processes as encountered in the processing of rich natural gas to meet pipeline quality specifications, the production of liquefied natural gas and liquefied petroleum gas, the production and refining of light oil, processes using mixtures of hydrocarbons as alternative refrigerants, and future applications with natural gas-hydrogen mixtures.

GERG-2004 is under consideration to be adopted as the ISO standard ISO 20765-2 for the calculation of thermodynamic properties of natural gases.

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