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Wide-Range Equation of State for Natural Gases and Other Mixtures

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

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Preface

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. The processing, transportation, and storage of natural gas 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 states. These data can advantageously be calculated from equations of state. To overcome the weaknesses and limitations of existing equations of state used in the natural gas industry, several years ago the Chair of Thermodynamics of the Ruhr-Universität Bochum decided to develop a new wide-range equation of state for natural gases and other mixtures of a quality that enables the equation to be adopted as a standard international reference equation suitable for all natural gas applications where thermodynamic properties are required. 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). Based on the new formulation, robust and efficient calculation routines (software) were developed in a second project, supported by the European natural gas companies mentioned before. The routines allow for "blind" calculations of the thermodynamic properties of mixtures at arbitrary conditions.

This monograph thoroughly presents the new equation of state, adopted by GERG in 2004 and called GERG-2004 equation of state or GERG-2004 for short. Firstly, a brief introduction to existing mixture models with particular focus on the equations of state commonly used in the natural gas industry is given, followed by the basic requirements that were defined for the new model. Similar to recent developments, the new wide-range formulation is explicit in the Helmholtz free energy. The mixture model uses accurate equations of state in the form of fundamental equations for each mixture component along with formulations developed for binary mixtures that take into account the residual mixture behaviour. Therefore, the pure substance equations of state and the general characteristics of the modern approach are described. However, the descriptions should be considered as background information and are not necessarily required for those who are only interested in the structure of the new equation of state. In Chap. 6, an overview of the experimental data used for the development and evaluation of the new mixture model is given. The quality and the extent of the available data limit the achievable accuracy of the equation. Detailed information on the mathematical structure of the new equation of state, its range of validity, the uncertainties in different thermodynamic properties, and the development of the binary equations is provided in Chap. 7. Moreover, it offers guidelines for the calculation of thermodynamic properties from the new equation of state along with some fundamental principles regarding advanced mixture property calculations using second order convergence methods. This includes stability analysis, the solution to flash specifications, the calculation of saturation points, and the construction of phase envelopes. The quality and predictive power of the new formulation is discussed in Chap. 8 by comparisons with experimental data and with results obtained from previous mixture models. Finally, recommendations for the potential further extension of the new equation of state are given.

The monograph is written in such a way that the complete numerical information, required for the calculation of thermodynamic properties from the new equation of state, such as density, enthalpy, entropy, isobaric heat capacity, and fugacity coefficients, is given in Chap. 7. However, special algorithms are needed to analyse the phase stability, i.e. to determine whether a mixture at the specified conditions is homogeneous or split in two (or more) phases, and to be able to perform phase equilibrium calculations. As mentioned above, the procedures used for this purpose in this work are also described in Chap. 7.

The authors are grateful to the members of the GERG Working Group 1.34 and the GERG Working Group 1.46 for the financial support of the respective research projects and for their very helpful collaboration and their patience. We are also grateful to all of the experimentalists who carried out measurements for the equation project, as well as to those who provided us with recently measured data prior to their publication or with (older) data that are not available in the open literature. Our special thanks go to M. L. Michelsen for providing us with the computer codes of algorithms for phase equilibrium calculations and for his help in understanding the sophisticated procedures. Moreover, we thank G. Lauermann and the Gas Processors Association for providing us with the GPA Thermodynamic Database. We wish to express our warmest thanks to D. Lecaplain, J. Kirschbaum, J. Bierwirth, and K. Göckeler, who, in different ways, contributed to certain parts of this work. In particular, one of us (O. K.) is very grateful to A. Grevé for her assistance in writing this monograph and for typing most of the equations of the manuscript. Finally, we thank E. W. Lemmon for carefully reading the entire manuscript, for helpful discussions and suggestions, and for improving the English style.

Bochum, April 2007

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Contents

Nomenclature

Symbols

a	Molar Helmoltz free energy Coefficient of the AGA8-DC92 equation of state Parameter of the Peng-Robinson equation of state Coefficient or parameter of an equation Activity
$\bar{a}$	Vector of the coefficients and parameters of an equation
A	Parameter Total Helmholtz free energy
b	Density exponent of the AGA8-DC92 equation of state Parameter of the Peng-Robinson equation of state (molar co-volume) Coefficient
B	Second virial coefficient Parameter
B^*	Composition-dependent coefficient of the AGA8-DC92 equation of state
c	Parameter of the AGA8-DC92 equation of state Density exponent Coefficient
c_p	Isobaric heat capacity
c_v	Isochoric heat capacity
C	Third virial coefficient Coefficient
C^*	Composition-dependent coefficient of the AGA8-DC92 equation of state
d	Differential Derivative
d	Density exponent
e	Mole number of the new phase
E	Parameter of the AGA8-DC92 equation of state
f	Weighting factor Composition-dependent factor of the departure function

	Fugacity
	Function
F	Parameter
	Number of degrees of freedom
	Function
$\overline{F}$	Vector of functions
g	Molar Gibbs free energy
$\hat{g}$	Partial molar Gibbs free energy
G	Total Gibbs free energy
h	Molar enthalpy
$\hat{h}$	Partial molar enthalpy
H	Total enthalpy
	Element of the Hessian matrix
$\boldsymbol{H}$	Hessian matrix
i	Serial number
I	Upper limit of serial number i
j	Serial number
J	Upper limit of serial number j
	Element of the Jacobian matrix
$\boldsymbol{J}$	Jacobian matrix
k	Serial number
K	Size parameter of the AGA8-DC92 equation of state
	Number of terms
	Equilibrium factor (*K*-factor), $K = x_i''/x_i'$
	Wilson *K*-factor
l	Serial number
	Molar liquid amount, $l_i = (1-\beta)\,x_i'$
$\bar{l}$	Liquid flows (vector of molar liquid amounts)
m	Serial number
M	Number of data points
	Molar mass
n	Serial number

	Coefficient Mole number of a component in the mixture Total mole number
$\bar{n}$	Coefficient vector Vector of mole numbers
N	Number of components in the mixture
p	Pressure Density exponent
P	Number of coexisting phases
q	Function
Q	Function
R	Molar gas constant, $R = 8.314\ 472\ \mathrm{J{\cdot}mol^{-1}{\cdot}K^{-1}}$ [see Mohr and Taylor (2005)]
R^*	Obsolete molar gas constant
s	Molar entropy
$\hat{s}$	Partial molar entropy
S	Total entropy Specification
t	Temperature exponent
tpd	Reduced tangent plane distance function, $tpd = TPD/(RT)$
T	Temperature in K (ITS-90)
TPD	Tangent plane distance function
u	Temperature exponent of the AGA8-DC92 equation of state Molar internal energy
U	Total internal energy
v	Molar volume Molar vapour amount, $v_i = \beta x_i''$
$\bar{v}$	Vapour flows (vector of molar vapour amounts)
$\hat{v}$	Partial molar volume
V	Total volume
w	Speed of sound Mole fraction of the component in the new phase Substance-dependent parameter

$\overline{w}$	Molar composition (vector of mole fractions) of the new phase
x	Mole fraction Variable Mole fraction in the saturated liquid phase
$\overline{x}$	Molar composition (vector of mole fractions) Molar composition (vector of mole fractions) of the saturated liquid phase
X	Variable
$\overline{X}$	Vector of the properties to be calculated at phase equilibrium
y	Variable Mole fraction in the saturated vapour phase
$\overline{y}$	Molar composition (vector of mole fractions) of the saturated vapour phase
Y	Reducing function for density or temperature Substitute for v and T
z	Any property
Z	Compression factor

Greek Symbols

α	Reduced molar Helmholtz free energy, $\alpha = a/(RT)$
β	Mole fraction exponent Parameter Vapour fraction, $\beta = n''/n$
β_a	Second acoustic virial coefficient
γ	Precorrelation factor, $\gamma = c_p/c_v$ Parameter Activity coefficient
δ	Reduced density, $\delta = \rho/\rho_\mathrm{r}$ Kronecker delta, $\delta_{ij} = 0$ for $i \neq j$, and $\delta_{ij} = 1$ for $i = j$ Differential amount
δ_T	Isothermal throttling coefficient
ε	Precorrelation factor, $\varepsilon = \left(c_p - c_v\right)/R$ Parameter Criterion of convergence
∂	Partial derivative

Δ	Difference Deviation
$\Delta\alpha$	Departure function for the reduced molar Helmholtz free energy
η	Parameter
ϑ	Parameter
φ	Fugacity coefficient
ϕ	Scaled composition derivative of $\ln\varphi_i$ Temperature or pressure derivative of $\ln\varphi_i$ Parameter
κ	Isentropic exponent
κ^{o}	Isentropic exponent of the ideal-gas mixture, $\kappa^{\mathrm{o}} = c_p^{\mathrm{o}} \big/ c_v^{\mathrm{o}}$
λ	Parameter
μ	Chemical potential
μ_{JT}	Joule-Thomson coefficient
π	Pressure derivative
θ	Parameter
ρ	Molar density
σ	Standard deviation
σ^2	Variance
τ	Inverse reduced temperature, $\tau = T_{\mathrm{r}}/T$
χ	Weighted residuum
χ^2	Weighted sum of squares
χ^{*2}	Reduced sum of squares
ω	Acentric factor
ψ	Temperature or total volume derivative of $\ln(f_i/n_i)$ Non-scaled composition derivative of $\ln(f_i/n_i)$
ζ	Parameter

Subscripts

a	Partial derivative with respect to the parameter a
c	At the critical point

calc	Calculated value
exp	Experimental value
Exp	Exponential term
gen	Generalised
i	Serial number
j	Serial number Partial derivative with respect to n_j
k	Serial number
l	Serial number
m	Serial number
max	Maximum value
n	Serial number
o	Property of the pure substance
p	Partial derivative with respect to p
Pol	Polynomial term
r	Reducing property
ref	Reference sum of squares
s	At saturation (phase equilibrium)
s	Variable to be specified
spec	Specified
t	At the triple point
tot	Total weighted variance
T	Partial derivative with respect to T
v	Partial derivative with respect to v
V	Partial derivative with respect to V
w	Speed of sound data
wt	Weighting
x	Standard deviation for variable x Partial derivative with respect to x
y	Standard deviation for variable y

Y	Parameter of a reducing function for density or temperature
z	Standard deviation for property z
δ	Partial derivative with respect to δ
τ	Partial derivative with respect to τ
0	Reference state, $T_0 = 298.15$ K, $p_0 = 0.101325$ MPa

Superscripts

E	Excess property
lin	Linearly combined residual parts of the pure substance equations of state
o	Ideal-gas state
p	Precorrelated
r	Residual part
T	Transponed
Δ	Part of the departure function
$'$	State of saturated liquid
$''$	State of saturated vapour
$*$	Intensive or extensive property of the segregated phase
( )	Equilibrium phase

Abbreviations

AAD	Average absolute deviation
Bias	Average deviation
Bu	Burnett apparatus
CNG	Compressed natural gas
DLL	Dynamic link library
GDMA	Two-sinker densimeter
LLE	Liquid-liquid equilibrium
LNG	Liquefied natural gas
LPG	Liquefied petroleum gas
min	Minimum

NGL	Natural gas liquids
Op	Optical interferometry method
RMS	Root-mean-squared deviation
SDV	Standard deviation
VLE	Vapour-liquid equilibrium
VLLE	Vapour-liquid-liquid equilibrium

Component Abbreviations and Chemical Formulas

Ar	Argon
CH_4	Methane
C_2H_6	Ethane
C_3H_8	Propane
CO	Carbon monoxide
CO_2	Carbon dioxide
H_2	Hydrogen
H_2O	Water
He	Helium
i-C_4	Isobutane (2-Methylpropane)
i-C_4H_{10}	Isobutane (2-Methylpropane)
i-C_5	Isopentane (2-Methylbutane)
i-C_5H_{12}	Isopentane (2-Methylbutane)
n-C_4	n-Butane
n-C_4H_{10}	n-Butane
n-C_5	n-Pentane
n-C_5H_{12}	n-Pentane
n-C_6	n-Hexane
n-C_6H_{14}	n-Hexane
n-C_7H_{16}	n-Heptane
n-C_8H_{18}	n-Octane
N_2	Nitrogen

NO_x	Oxides of nitrogen
O_2	Oxygen
R-22	Chlorodifluoromethane
R-32	Difluoromethane
R-125	1,1,1,2,2-Pentafluoroethane
R-134a	1,1,1,2-Tetrafluoroethane
R-143a	1,1,1-Trifluoroethane
R-152a	1,1-Difluoroethane

1 Introduction

Aside from crude oil and coal, natural gas is one of the most important primary energy sources accounting for almost one fourth of the world primary energy consumption [BP (2006)]. Due to its longer estimated future availability compared to crude oil, it increasingly gains in importance. Although natural gas belongs to the fossil fuels, it is comparatively environmentally sound.

Natural gas is a multi-component mixture of widely varying composition with methane as the main constituent and further essential components such as nitrogen, carbon dioxide, ethane, propane, and heavier hydrocarbons. Nowadays, natural gas is used for space heating, cooking, electric power generation, and as raw material in the chemical industry. Driven by the need to satisfy new and more stringent environmental emissions standards as well as for economic reasons, natural gas is considered as a clean-burning, alternative fuel for the transportation sector. Natural gas vehicles using compressed natural gas (CNG) at pressures $p \geq 20$ MPa are increasing in abundance and popularity. Aside from CNG, some natural gas vehicles are fuelled by liquefied natural gas (LNG), and others are bi-fuel vehicles using gasoline or natural gas, allowing for more flexibility in fuel choice. Future developments include, for example, natural-gas-powered fuel cells for the clean and efficient generation of electricity for residential, commercial, industrial, and even transportation settings, and the use of natural gas–hydrogen mixtures as an alternative fuel enabling the further reduction of the emissions of CO, CO_2, NO_x, and hydrocarbons of gasoline or natural-gas-powered vehicles [Akansu *et al.* (2004)], representing the next step on the path to an ultimate hydrogen economy.

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 commonly using equations of state are processing, transportation through pipelines or by shipping, and storage of natural gas:

- To meet pipeline quality specifications or for commercial use as a fuel, natural gas in its raw form in general needs to be processed ahead of the feed into the gas pipeline system or a liquefaction facility. This involves separation of a number of components which are either undesirable or have more value on their own than when left in the natural gas. Raw natural gas contains varying and comparatively large amounts of ethane, propane, butane, and heavier hydrocarbons (natural gasoline), which are known as natural gas liquids

(NGL). The separation of these components requires the design of fractionation units, where they are removed from the raw gas and further fractionated for individual sale as ethane, propane, liquefied petroleum gas (LPG), and other products. Among others, carbon dioxide and water are undesirable components and are removed as well.

- Natural gas is transported in gaseous form through pipelines at pressures between 8 MPa and 12 MPa. Compressor stations placed periodically along the pipeline ensure that the natural gas remains pressurised. In addition, metering stations allow for monitoring and managing the natural gas in the pipes. Small differences in methods used to calculate volumetric flow rates in large scale metering can introduce large cost uncertainties. To match supply and demand, natural gas is injected at pressures up to 30 MPa into underground storage facilities, such as depleted gas reservoirs, aquifers, and salt caverns.
- Natural gas deposits are unequally divided over the world. In situations where the economics of major gas transmission pipelines are not viable (primarily across oceans), natural gas is reduced to about one six-hundredth of its volume by cooling to about 110 K at atmospheric pressure, resulting in the condensation of the gas into liquid form, known as LNG, thus making it transportable by specialised tanker ships. At the receiving terminal, the LNG is pumped into onshore storage tanks and can then be regasified and distributed into the pipeline system. State-of-the-art and highly-efficient liquefaction processes use mixtures of natural gas components as refrigerants in the pre-cooling, liquefaction, and sub-cooling cycles [Knott (2001), Lee *et al.* (2002), and Berger *et al.* (2003)]. Thus a significant amount of information regarding the thermal and caloric properties of natural gases and mixtures of natural gas components is needed for compressor and heat exchanger design.

Currently, there are not any equations 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. Therefore, several years ago the Chair of Thermodynamics of the Ruhr-Universität Bochum 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.

The new equation of state for natural gases and other mixtures developed in this work results from the continuation of the preceding study of Klimeck (2000), who established the essential tools required for the development of an accurate and wide ranging equation of state for mixtures. Aside from a new class of highly accurate equations of state for the natural gas components methane, nitrogen, carbon dioxide, and ethane, representing the main constituents of common natural gases, Klimeck (2000) developed a preliminary model for natural gas mixtures consisting of up to seven natural gas components to demonstrate the predictive capability of the pursued approach. The completely revised, new formulation presented in this work removes the limitation of the small number of components available and the physically incorrect behaviour in calculated vapour-liquid equilibrium states built unintentionally into the preliminary work.

Similar to recent developments, the new equation of state for natural gases, similar gases, and other mixtures is based on a multi-fluid approximation. The mixture model uses accurate equations of state in the form of fundamental equations for each mixture component along with functions developed for the binary mixtures of the components that take into account the residual mixture behaviour. The new formulation enables the calculation of thermal and caloric properties for natural gases and other mixtures consisting of the 18 components methane, nitrogen, carbon dioxide, ethane, propane, n-butane, isobutane, n-pentane, isopentane, n-hexane, n-heptane, n-octane, hydrogen, oxygen, carbon monoxide, water, helium, and argon.

Based on this new mixture model, robust and efficient calculation routines were developed in this work, supported by the European natural gas companies mentioned above, enabling the “blind” calculation of the thermodynamic properties in the different fluid regions and also allowing for extensive VLE calculations for any binary and multi-component mixture of the considered components and at arbitrary mixture conditions.

Briefly, Chap. 2 gives an introduction to existing mixture models and particularly focuses on the equations of state commonly used in the natural gas industry. In Chap. 3, the basic requirements for the new equation of state are defined. Chapter 4 deals with the equations of state used for the components forming the basis of the mixture model developed here. Chapter 5 focuses on the general characteristics of mixture models based on multi-fluid approximations and summarises some basics of the development of the different binary formulations. An overview of the experimental data used for the development and evaluation of the new mixture model is given in Chap. 6. Detailed information on the mathematical structure of the new equation of state, its range of validity, and the development of the various binary equations is provided in Chap. 7. Moreover, it offers guidelines for the calculation of thermodynamic properties from the multi-fluid model along with some fundamental principles regarding advanced mixture property calculations based on the essentials given in Chap. 5. The quality and predictive power of the new formulation is discussed in Chap. 8 by comparisons with experimental data and results obtained from previous equations of state. Chapter 9 gives recommendations for the potential further extension of the property model.

2 Previous Equations of State for Mixtures

This chapter gives a brief introduction to existing mixture models. Of particular interest are the equations of state which are commonly used in the natural gas industry.

In the literature, a large number of mixture models is available. The models differ in both structure and accuracy. One group of models describes the behaviour of mixtures through the use of excess properties. For instance, many models have been developed for the excess Gibbs free energy $g^{\mathrm{E}}(T,p,\bar{x})$ [e.g. van Laar (1910), Gmehling *et al.* (1993)] as well as for the excess Helmholtz free energy $a^{\mathrm{E}}(T,p,\bar{x})$ [e.g. Huron and Vidal (1979), Heidemann (1996)]. To use these models, the pure components as well as the mixture itself must be in the same state at a given temperature and pressure [Orbey and Sandler (1995)]. As a result of this precondition, these models are not suitable for most engineering problems when taking into account the involved components and the covered fluid regions.

The thermodynamic properties of mixtures can be calculated in a very convenient way from equations of state[1]. Most of these equations are explicit in pressure, as for example well-established cubic equations of state. Cubic equations are still widely used in many technical applications due to their simple mathematical structure. For technical applications with high demands on the accuracy of the calculated mixture properties, these equations show major weaknesses with respect to the representation of thermal properties in the liquid phase and the description of caloric properties [e.g. Soave (1995), Klimeck *et al.* (1996)].

Empirical equations of state, such as the equations of Bender (1973) and of Starling (1973), yield an improved description of the properties of mixtures especially in the homogeneous region. These models are explicit in pressure as well. Bender (1973) used mixing rules to describe the composition dependence of the coefficients and the temperature-dependent functions of the equation of state. Starling (1973) used mixing rules for each coefficient of the equation of state.

The work of Leland *et al.* [Leach *et al.* (1968), Leland and Chapelear (1968)] laid the basis for the application of extended corresponding states models to mixtures. Based on this work, Ely (1990) developed the exact shape factor concept. Later, Marrucho *et al.* (1994) presented an improved extended corresponding states theory for natural gas mixtures. Recently, Trusler *et al.* [Estela-Uribe and Trusler (2003), Estela-Uribe *et al.* (2004)] reported two separate extended corresponding states models for natural gases and similar mixtures. One was a wide ranging equation and the other was limited to the custody transfer region. The wide ranging model yields an accuracy which is, on average, similar to or even slightly better than other commonly used equations for natural gases.

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[1] For instance, equations of state do not rely on activity coefficient concepts.

Recent developments, including the mixture model developed in this work, are based on multi-fluid approximations [Tillner-Roth (1993), Lemmon (1996)]. These models use equations of state in the form of fundamental equations for each mixture component along with further correlation equations to take into account the residual mixture behaviour. The equations are explicit in the Helmholtz free energy. The basic principles for the development of these mixture models are strongly related to the development of empirical equations of state for pure substances. The models enable the accurate description of the thermodynamic properties of mixtures in the extended fluid region for wide ranges of temperature, pressure, and composition. Examples that demonstrate the capabilities of mixture models based on multi-fluid approximations were shown by Tillner-Roth and Friend (1998) for the binary system water–ammonia, whereas Lemmon and Jacobsen (1999) describe multi-component mixtures of polar and nonpolar substances including natural gas components. A model for the properties of dry air and similar mixtures was developed by Lemmon *et al.* (2000). Recent developments were reported for mixtures of hydrocarbon refrigerants [Miyamoto and Watanabe (2003)] and for hydrofluorocarbon refrigerant mixtures [Lemmon and Jacobsen (2004)]. The new equation of state for natural gases and other mixtures developed in this work results from the continuation of the preceding work of Klimeck (2000), who established the essential tools required for the development of an accurate and wide ranging mixture model based on a multi-fluid approximation; for further details see Chaps. 5 and 7.

2.1 Examples of Equations of State Commonly Applied in the Natural Gas Industry

Many different types of equations of state are applied in the natural gas industry. The use of a certain equation depends on the fluid region where the calculation of the thermodynamic properties is required. For pipeline applications, which mainly deal with the gas phase properties of natural gases, several equations of comparatively high accuracy exist. For certain applications, simplified equations were developed, e.g. the SGERG equation of Jaeschke and Humphreys (1992). These equations use the mole fractions of specific natural gas components (e.g. nitrogen and carbon dioxide) in combination with physical properties, such as the relative density and the superior calorific value, as input variables instead of the complete molar composition analysis. In the liquid phase and for phase equilibrium calculations, cubic equations of state [e.g. Peng and Robinson (1976)], which show poor accuracy in the description of many thermodynamic properties (see Sec. 2.1.2), are commonly used. A more accurate description of, for example, the $p\rho T$ relation in the liquid phase, is achieved by equations with very limited ranges of validity for temperature, pressure and composition [e.g. McCarty (1982)]. They are typically only applicable in the subcritical range. As a result of the use of individual equations for different fluid regions, there are inconsistencies in calculations when moving from one region to another and when more than one phase is involved, i.e. for phase equilibrium calculations.

As most of the standard natural gas applications, such as gas transmission and storage, are located in the “classical” natural gas region, i.e. the gas phase at temperatures from 250 K to 350 K and pressures up to 30 MPa, this range is of main interest for the calculation of thermodynamic properties. The internationally accepted standard for the calculation of compression factor in this region is, according to ISO 12213 “Natural Gas – Calculation of Compression Factor” [ISO (1997)], the AGA8-DC92 equation of state of Starling and Savidge (1992).

2.1.1 The AGA8-DC92 Equation of State of Starling and Savidge (1992)

The range of validity of the AGA8-DC92 equation of state is limited to the gas phase. Basically, this equation of state enables the calculation of thermodynamic properties of natural gases consisting of up to 21 components. The equation for the residual part of the reduced Helmholtz free energy is given by

$$\frac{a^{\mathrm{r}}}{RT} = \alpha^{\mathrm{r}}(\delta,\tau,\bar{x}) = \delta\frac{B}{K^3} - \delta\sum_{n=13}^{18} C_n^* \tau^{u_n} + \sum_{n=13}^{58} C_n^* \tau^{u_n} \delta^{b_n} \exp\left(-c_n \delta^{b_n}\right), \tag{2.1}$$

where the second virial coefficient B is calculated by means of binary parameters for the 21 considered components according to

$$B = \sum_{n=1}^{18} a_n \tau^{u_n} \sum_{i=1}^{21}\sum_{j=1}^{21} x_i x_j E_{ij}^{u_n} \left(K_i K_j\right)^{3/2} B_{nij}^* \tag{2.2}$$

with $\delta = K^3\rho$ and $\tau = T_{\mathrm{r}}/T$, where T_{r} = 1 K. The size parameter K depends on the mixture composition and is calculated by using binary parameters. The coefficients C_n^* and B_{nij}^* also depend on the composition and contain further binary parameters which take into account different physical properties, as for example dipole and quadrupole characteristics, of the considered components. The structure of the AGA8-DC92 equation of state is based on a total of 58 polynomial terms and polynomial terms in combination with exponential functions which require 860 different parameters.

The AGA8-DC92 equation developed by Starling and Savidge (1992) was originally designed as a thermal equation of state explicit in compression factor. The range of validity covers the gas phase at temperatures 143 K ≤ T ≤ 673 K and pressures up to 280 MPa. Due to the data situation, a well-founded estimation of the uncertainty in the description of thermal properties of natural gases is only feasible in the temperature range 250 K ≤ T ≤ 350 K at pressures up to 30 MPa. Detailed investigations concerning the uncertainty of the AGA8-DC92 equation in the description of thermal properties have been published by numerous authors [e.g. ISO (1997) and Jaeschke and Schley (1996)].

Within the framework of the research project “Fundamental Equation for Calorific Properties of Natural Gases” Klimeck *et al.* (1996) investigated the description of caloric properties, such as the speed of sound, the isobaric heat capacity and enthalpy differences. Data calculated from different equations of state were compared with experimental data for the pure natural gas components, their binary mixtures, and natural gases. In order to enable these calculations, the AGA8-DC92 equation was combined with equations of Jaeschke and Schley (1995) for the isobaric heat capacity in the ideal gas state of the pure components.

The results of the investigations mentioned above can be summarised as follows:

- The uncertainty in the description of the $p\rho T$ relation of typical natural gases of pipeline quality[2] amounts to 0.1% in density. This uncertainty is achieved for temperatures ranging from 290 K to 350 K at pressures up to 30 MPa.
- For the calculation of caloric properties at temperatures above 270 K the uncertainty in the speed of sound amounts to approximately 0.2%. The uncertainty in the isobaric heat capacity and isobaric enthalpy differences is about 1%.

Nevertheless, the investigations revealed several shortcomings of the AGA8-DC92 equation of state, which is currently the internationally accepted standard for the gas phase:

- The development of the AGA8-DC92 equation of state was based mainly on mixture data at temperatures above 270 K. Comparisons with the limited density data for natural gas mixtures in the temperature range from 250 K to 270 K indicate a higher uncertainty in the prediction of thermal properties in this region. Moreover, at higher temperatures up to 290 K, the uncertainty of $\Delta\rho/\rho \leq 0.1\%$ is restricted to pressures less than 12 MPa.
- For natural gases containing higher fractions of nitrogen, carbon dioxide, ethane, or heavier alkanes, larger uncertainties have to be taken into account for the calculation of thermal properties from the AGA8-DC92 equation of state in the lower temperature range.
- Significant deviations between calculated and measured caloric properties occur at temperatures below 270 K even for typical natural gases of pipeline quality. For example, speed of sound deviations increase at higher pressures and reach a value of about −1% at a pressure of 20 MPa.
- An increase of the uncertainty in caloric properties for natural gases containing higher fractions of heavier alkanes such as propane and the butanes has to be taken into account even at higher temperatures. This shortage of the AGA8-DC92 equation becomes even more evident for increasing pressures while the temperature decreases.

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[2] In this work, the expression “pipeline quality” refers to the definition of the international standard ISO 12213 “Natural Gas – Calculation of Compression Factor” [ISO (1997)]. According to that, natural gases of pipeline quality are processed natural gases of a composition which is typical for sales gas.

2.1.2 The Cubic Equation of State of Peng and Robinson (1976)

Due to their simple mathematical structure, cubic equations of state along with their huge amount of existing modifications are still commonly used for technical applications. These equations are explicit in pressure, but can be transformed to an equation for the residual Helmholtz free energy a^{r}. The dimensionless form of the residual Helmholtz free energy derived from the well-known cubic equation of state of Peng and Robinson (1976) reads:

$$\frac{a^{\mathrm{r}}}{RT} = \alpha^{\mathrm{r}}(\rho, T, \bar{x}) = \ln\left(\frac{1}{1 - b\rho}\right) - \frac{a}{2\sqrt{2}\,RT}\ln\left(\frac{1 + (\sqrt{2} + 1)\,b\rho}{1 - (\sqrt{2} - 1)\,b\rho}\right). \tag{2.3}$$

The equation contains two parameters. The parameter b depends only on the mixture composition, whereas the parameter a additionally depends on temperature. Basically, these parameters are calculated by means of different mixing rules using binary interaction parameters; see Peng and Robinson (1976) for further details.

The investigations of Klimeck *et al.* (1996) (see Sec. 2.1.1) on the suitability of the Peng-Robinson equation of state for use in technical applications which require high accuracy predictions of the properties of natural gases quickly revealed serious deficiencies. Many cubic equations of state have these weaknesses in common due to their structure:

- Major shortcomings already occur for the description of the $p\rho T$ relation of pure methane at temperatures and pressures typically encountered in standard applications related to transmission and distribution of pipeline quality gases. For instance, density values calculated from the Peng-Robinson equation deviate from the reference equation of state of Setzmann and Wagner (1991) by up to +5% at pressures below 30 MPa.
- Comparisons of calculated values for the speed of sound show deviations of more than ±10% in the same temperature and pressure ranges.
- A similar insufficient behaviour is observed in the calculation of properties in the liquid phase. Calculated saturated liquid densities deviate from experimental data of natural gases and state-of-the-art measurements of pure substances by up to −15%. This incorrect calculation in the phase equilibrium exists in the liquid phase densities as well[3].

These results demonstrate that the Peng-Robinson equation of state is not suitable for the accurate description of thermal and caloric properties in the homogeneous region and for saturated liquid densities. Nevertheless, for the calculation of vapour pressures and equilibrium phase compositions of mixtures, and for the evaluation of corresponding experimental data, the use of cubic equations of state is quite functional as they yield fairly

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[3] The poor quality of cubic equations of state in the description of liquid phase densities is generally known. One method that has become quite popular for improving the density calculation from cubic equations of state is called “volume shifting” [Aavatsmark (1995)]. However, the validity of this correction is restricted to a limited range of the liquid phase.

accurate results. For example, experimental data for the vapour pressure of many binary mixtures of natural gas components are reproduced by the Peng-Robinson equation of state over wide temperature and composition ranges to within ±(3 – 5)%, which is in most cases in agreement with the experimental uncertainty.

3 Requirements for the New Equation of State for Natural Gases

Based on the investigations concerning the AGA8-DC92 equation of state, several years ago the Chair of Thermodynamics of the Ruhr-Universität Bochum decided to develop a new wide-range equation of state for natural gases in cooperation with 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 research project aimed to develop an equation of state that is suitable for all technical applications using natural gases and other mixtures consisting of natural gas components.

The AGA8-DC92 equation of state of Starling and Savidge (1992) is known to be a very accurate standard for the calculation of the thermodynamic properties of natural gases at typical pipeline conditions, i.e. for temperatures $270\text{ K} \le T \le 330\text{ K}$ at pressures up to 12 MPa. As mentioned in Chap. 2, the AGA8-DC92 equation shows significant shortcomings regarding, for example, the range of validity, the uncertainty in the description of natural gases at temperatures below 290 K and mixtures of unusual composition. These insufficiencies had to be reduced by the development of a new equation of state. The basic requirements on the new natural gas model were defined as follows:

- The new equation of state for natural gases should be valid in the entire fluid region, i.e. in the gas phase, the liquid phase, the supercritical region, and for vapour-liquid equilibrium (VLE) states. This wide range of validity enables the use of the equation in both standard and advanced technical applications for natural gases, such as pipeline transport, natural gas storage, and improved processes with liquefied natural gas[4] (LNG). The extended range of validity represents the most important requirement regarding the basic structure of the new fundamental equation for natural gases.
- The highest demands on the accuracy of the new mixture model occur in standard natural gas applications, including gas metering, transmission, and storage. This requires the accurate description of the thermodynamic properties of different types of natural gases in the temperature range from 250 K to 350 K and at pressures up to 30 MPa. Therefore, the new equation of state had to achieve a very high accuracy in the gas phase with uncertainties of less than 0.1% in density and speed of sound. The targeted uncertainty in

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[4] The development of modern natural gas liquefaction processes for LNG baseload plants requires a significant amount of information regarding the thermal and caloric properties of natural gases and mixtures of natural gas components, which are used as refrigerants in the pre-cooling, liquefaction, and sub-cooling cycles. Besides the mixture densities, further properties, such as enthalpy, entropy, and isobaric heat capacity, are needed for compressor and heat exchanger design.

the prediction of other caloric properties, such as the isobaric heat capacity and isobaric enthalpy differences, was defined to be less than 1%. This is in agreement with the recommendations of Klimeck *et al.* (1996), who investigated the representation of accurate experimental data for different caloric properties by previous equations of state including the AGA8-DC92 equation. The authors revealed significant shortcomings for all commonly used equations for industrial applications.

- The mentioned uncertainties are required for the prediction of properties of processed natural gases of sales quality. For natural gases of uncommon compositions, the uncertainties in density and speed of sound should not exceed 0.2% in the mentioned temperature and pressure ranges.
- Since the data situation for properties of natural gases is known to be poor in the liquid phase, the development of a new equation of state is mainly based on experimental density data in this region. For the use of the new equation in LNG custody transfer operations and the design of improved natural gas liquefaction processes, the uncertainty in liquid phase density should be less than (0.1 – 0.3)% in the temperature range from 100 K to 140 K.
- For the calculation of vapour pressures and phase compositions in vapour-liquid equilibrium, the use of cubic equations of state is very common. Therefore, the new equation of state for natural gases had to achieve an accuracy which at least corresponds to some of the best cubic equations of state. Thus, the targeted uncertainty in vapour pressure should be (3 – 5)%. Due to the poor data situation for phase equilibrium properties of natural gases, this requirement is applied mostly to the description of experimental VLE data for binary mixtures of the considered natural gas components. This is especially true for the binary mixtures consisting of the main natural gas components, namely methane, nitrogen, carbon dioxide, and ethane, which are of major interest. Nevertheless, in order to accurately predict dew and bubble points of natural gases containing further components, the accurate description of the VLE properties of mixtures containing the secondary alkanes from propane to n-octane and further secondary components was also required. For the accurate description of saturated liquid densities, the new equation of state should achieve a similar accuracy as that aimed for liquid phase densities. This would result in an enormous improvement compared to the poor performance of cubic equations of state in the liquid phase.
- In contrast to the preliminary equation of state developed by Klimeck (2000), the new reference equation of state had to behave reasonably in regions characterised by poor data. This requirement is mostly related to the description of phase equilibrium properties in the critical region of binary mixtures (see Sec. 7.11).
- The structure of the new equation of state for natural gases should allow the extension of the mixture model to further components in a reasonable way without affecting the representation of mixtures of the so far considered components. Aside from the extension

to higher alkanes, such as n-nonane and n-decane, the addition of hydrogen sulphide is worthwhile in order to accurately describe the thermodynamic properties of acid gases[5] and raw natural gases[6]. Moreover, natural gases may also contain small amounts of ethylene, propylene, benzene and toluene.

- Considering the use of the new equation of state for natural gases in technical applications and with regard to complex phase equilibrium calculations[7], the structure of the mixture model had to be kept as simple as possible. In practice, this enables sound programming and computing time-saving algorithms, and with that the development of user-friendly software. Within the framework of the equation project, a comprehensive software package had to be developed (see Sec. 7.14). This enabled the calculation of the thermodynamic properties in the homogeneous gas, liquid, and supercritical regions, and also allowed calculations of extensive VLE properties, including flash, phase envelope, dew point, and bubble point calculations for any binary and multi-component mixture.

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[5] Acid gases mainly consist of carbon dioxide and hydrogen sulphide with minor traces of hydrocarbons (methane and water are important secondary components). Nowadays, these mixtures are injected, analogue to carbon dioxide geological storage, into deep saline aquifers and depleted hydrocarbon reservoirs driven by the need to dispose of hydrogen sulphide produced with natural gas from sour gas reservoirs. The injection of acid gases occurs over a wide range of aquifer and reservoir characteristics, acid gas compositions, and operating conditions [e.g. Boyle and Carroll (2002), Carroll (2002a,b)].

[6] For instance, hydrogen sulphide must be removed from natural gases because of its high toxicity and strong, offensive odour. Carbon dioxide is removed because it has no heating value. Moreover, these gases are corrosive as they form weak acids when dissolved in water.

[7] Such calculations require extensive and sophisticated derivatives of the equation of state with respect to density, temperature, and composition (see Sec. 7.3).

4 Equations of State for Pure Substances

Within the past 20 years highly accurate equations of state have been developed for many industrial fluids including substances relevant to natural gas such as methane [Setzmann and Wagner (1991)], nitrogen [Span *et al.* (2000)], carbon dioxide [Span and Wagner (1996)], ethylene [Smukala *et al.* (2000)] and water [Wagner and Pruß (2002)]. Most of these modern equations of state are fundamental equations explicit in the Helmholtz free energy as a function of density and temperature. Recently, further high accuracy fundamental equations were reported by Bücker and Wagner (2006a) for the main natural gas component ethane and the secondary components n-butane and isobutane [Bücker and Wagner (2006b)]. Moreover, in cooperation with the group of Wagner at the Ruhr-Universität Bochum, Germany, a new fundamental equation for propane has recently been developed at the National Institute of Standards and Technology (NIST), Boulder, USA [Lemmon *et al.* (2007)]. Selected examples of such reference quality equations of state are listed in Table 4.1. Comprehensive surveys of recommended reference equations of state for pure substances can be found in Span *et al.* (2001) and Jacobsen *et al.* (2000).

Table 4.1 Selected examples of reference quality equations of state explicit in the Helmholtz free energy for components relevant to natural gas

Pure substance	Reference	Range of validity[a] Temperature $T_{\max}$/K	 Pressure $p_{\max}$/MPa	Number of terms
Methane[b]	Setzmann & Wagner (1991)	625	1000	40
Nitrogen	Span *et al.* (2000)	1000	2200	36
Carbon dioxide	Span & Wagner (1996)	1100	800	42
Ethane	Bücker & Wagner (2006a)	673	900	44
Ethylene	Smukala *et al.* (2000)	450	300	35
Propane	Lemmon *et al.* (2007)	650	1000	18
n-Butane	Bücker & Wagner (2006b)	573	69	25
Isobutane	Bücker & Wagner (2006b)	573	35	25
Water[c]	Wagner & Pruß (2002)	1273	1000	56
Oxygen[b]	Schmidt & Wagner (1985)	300	82	32
Argon	Tegeler *et al.* (1999)	700	1000	41

[a] The range of validity covers temperatures ranging from the triple point or melting line of the respective substance up to the maximum value listed in the temperature column.

[b] Recommended as a standard by the International Union of Pure and Applied Chemistry (IUPAC).

[c] Recommended as a standard by the International Association for the Properties of Water and Steam (IAPWS).

All of the reference equations of state listed in Table 4.1 are explicit in the Helmholtz free energy and have the following characteristics in common:

- State-of-the-art experimental data for the thermodynamic properties of the respective fluid are represented to within their experimental uncertainty.
- The mathematical form of the equation of state was determined by applying state-of-the-art structure-optimisation techniques.
- The developed equations consist of a large number of terms (except for propane) ranging from 25 to more than 50 terms with complex functional forms, which are required for the accurate description of properties in the critical region.
- The coefficients of the equations were fitted simultaneously to the experimental data of many different properties (so-called multi-property fitting), e.g. density, speed of sound, isochoric and isobaric heat capacity, and phase equilibrium properties.
- The equations are valid over a wide range of temperature (e.g. from the melting line up to 1000 K) and pressure (e.g. up to 1000 MPa).
- The equations behave reasonably in regions characterised by poor data only.
- The extrapolation to temperatures and pressures far beyond the range of validity, which is determined by the available and selected data used for the development of the equation of state, yields reasonable results.

However, the large number of terms and the use of complex functional forms of these high accuracy equations of state adversely affect the complexity of modern mixture models (see Chaps. 5 and 7). These models use both pure substance equations of state for each component in the mixture and a number of further correlation equations developed with experimental data for many binary mixtures.

Considering the use of a new formulation for mixtures of natural gas components in technical applications, the structure of the mixture model has to be kept as simple as possible. In practice, this enables sound programming and computing-time saving algorithms. At the same time, accurate experimental data for the thermodynamic properties of natural gases and other mixtures have to be represented by the new mixture model to within the uncertainty of the measurements. In order to meet these conflicting requirements, accurate technical equations of state along with highly accurate equations of state with only 12 to 24 terms and a less complex structure make up the pure substance basis for the new mixture model developed in this work[8]. Many of these equations for the natural gas main and secondary components, such as methane, nitrogen, carbon dioxide, ethane, propane, and heavier alkanes, as well as oxygen

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[8] All types of equations of state can be used in the mixture model form developed here. However, due to the lack of highly accurate experimental data in the critical region, high accuracy pure substance equations of state are not required for mixture calculations.

and argon, were developed in preceding studies [Klimeck (2000), Span (2000a), Span and Wagner (2003a,b)]. Further equations of state for hydrogen, carbon monoxide, water and helium were developed in this work prior to the development of the new equation of state for natural gases and other mixtures. Details on the development of pure substance equations of state for the 18 natural gas components considered here are given in this chapter. A list of these components and their equations of state is presented in Table 4.2.

Table 4.2 List of the 18 main and secondary natural gas components considered in the developed mixture model and their equations of state[a]

Pure substance	Reference	Range of validity Temperature T/K	 Pressure p_{max}/MPa	Number of terms
Main components				
Methane	Klimeck (2000)	90 – 623	300	24
Nitrogen	Klimeck (2000)	63 – 700	300	24
Carbon dioxide	Klimeck (2000)	216[b] – 900	300	22
Ethane	Klimeck (2000)	90 – 623	300	24
Secondary alkanes				
Propane	Span & Wagner (2003b)	85 – 623	100	12
n-Butane	Span & Wagner (2003b)	134 – 693	70	12
Isobutane	Span & Wagner (2003b)	113 – 573	35	12
n-Pentane	Span & Wagner (2003b)	143 – 573	70	12
Isopentane	Span (2000a)	112 – 500	35	12
n-Hexane	Span & Wagner (2003b)	177 – 548	100	12
n-Heptane	Span & Wagner (2003b)	182 – 523	100	12
n-Octane	Span & Wagner (2003b)	216 – 548	100	12
Other secondary components				
Hydrogen[c]	This work	14 – 700	300	14
Oxygen	Span & Wagner (2003b)	54 – 303	100	12
Carbon monoxide	This work	68 – 400	100	12
Water	This work	273 – 1273	100	16
Helium[d]	This work	2.2 – 573	100	12
Argon	Span & Wagner (2003b)	83 – 520	100	12

[a] The tabulated references correspond to the equations for the residual part of the Helmholtz free energy of the considered pure substances. The equations of Jaeschke and Schley (1995) for the isobaric heat capacity in the ideal-gas state were used to derive the Helmholtz free energy of the ideal gas for all components.

[b] The equation can be extrapolated from the triple point temperature down to 90 K (see Sec. 4.11.1).

[c] Represents equilibrium hydrogen.

[d] Represents helium-4. The lower temperature limit of the equation of state is the lambda point at which helium I transitions to helium II.

The equations of state developed in the preceding works mentioned above as well as those developed in this work are empirical descriptions of the Helmholtz free energy. The development of these empirical formulations is based on the application of linear optimisation procedures and nonlinear multi-property fitting algorithms. Furthermore, for certain natural gas components, equations of state were applied which were developed with an optimisation algorithm considering experimental data of different fluids simultaneously. The optimisation and fitting strategies are state-of-the-art and have already been described in detail in the literature [e.g. Setzmann and Wagner (1989), (1991), Wagner and de Reuck (1996), Span *et al.* (1998), Span (2000b), and Wagner and Pruß (2002)]. Thus, the following sections briefly summarise some of the basic facts which are required for a rough understanding of the sophisticated procedures that were used for the development of the pure substance equations of state forming the basis of the developed mixture model.

4.1 Basic Structure of an Equation of State Explicit in the Helmholtz Free Energy

The equations of state described in this chapter are fundamental equations explicit in the Helmholtz free energy a with the independent variables density ρ and temperature T. The function $a(\rho,T)$ is commonly split into a^{o}, which represents the properties of the ideal gas at a given T and ρ, and a^{r}, which takes into account the residual fluid behaviour. This convention can be written as

$$a(\rho,T) = a^{\mathrm{o}}(\rho,T) + a^{\mathrm{r}}(\rho,T). \tag{4.1}$$

Usually, the Helmholtz free energy is used in its dimensionless form $\alpha = a/(RT)$. Thus, Eq. (4.1) becomes

$$\alpha(\delta,\tau) = \alpha^{\mathrm{o}}(\delta,\tau) + \alpha^{\mathrm{r}}(\delta,\tau), \tag{4.2}$$

where $\delta = \rho/\rho_{\mathrm{c}}$ is the reduced density and $\tau = T_{\mathrm{c}}/T$ is the inverse reduced temperature with ρ_{c} as the critical density and T_{c} as the critical temperature of the considered fluid.

4.2 The Calculation of Thermodynamic Properties Derived from the Helmholtz Free Energy

Since the Helmholtz free energy as a function of density and temperature is one of the four fundamental forms of an equation of state, all thermodynamic properties of a pure substance can be obtained by combining derivatives of Eq. (4.2). For example, in the homogeneous gas, liquid, and supercritical regions, the pressure p, enthalpy h, and entropy s can be determined from the following equations[9]:

$$\frac{p(\delta,\tau)}{\rho RT} = 1 + \delta\alpha_\delta^{\mathrm{r}}, \tag{4.3}$$

$$\frac{h(\delta,\tau)}{RT} = 1 + \tau\left(\alpha_\tau^{\mathrm{o}} + \alpha_\tau^{\mathrm{r}}\right) + \delta\alpha_\delta^{\mathrm{r}}, \tag{4.4}$$

$$\frac{s(\delta,\tau)}{R} = \tau\left(\alpha_\tau^{\mathrm{o}} + \alpha_\tau^{\mathrm{r}}\right) - \alpha^{\mathrm{o}} - \alpha^{\mathrm{r}}. \tag{4.5}$$

Further relations between Eq. (4.2), its derivatives, and the thermodynamic properties considered in many technical applications are listed in Table 7.1, which gives the relationship among thermodynamic properties and the dimensionless Helmholtz free energy for the mixture model developed here[10] (see Chaps. 5 and 7).

4.2.1 The Calculation of Phase Equilibrium Properties

In addition to the calculation of thermodynamic properties in the homogeneous region of the fluid surface, phase equilibrium properties, such as vapour pressure and saturated liquid (indicated by a single prime) and vapour (indicated by a double prime) density, can be determined from fundamental equations explicit in the Helmholtz free energy. Therefore, the following phase equilibrium conditions must be satisfied:

- equality of temperature $T' = T'' = T$, (4.6)
- equality of pressure $p' = p'' = p_{\mathrm{s}}$, (4.7)
- equality of chemical potential $\mu' = \mu''$. (4.8)

For a pure substance the chemical potential μ equals the Gibbs free energy g. Thus, applying the relations between Eq. (4.2), its derivatives, and the thermodynamic properties to Eqs. (4.6) – (4.8) yields the equations

$$\frac{p_{\mathrm{s}}}{\rho' RT} = 1 + \delta'\alpha_\delta^{\mathrm{r}}(\delta',\tau), \tag{4.9}$$

$$\frac{p_{\mathrm{s}}}{\rho'' RT} = 1 + \delta''\alpha_\delta^{\mathrm{r}}(\delta'',\tau), \tag{4.10}$$

$$\frac{p_{\mathrm{s}}}{RT}\left(\frac{1}{\rho''} - \frac{1}{\rho'}\right) - \ln\left(\frac{\rho'}{\rho''}\right) = \alpha^{\mathrm{r}}(\delta',\tau) - \alpha^{\mathrm{r}}(\delta'',\tau). \tag{4.11}$$

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[9] $\alpha_\delta = (\partial\alpha/\partial\delta)_\tau$, $\alpha_\tau = (\partial\alpha/\partial\tau)_\delta$.

[10] The Helmholtz free energy of a mixture is a function of density, temperature, and the mixture composition. The thermodynamic properties in the homogeneous gas, liquid, and supercritical regions of a mixture are related only to derivatives with respect to density and temperature. Thus, in the homogeneous region, the same relations can be applied to both pure substance equations and equations of state for mixtures explicit in the Helmholtz free energy.

At a given temperature, the vapour pressure and the densities of the coexisting phases can be determined from the equation of state by simultaneous solution of Eqs. (4.9) – (4.10)[11].

The simultaneous solution of the phase equilibrium conditions requires the use of an iterative procedure. Suitable initial values for the unknown variables p_s, δ', and δ'' can be obtained from auxiliary equations for the saturated properties of the respective pure substance.

4.3 The Equation for the Helmholtz Free Energy of the Ideal Gas

The Helmholtz free energy of the ideal gas is given by

$$a^\mathrm{o}(\rho,T) = h^\mathrm{o}(T) - RT - Ts^\mathrm{o}(\rho,T). \tag{4.12}$$

For the ideal gas, the enthalpy h^o is a function of temperature only, whereas the entropy s^o depends on temperature and density. Both properties can be derived from an equation for the ideal-gas heat capacity $c_p^\mathrm{o}(T)$. When c_p^o is inserted into the expression for $h^\mathrm{o}(T)$ and $s^\mathrm{o}(\rho,T)$ in Eq. (4.12), one obtains

$$a^\mathrm{o}(\rho,T) = \left[\int_{T_0}^{T} c_p^\mathrm{o}\,\mathrm{d}T + h_0^\mathrm{o}\right] - RT - T\left[\int_{T_0}^{T} \frac{c_p^\mathrm{o} - R}{T}\,\mathrm{d}T - R\ln\left(\frac{\rho}{\rho_0^\mathrm{o}}\right) + s_0^\mathrm{o}\right], \tag{4.13}$$

where all variables with the subscript "0" refer to an arbitrary reference state. Occasionally, the enthalpy h_0^o and the entropy s_0^o are taken to be zero for $T_0 = 298.15$ K, $p_0 = 0.101325$ MPa, and the corresponding density $\rho_0^\mathrm{o} = p_0/(RT_0)$.

In order to obtain the equations for $a^\mathrm{o}(\rho,T)$ and $\alpha^\mathrm{o}(\delta,\tau)$, the equations of Jaeschke and Schley (1995) were used for the isobaric heat capacity in the ideal-gas state, $c_p^\mathrm{o}(T)$, for the 18 natural gas components[12] considered for the mixture model developed in this work (see Table 4.2). These equations use the functional form

$$\frac{c_p^\mathrm{o}}{R} = b_0 + \sum_{k=1,3} b_k\left(\frac{\theta_k/T}{\sinh(\theta_k/T)}\right)^2 + \sum_{k=2,4} b_k\left(\frac{\theta_k/T}{\cosh(\theta_k/T)}\right)^2. \tag{4.14}$$

Jaeschke and Schley (1995) determined the coefficients b_0, b_k and parameters θ_k by fitting to selected c_p^o values available in the literature, taking into account data at temperatures ranging from 10 K to 1000 K. After rearranging the coefficients and parameters, namely $n_3^\mathrm{o} = b_0 - 1$, and $n_{k+3}^\mathrm{o} = b_k$ and $\vartheta_{k+3}^\mathrm{o} = \theta_k/T_\mathrm{c}$ for $k = 1$ to 4, one obtains from Eq. (4.14)

$$\frac{c_p^\mathrm{o}}{R} = 1 + n_3^\mathrm{o} + \sum_{k=4,6} n_k^\mathrm{o}\left(\frac{\vartheta_k^\mathrm{o}\tau}{\sinh(\vartheta_k^\mathrm{o}\tau)}\right)^2 + \sum_{k=5,7} n_k^\mathrm{o}\left(\frac{\vartheta_k^\mathrm{o}\tau}{\cosh(\vartheta_k^\mathrm{o}\tau)}\right)^2 \tag{4.15}$$

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[11] Equation (4.11) represents the integral criterion of Maxwell (Maxwell criterion).

[12] For the temperatures considered in this work, only the translational contribution to the ideal-gas heat capacity of helium and argon has to be taken into account: $c_{p,\mathrm{He}}^\mathrm{o} = c_{p,\mathrm{Ar}}^\mathrm{o} = 2.5R$.

with $\tau = T_c / T$. The values of the coefficients and parameters of Eq. (4.15) are given in Table A3.1[13] of the appendix.

Combining $c_p^o(T)$ in Eq. (4.15) with a^o in Eq. (4.13) results in the dimensionless form of the Helmholtz free energy in the ideal-gas state α^o [see Eq. (4.2)] for the 18 components considered in this work, given as Eq. (7.5).

4.4 Fitting and Optimising the Structure of an Equation for the Residual Part of the Helmholtz Free Energy

While statistical thermodynamics can predict the behaviour of fluids in the ideal-gas state with high accuracy, no physically founded equation is known which accurately describes the real thermodynamic behaviour of fluids over the whole fluid region. Thus, for this purpose an equation for the residual fluid behaviour, in this case for the residual part of the Helmholtz free energy α^r, must be determined in an empirical way. Since the Helmholtz free energy itself is not accessible by direct measurements, it is necessary to determine the unknown mathematical structure and the unknown coefficients of the residual part of the dimensionless Helmholtz free energy from properties for which experimental data are available.

In this context, the development of the final form of an equation for α^r requires the following steps:

- Selection of the final data set.
- Weighting of the data.
- Precorrelation of auxiliary quantities.
- Linear least-squares fitting in connection with the structure-optimisation method.
- Nonlinear least-squares fitting.

In this work, only basic statements on the fitting and optimisation procedures applied to develop an equation for α^r for the considered substance are made. More detailed descriptions of the algorithms used are provided by Wagner and Pruß (2002) and Span (2000b).

4.4.1 Fitting an Equation for α^r to Data

If a certain functional form has been selected for $\alpha^r(\delta, \tau, \bar{n})$, data for J different properties z_j (e.g. pressure p, speed of sound w, etc.) can be used to determine the unknown coefficients n_i (expressed as the vector $\bar{n}$) by minimising the following sum of squares:

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[13] To denote the pure substance as a component in a mixture, the subscripts "o" (referring to pure substance) and "i" (referring to the considered component) are introduced (see Chaps. 5 and 7).

$$\chi^2 = \sum_{j=1}^{J} \chi_j^2 = \sum_{j=1}^{J} \sum_{m=1}^{M_j} \left[\left[z_{\mathrm{exp}} - z_{\mathrm{calc}}\left(x_{\mathrm{exp}}, y_{\mathrm{exp}}, \bar{n} \right) \right]^2 \right]_{j,m} \cdot \sigma_{\mathrm{tot},m}^{-2}, \tag{4.16}$$

where M_j is the number of data points used for the jth property, z_{exp} is the experimental value for any property z, and z_{calc} is the value for the property calculated from the equation for α with the parameter vector $\bar{n}$ at x_{exp} and y_{exp}. The measured independent values of x and y may vary for the different properties of z, but usually one of them corresponds to the temperature T, while the other corresponds to the density ρ or pressure p (e.g. $p(T,\rho)$ or $w(T,p)$). When data sets of different properties are used for the development of a correlation equation, then the residuum $\Delta z = \left(z_{\mathrm{exp}} - z_{\mathrm{calc}} \right)$ of Eq. (4.16) is reduced with a suitable measure for the uncertainty of the data point considered. According to the Gaussian error propagation formula, the uncertainty of a measured data point is given by

$$\sigma_{\mathrm{exp}}^2 = \left[\frac{\partial \Delta z}{\partial x} \right]_{y,z}^2 \cdot \sigma_x^2 + \left[\frac{\partial \Delta z}{\partial y} \right]_{x,z}^2 \cdot \sigma_y^2 + \left[\frac{\partial \Delta z}{\partial z} \right]_{x,y}^2 \cdot \sigma_z^2, \tag{4.17}$$

where σ_x, σ_y, and σ_z are the isolated uncertainties of the single variables x, y, and z, respectively. The partial derivatives of Δz have to be calculated from a preliminary equation of state.

In order to have an additional influence on the data set, a weighting factor f_{wt} is introduced. The total variance σ_{tot}^2 of a data point used in Eq. (4.16) is defined as

$$\sigma_{\mathrm{tot}}^2 = \sigma_{\mathrm{exp}}^2 \big/ f_{\mathrm{wt}}^2 . \tag{4.18}$$

In this way, weighting factors $f_{\mathrm{wt}} > 1$ increase the influence of a data point with respect to the sum of squares and weighting factors $f_{\mathrm{wt}} < 1$ reduce it. Usually f_{wt} is equal to one and σ_{tot}^2 is equal to σ_{exp}^2. However, in some cases different weighting factors are used to compensate for effects caused by the structure of the data set.

The determination of $\bar{n}$ by minimising χ^2 for data of more than one property is called “multi-property fitting”. This problem will lead to a linear system of normal equations if each of the properties z depends on the same independent variables as the function used (e.g. T and ρ for the Helmholtz free energy) and if the relations between z and the function or its derivatives is linear for all considered properties. Data for such properties are called “linear data”. For functions in terms of the Helmholtz free energy, examples of such properties are $p(T,\rho)$ and $c_v(T,\rho)$ (see Table 4.3). If one or both of these conditions is not fulfilled (e.g. for $h(T,p)$, $w(T,p)$, $c_p(T,p)$), those data are called “nonlinear data” and more complicated and time-consuming nonlinear algorithms must be used to minimise the sum of squares, Eq. (4.16). Table 4.3 lists selected sums of squares of the linear and nonlinear data used for the development of the equations presented in this work. The total sum of squares is obtained as given by Eq. (4.16).

Table 4.3 Contribution of selected linear, nonlinear, and linearised data to the weighted sum of squares for the fitting and optimisation process[a–c]

j	Type of data	Weighted sum of squares
		Linear data
1	$p(T,\rho)$	$\chi_1^2 = \sum\limits_{m=1}^{M_1} \left[\frac{p-\rho RT}{\rho^2 RT} - \rho_\mathrm{r}^{-1}\,\alpha_\delta^\mathrm{r} \right]_m^2 \cdot \sigma_m^{-2}$
2	$c_v(T,\rho)$	$\chi_2^2 = \sum\limits_{m=1}^{M_2} \left[\frac{c_v}{R} + \tau^2 \left(\alpha_{\tau\tau}^\mathrm{o} + \alpha_{\tau\tau}^\mathrm{r} \right) \right]_m^2 \cdot \sigma_m^{-2}$
3	$B(T)$	$\chi_3^2 = \sum\limits_{m=1}^{M_3} \left[B\rho_\mathrm{r} - \lim\limits_{\delta\to 0} \alpha_\delta^\mathrm{r} \right]_m^2 \cdot \sigma_m^{-2}$
4	$\beta_\mathrm{a}(T)$	$\chi_4^2 = \sum\limits_{m=1}^{M_4} \left[\beta_\mathrm{a}\rho_\mathrm{r} - \lim\limits_{\delta\to 0} \left[2\alpha_\delta^\mathrm{r} - 2\frac{\kappa^\mathrm{o}-1}{\kappa^\mathrm{o}}\tau\alpha_{\delta\tau}^\mathrm{r} + \frac{\left(\kappa^\mathrm{o}-1\right)^2}{\kappa^\mathrm{o}}\tau^2\alpha_{\delta\tau\tau}^\mathrm{r} \right] \right]_m^2 \cdot \sigma_m^{-2}$
		Nonlinear data
5	$w(T,p)$	$\chi_5^2 = \sum\limits_{m=1}^{M_5} \left[\frac{w^2 M}{RT} - \left[1 + 2\delta\alpha_\delta^\mathrm{r} + \delta^2\alpha_{\delta\delta}^\mathrm{r} - \frac{\left(1+\delta\alpha_\delta^\mathrm{r} - \delta\tau\alpha_{\delta\tau}^\mathrm{r}\right)^2}{\tau^2\left(\alpha_{\tau\tau}^\mathrm{o} + \alpha_{\tau\tau}^\mathrm{r}\right)} \right] \right]_m^2 \cdot \sigma_m^{-2}$
6	$c_p(T,p)$	$\chi_6^2 = \sum\limits_{m=1}^{M_6} \left[\frac{c_p}{R} + \tau^2\left(\alpha_{\tau\tau}^\mathrm{o} + \alpha_{\tau\tau}^\mathrm{r}\right) - \frac{\left(1+\delta\alpha_\delta^\mathrm{r} - \delta\tau\alpha_{\delta\tau}^\mathrm{r}\right)^2}{1 + 2\delta\alpha_\delta^\mathrm{r} + \delta^2\alpha_{\delta\delta}^\mathrm{r}} \right]_m^2 \cdot \sigma_m^{-2}$
7	$h_2(T_2,p_2)$ $-h_1(T_1,p_1)$	$\chi_7^2 = \sum\limits_{m=1}^{M_7} \left[\frac{h_2}{RT_2} - \frac{h_1}{RT_1} - \left[\tau\left(\alpha_\tau^\mathrm{o} + \alpha_\tau^\mathrm{r}\right) + \delta\alpha_\delta^\mathrm{r}\right]_2 + \left[\tau\left(\alpha_\tau^\mathrm{o} + \alpha_\tau^\mathrm{r}\right) + \delta\alpha_\delta^\mathrm{r}\right]_1 \right]_m^2 \cdot \sigma_m^{-2}$
8	$p_\mathrm{s}(T)$	$\chi_8^2 = \sum\limits_{m=1}^{M_8} \left[\frac{p_\mathrm{s} - p_\mathrm{s,calc}}{\rho_\mathrm{r} R T_\mathrm{r}} \right]_m^2 \cdot \sigma_m^{-2}$
9	$\rho'(T)$	$\chi_9^2 = \sum\limits_{m=1}^{M_9} \left[\frac{\rho' - \rho'_\mathrm{calc}}{\rho_\mathrm{r}} \right]_m^2 \cdot \sigma_m^{-2}$
10	$\rho''(T)$	$\chi_{10}^2 = \sum\limits_{m=1}^{M_{10}} \left[\frac{\rho'' - \rho''_\mathrm{calc}}{\rho_\mathrm{r}} \right]_m^2 \cdot \sigma_m^{-2}$
		Linearised data
11	$w(T,\rho^\mathrm{p},\gamma^\mathrm{p})$	$\chi_{11}^2 = \sum\limits_{m=1}^{M_{11}} \left[\frac{w^2 M}{RT} - \gamma^\mathrm{p}\left(1 + 2\delta\alpha_\delta^\mathrm{r} + \delta^2\alpha_{\delta\delta}^\mathrm{r}\right) \right]_m^2 \cdot \sigma_m^{-2}$
12	$c_p(T,\rho^\mathrm{p},\varepsilon^\mathrm{p})$	$\chi_{12}^2 = \sum\limits_{m=1}^{M_{12}} \left[\frac{c_p}{R} + \tau^2\left(\alpha_{\tau\tau}^\mathrm{o} + \alpha_{\tau\tau}^\mathrm{r}\right) - \varepsilon^\mathrm{p} \right]_m^2 \cdot \sigma_m^{-2}$

Table 4.3 (continued)

j	Type of data	Weighted sum of squares
		Linearised data (continued)
13	$h_2(T_2,\rho_2^{\mathrm{p}})$ $-h_1(T_1,\rho_1^{\mathrm{p}})$	$\chi_{13}^2=\sum\limits_{m=1}^{M_{13}}\left[\frac{h_2}{RT_2}-\frac{h_1}{RT_1}-\left[\tau\left(\alpha_\tau^{\mathrm{o}}+\alpha_\tau^{\mathrm{r}}\right)+\delta\alpha_\delta^{\mathrm{r}}\right]_2+\left[\tau\left(\alpha_\tau^{\mathrm{o}}+\alpha_\tau^{\mathrm{r}}\right)+\delta\alpha_\delta^{\mathrm{r}}\right]_1\right]_m^2\cdot\sigma_m^{-2}$
14	$p(T,\rho'^{\mathrm{p}})$	$\chi_{14}^2=\sum\limits_{m=1}^{M_{14}}\left[\frac{p_{\mathrm{s}}-\rho' RT}{(\rho')^2 RT}-\rho_{\mathrm{r}}^{-1}\,\alpha_\delta^{\mathrm{r}}(\delta',\tau)\right]_m^2\cdot\sigma_m^{-2}$
15	$p(T,\rho''^{\mathrm{p}})$	$\chi_{15}^2=\sum\limits_{m=1}^{M_{15}}\left[\frac{p_{\mathrm{s}}-\rho'' RT}{(\rho'')^2 RT}-\rho_{\mathrm{r}}^{-1}\,\alpha_\delta^{\mathrm{r}}(\delta'',\tau)\right]_m^2\cdot\sigma_m^{-2}$
16	Maxwell criterion	$\chi_{16}^2=\sum\limits_{m=1}^{M_{16}}\left[\frac{p_{\mathrm{s}}}{RT}\left(\frac{1}{\rho''}-\frac{1}{\rho'}\right)-\ln\left(\frac{\rho'}{\rho''}\right)-\left[\alpha^{\mathrm{r}}(\delta',\tau)-\alpha^{\mathrm{r}}(\delta'',\tau)\right]\right]_m^2\cdot\sigma_m^{-2}$

[a] For the relations between the different thermodynamic properties and α^{o} and α^{r} and their derivatives see Table 7.1; for a pure substance $\rho_{\mathrm{r}}=\rho_{\mathrm{c}}$.

[b] For the weighted sum of squares the following abbreviations and definitions are used:

- $\alpha_\delta=\left(\frac{\partial\alpha}{\partial\delta}\right)_\tau$, $\alpha_{\delta\delta}=\left(\frac{\partial^2\alpha}{\partial\delta^2}\right)_\tau$, $\alpha_\tau=\left(\frac{\partial\alpha}{\partial\tau}\right)_\delta$, $\alpha_{\tau\tau}=\left(\frac{\partial^2\alpha}{\partial\tau^2}\right)_\delta$, $\alpha_{\delta\tau}=\left(\frac{\partial^2\alpha}{\partial\delta\,\partial\tau}\right)$
- The weight σ_m corresponds to the quantity σ_{tot} according to Eq. (4.18).
- The superscript “p” means precorrelated.
- $\gamma^{\mathrm{p}}=\frac{c_p(T,\rho^{\mathrm{p}})}{c_v(T,\rho^{\mathrm{p}})}$, $\varepsilon^{\mathrm{p}}=\frac{c_p-c_v}{R}=\left[\frac{\left(1+\delta\alpha_\delta^{\mathrm{r}}-\delta\tau\alpha_{\delta\tau}^{\mathrm{r}}\right)^2}{1+2\delta\alpha_\delta^{\mathrm{r}}+\delta^2\alpha_{\delta\delta}^{\mathrm{r}}}\right]_{\tau,\delta^{\mathrm{p}}}$
- $\kappa^{\mathrm{o}}=c_p^{\mathrm{o}}/c_v^{\mathrm{o}}$ is the isentropic exponent of the ideal-gas mixture.

[c] All precorrelated quantities are calculated from a preliminary equation of state.

4.4.2 Basic Statements for Optimising the Mathematical Form of α^{r}

Since the functional form of an equation for the residual part of the Helmholtz free energy is not initially known, a suitable mathematical structure must be established before any coefficients n_i can be fitted to the data. In the past, the structure of most correlation equations was determined subjectively, based on the experience of the correlator or by trial and error. To improve this situation, Wagner and co-workers developed different optimisation strategies [Wagner (1974), Ewers and Wagner (1982), Setzmann and Wagner (1989), and Tegeler *et al.* (1999)], which introduce objective criteria for the selection of the mathematical structure of such equations.

The entire strategy of the structure optimisation of an equation for α^{r} consists of two basic steps:

- Formulation of a comprehensive set of mathematical functions of the reduced density and inverse reduced temperature that is used as a "bank of terms".
- From this bank of terms, the structure-optimisation method determines with mathematical statistical and stochastic methods the best combination of a certain number of terms.

In order to determine suitable mathematical structures for the residual part of the Helmholtz free energy of the equations of state developed in this work[14], a modified form of the structure-optimisation method developed by Setzmann and Wagner (1989) was used. The most significant changes, which were introduced by Span and Wagner (1996), regard the handling of different functional forms in the bank of terms as described in the following paragraph.

A sophisticated correlation equation for the residual part of the Helmholtz free energy consists of an extensive sum of terms. Hence, the mathematical form of a single term can be associated with different functional groups ranging from simple polynomials in the reduced density δ and the inverse reduced temperature τ to complicated exponential expressions [see the different banks of terms given by Eq. (4.26) and Eqs. (7.165) – (7.167)]. Additional limitations with respect to the number of terms belonging to certain functional groups turned out to be useful [Span and Wagner (1996)] and the optimisation algorithm was modified to allow such limitations; for further details see Span (2000b).

The used structure-optimisation method only works with linear data (see Sec. 4.4.1). Thus, to take into account in the optimisation process, at least partly, the experimental information for the nonlinear data, the nonlinear relations between these properties and the derivatives of α^{o} and α^{r} were linearised. The results of this linearisation for the sum of squares of selected nonlinear properties, which were considered for the development of the equations of state presented in this work, are listed in Table 4.3. An example of such a linearisation is shown in the following for the property speed of sound w.

According to the relation between the property $z = w$ and the derivatives of α^{o} and α^{r} given by

$$\frac{w^2(\delta,\tau)\,M}{RT} = 1 + 2\delta\alpha_{\delta}^{\mathrm{r}} + \delta^2\alpha_{\delta\delta}^{\mathrm{r}} - \frac{\left(1+\delta\alpha_{\delta}^{\mathrm{r}} - \delta\tau\alpha_{\delta\tau}^{\mathrm{r}}\right)^2}{\tau^2\left(\alpha_{\tau\tau}^{\mathrm{o}} + \alpha_{\tau\tau}^{\mathrm{r}}\right)}, \tag{4.19}$$

the sum of squares [see Eq. (4.16)] for fitting an equation for α^{r} to M_w experimental data of w [w is the jth property in Eq. (4.16) considered in the entire multi-property fitting process] reads:

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[14] The residual part of the Helmholtz free energy of the equations of state for the pure substances hydrogen, water and helium as well as the correlation equations for many binary mixtures were determined with the structure-optimisation method described in this section. The equation of state for carbon monoxide was developed by fitting the coefficients of an existing simultaneously optimised structure to data.

$$\chi_j^2 = \sum_{m=1}^{M_w} \left[\frac{w^2 M}{RT} - 1 - 2\delta\alpha_\delta^{\mathrm{r}} - \delta^2\alpha_{\delta\delta}^{\mathrm{r}} + \frac{\left(1 + \delta\alpha_\delta^{\mathrm{r}} - \delta\tau\alpha_{\delta\tau}^{\mathrm{r}}\right)^2}{\tau^2\left(\alpha_{\tau\tau}^{\mathrm{o}} + \alpha_{\tau\tau}^{\mathrm{r}}\right)} \right]_m^2 \cdot \sigma_{\mathrm{tot},m}^{-2} . \tag{4.20}$$

This type of sum of squares leads to a nonlinear system of normal equations when determining the coefficients $\bar{n}$ in the equation for $\alpha^{\mathrm{r}}(\delta,\tau,\bar{n})$. However, the structure-optimisation method used here cannot cope with such a nonlinear system. A further difficulty arises because the speed of sound is not measured as a function of density and temperature, which are the independent variables of the equation for α^{r}, but of pressure and temperature. Thus, the sum of squares according to Eq. (4.20) is implicitly nonlinear. As shown by Schmidt and Wagner (1985), this implicitly nonlinear relation can be linearised by using the following sum of least squares:

$$\chi_j^2 = \sum_{m=1}^{M_w} \left[\frac{w^2 M}{RT} - \gamma^{\mathrm{p}} \cdot \left(1 + 2\delta\alpha_\delta^{\mathrm{r}} + \delta^2\alpha_{\delta\delta}^{\mathrm{r}}\right) \right]_m^2 \cdot \sigma_{\mathrm{tot},m}^{-2} \tag{4.21}$$

with the so-called precorrelation factor γ^{p} according to

$$\gamma^{\mathrm{p}} = \frac{c_p\left(\rho^{\mathrm{p}},T\right)}{c_v\left(\rho^{\mathrm{p}},T\right)} . \tag{4.22}$$

The density ρ^{p} and the precorrelation factor γ^{p} have to be precalculated by a preliminary equation of state.

Because the linearisations of the nonlinear sums of squares require precalculations with preliminary equations of state, the entire process of optimising the structure of the α^{r} equation is a recursive process; see Wagner and Pruß (2002) and Span (2000b) for further details.

4.5 The Simultaneous Optimisation Method

Based on the structure-optimisation algorithm developed by Setzmann and Wagner (1989) (see Sec. 4.4.2), an algorithm for the optimisation of functional forms of empirical equations of state which considers data sets of different substances simultaneously was developed by Span *et al.* (1998). In this way, equations for the residual part of the Helmholtz free energy can be developed which yield, on average, the best representation of the thermodynamic properties of all substances within larger groups of substances (e.g. nonpolar and polar substances).

For the simultaneous optimisation, mathematical functions of the reduced variables δ and τ are used to define a bank of terms which is shared by all considered substances. The use of such a simple corresponding states similarity makes it possible to develop more accurate equations of state for substances characterised by a poor data situation when data for well-measured substances are added to the regression matrices.

In order to determine the best mathematical structure of an equation for the residual part of the Helmholtz free energy, a criterion which gives assessment to the quality of the resulting equation of state is needed for any optimisation method. The sum of squares χ^2 according to Eq. (4.16) represents such a criterion in the algorithm of Setzmann and Wagner (1989). In the simultaneous optimisation procedure, the corresponding sum of squares χ_i^2 has to be calculated from each of the I regression matrices, which represent the data sets of the I considered substances. Equivalent to χ^2 the sum of squares is then defined as

$$\chi^{*2} = \sum_{i=1}^{I} \chi_i^{*2} = \sum_{i=1}^{I} \chi_i^2 \big/ \chi_{\mathrm{ref},i}^2 , \tag{4.23}$$

where the reference sums of squares $\chi_{\mathrm{ref},i}^2$ are used to reduce the sums of squares χ_i^2 in order to compensate for the larger influence of extensive data sets for well-measured substances on the total sum of squares[15]. The sum of squares $\chi_{\mathrm{ref},i}^2$ results from an equation of state of the same length which is individually optimised for the corresponding substance i. Thus, in the simultaneous optimisation the reduced sum of squares of substance i, $\chi_i^{*2} = \chi_i^2 \big/ \chi_{\mathrm{ref},i}^2$, will equal 1 if the current simultaneously optimised formulation describes the data set as well as the individually optimised equation of state.

Based on this optimisation method, accurate equations of state for technical applications of a group of non- and weakly polar substances with an identical mathematical structure were developed by Span and Wagner (2003a,b) and Span (2000a). This development was important for this work to realise a wide-range equation of state for mixtures of natural gas components with a structure as simple as possible. Thus, the equations for the normal alkanes from propane to n-octane, and the fluids oxygen, argon, isobutane and isopentane were used (see Table 4.1 and Sec. 4.9).

For extensions of the presented mixture model, there are further pure substance equations of state of interest, e.g. the equation for ethylene [Span and Wagner (2003b)] and the equations for n-nonane, n-decane, hydrogen sulphide, and toluene [Lemmon and Span (2006)]. The equations of state recently developed by Lemmon and Span (2006) maintain the simultaneously optimised structure developed by Span and Wagner (2003b), only the coefficients were fitted to the experimental data of the respective substances.

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[15] Extensive data sets of well-measured substances will result in high values for χ_i^2 even if the representation of the data is satisfactory.

4.6 Functional Forms for α^{r} and the Bank of Terms

For the development of a suitable form of the equation for the residual part α^{r} of any wide-range equation of state, the collection of the comprehensive set of functional forms for the bank of terms is of great importance.

The pure substance equations of state developed in this work and those from preceding works selected to form the basis of the developed wide-range equation of state for natural gases and other mixtures use the following different functional forms:

- polynomial terms and
- polynomial terms in combination with exponential functions.

These two functional forms are used in many formulations for the residual Helmholtz free energy, especially for equations of state for those substances which are mainly of engineering interest. Some of the characteristics of these terms are briefly described in Secs. 4.6.1 and 4.6.2.

More complex functional forms are commonly used for highly accurate equations of state for selected substances of particular scientific and engineering interest (see Table 4.1). To improve the representation of properties in the extended critical region, sophisticated functional forms have been introduced in such reference equations of state, such as modified Gaussian bell-shaped terms [Setzmann and Wagner (1991)] and nonanalytical terms [Span and Wagner (1996)]. Recently, to eliminate certain undesirable characteristics of modern multi-parameter equations of state, which exhibit a behaviour in the two-phase region that is inconsistent with the physical behaviour of fluids, a further type of functional form has been developed by Lemmon and Jacobsen (2005). This type of term overcomes the mentioned dilemma and results in equations of state for pure fluids that are more fundamentally consistent.

4.6.1 Polynomial Terms

Polynomial terms have been part of all previous wide-range equations of state. They are a part of the bank of terms in the following form:

$$\alpha_i^{\mathrm{r}} = n_i \, \delta^{d_i} \tau^{t_i} \tag{4.24}$$

with $\delta = \rho/\rho_{\mathrm{c}}$ and $\tau = T_{\mathrm{c}}/T$. To achieve good extrapolation for the equation of state to be developed, the values of the density exponents d_i should be limited to the range from 1 to 5 with integral step sizes. This limitation is particularly important when extrapolating to high densities. For the same reason, the values of the temperature exponents t_i should be limited to a small range as well. Moreover, the temperature exponent t_i of the polynomial term with the highest density exponent d_i (the leading term when extrapolating the equation to high densities) should be between $0 < t_i \leq 1$; for further details and discussions of these considerations see Span and Wagner (1997). In order to provide a sufficiently large selection of these functional terms despite the small range for t_i, a step size of 0.125 is commonly used for the temperature exponents of the polynomial terms.

4.6.2 Polynomial Terms in Combination with Exponential Terms

The mathematical structure of polynomial terms in combination with exponential functions is illustrated by the equation

$$\alpha_i^{\mathrm{r}} = n_i \, \delta^{d_i} \tau^{t_i} e^{-\delta^{c_i}} . \tag{4.25}$$

Terms with $c_i = 2$ are known as Benedict, Webb, and Rubin (BWR)-type terms, see Benedict *et al.* (1940). In an extended form, namely with density exponents up to $c_i = 6$, these terms are nowadays considered to be the standard functional forms of modern, wide-range, pure-substance equations of state.

In order to avoid unwanted influences of the polynomial terms coupled with the exponential functions when extrapolating an equation of state, the temperature exponent t_i in Eq. (4.25) should be greater or equal to one in the bank of terms, but is not compulsory.

4.6.3 The Bank of Terms

Based on the various functional forms selected by the correlator, the general expression of the bank of terms for the residual part α^{r} of the dimensionless Helmholtz free energy equation is the sum of all considered functional forms. Such a bank of terms typically consists of 500 to 1000 terms.

The bank of terms used in the development of the equations of state for hydrogen, water and helium consisted of 562 terms and can be written as

$$\begin{aligned}
\alpha^{\mathrm{r}} = {} & \sum_{k=1}^{4}\sum_{l=0}^{16} n_{kl}\, \delta^{k} \tau^{l/8} \\
& + \exp(-\delta) \sum_{k=1}^{6}\sum_{l=0}^{22} n_{kl}\, \delta^{k} \tau^{l/8} \quad + \exp\left(-\delta^{2}\right) \sum_{k=1}^{4}\sum_{l=0}^{20} n_{kl}\, \delta^{k} \tau^{l/4} \\
& + \exp\left(-\delta^{3}\right) \sum_{k=1}^{5}\sum_{l=4}^{36} n_{kl}\, \delta^{k} \tau^{l/2} \quad + \exp\left(-\delta^{4}\right) \sum_{k=4}^{5}\sum_{l=0}^{16} n_{kl}\, \delta^{k} \tau^{l} \\
& + \exp\left(-\delta^{5}\right) \sum_{k=1}^{2}\sum_{l=2}^{10} n_{kl}\, \delta^{2k-1} \tau^{2l} + \exp\left(-\delta^{6}\right) \sum_{k=4}^{8}\sum_{l=8}^{18} n_{kl}\, \delta^{k} \tau^{2l} .
\end{aligned} \tag{4.26}$$

4.7 The Structure of the Equations of State Used for the New Mixture Model

The wide-range equation of state for natural gases and other mixtures presented in this work is based on equations of state in the form of the fundamental equation for the Helmholtz free energy for the pure natural gas components (see Chaps. 5 and 7). Thus, the uncertainties of the pure substance equations of state directly influence the accuracy in the description of the thermodynamic properties of mixtures. High accuracy equations of state are available for many of the natural gas components considered in the new mixture model (see Table 4.1). The complex mathematical structures of these equations would adversely affect the complexity of the mixture model, which uses a number of further correlation equations to accurately describe the behaviour of binary and multi-component mixtures. Therefore, the pure substance equations of state developed in this work and those from preceding works, selected to form the basis of the wide-range equation of state for natural gases and other mixtures, consist of only polynomial terms and polynomial terms in combination with exponential terms (see Sec. 4.6). Hence, a similar structure is realised for the pure substance basis of the mixture model. According to Eqs. (4.24) and (4.25), the equations for the residual part of the dimensionless Helmholtz free energy read[16]

$$\alpha^{\mathrm{r}}(\delta,\tau) = \sum_{k=1}^{K_{\mathrm{Pol}}} n_k\, \delta^{d_k}\, \tau^{t_k} + \sum_{k=K_{\mathrm{Pol}}+1}^{K_{\mathrm{Pol}}+K_{\mathrm{Exp}}} n_k\, \delta^{d_k}\, \tau^{t_k}\, e^{-\delta^{c_k}} . \tag{4.27}$$

The maximum number of terms, which is the sum of the number of polynomial terms K_{Pol} and of polynomial terms in combination with exponential expressions K_{Exp}, ranges from 12 to 24 for the equations used here. The values of the coefficients and exponents of Eq. (4.27) are given in Tables A3.2 – A3.4 for all considered pure substances, see also Sec. 7.1.

The use of a similar and comparatively simple mathematical structure for the equations of state of all considered substances enables sound programming and computing time saving algorithms. This feature is important when considering the use of the new equation of state for mixtures of natural gas components in technical applications and with regard to complex phase equilibrium calculations. Such calculations require extensive and sophisticated derivatives of the residual Helmholtz free energy of the mixture model with respect to density, temperature, and composition (see Sec. 7.3).

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[16] To denote the pure substance as a component in a mixture the subscripts "o" (referring to pure substance) and "i" (referring to the considered component) is used in Chaps. 5 and 7. Equation (4.26) then reads

$$\alpha^{\mathrm{r}}_{\mathrm{o}i}(\delta,\tau) = \sum_{k=1}^{K_{\mathrm{Pol},i}} n_{\mathrm{o}i,k}\, \delta^{d_{\mathrm{o}i,k}}\, \tau^{t_{\mathrm{o}i,k}} + \sum_{k=K_{\mathrm{Pol},i}+1}^{K_{\mathrm{Pol},i}+K_{\mathrm{Exp},i}} n_{\mathrm{o}i,k}\, \delta^{d_{\mathrm{o}i,k}}\, \tau^{t_{\mathrm{o}i,k}}\, e^{-\delta^{c_{\mathrm{o}i,k}}} . \tag{4.27a}$$

Nevertheless, with regard to technical applications, the demands on the accuracy of both the pure substance equations of state and the wide-range equation of state for mixtures of natural gas components are rather high. Thus, a new class of highly accurate equations of state was developed by Klimeck (2000) for the natural gas components methane, nitrogen, carbon dioxide and ethane, which are the main constituents of common natural gases. The new equations satisfy the high demands on the accuracy while maintaining a mathematically simple structure. Further details on these equations and those used for the secondary natural gas components, such as propane and heavier alkanes, hydrogen, oxygen, and water, are given in the following sections.

4.8 The Equations of State for the Main Natural Gas Components

For the development of a wide-range equation of state for natural gas mixtures, the accuracy of the equations for the main natural gas components, namely methane, nitrogen, carbon dioxide and ethane, is of fundamental importance as these components cover about 97% of the composition of typical natural gas mixtures.

The use of the developed mixture model in standard natural gas applications, such as pipeline transport and natural gas storage, requires the accurate description of the thermodynamic properties of natural gases in the temperature range from 250 K to 350 K at pressures up to 30 MPa. In reduced properties, this range corresponds to reduced temperatures ranging from $T/T_\mathrm{r} = 1.2$ to $T/T_\mathrm{r} = 1.8$, where T_r is an estimate for the reducing temperature of a typical natural gas[17]. For a pure component, the reducing temperature T_r equals the critical temperature of the respective substance. The temperature range which is of main interest for a pure substance then corresponds to the reduced temperature range $1.2 \leq T/T_\mathrm{c} \leq 1.8$. Therefore, the highest demands on the accuracy of the equations of state for the main natural gas components have to be satisfied for this range of supercritical temperatures. Due to that reason, the development of the pure substance equations of state was focused on the supercritical region at pressures up to 30 MPa.

In other regions of the thermodynamic surface, the demands on the accuracy of the pure substance equations were higher than required for the mixture model. However, a highly accurate description of the properties of the main natural gas components is not necessary for temperatures $T \geq 3T_\mathrm{c}$.

The equations used in this work for the four mentioned main natural gas components were developed in a preceding project by Klimeck (2000). This new class of highly accurate equations of state has the following characteristics:

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[17] The reducing temperature varies due to different natural gas compositions.

- The development was based mainly on the comprehensive data sets of various thermal and caloric properties that were used for the development of the reference equations of state for methane [Setzmann and Wagner (1991)], nitrogen [Span *et al.* (2000)], carbon dioxide [Span and Wagner (1996)] and ethane[18] [Bücker and Wagner (2006a)]. In addition, state-of-the-art density and speed of sound measurements for methane and carbon dioxide, which were not available at the time the corresponding reference equations of state were developed, were used for the development of the new equations [e.g. Trusler and Costa Gomes (1996), Estrada-Alexanders and Trusler (1998), Klimeck *et al.* (2001)]. Thus, compared to the respective reference equation of state, the description of the thermal and caloric properties of methane was significantly improved for temperatures between 240 K and 300 K (see Figs. 4.1 and 4.2).
- In addition to the updated data sets, certain properties were calculated from the corresponding reference equations of state and from auxiliary equations to be used in fitting.
- The new equations of state were developed by using the multi-property fitting and optimisation methods described in Secs. 4.4 and 4.5. The equations for methane, nitrogen and ethane use an identical simultaneously optimised structure with 24 terms. The shared structure yields a similar description of the thermodynamic properties of the pure components. The equation for carbon dioxide was developed separately[19] and consists of 22 terms.
- The equations are valid over wide ranges of temperature and at pressures up to 300 MPa (see Table 4.2).
- The new equations of state describe the thermodynamic properties of the respective pure substances more accurately than is required for the calculation of the thermodynamic properties of mixtures.
- At supercritical temperatures and at pressures up to 30 MPa the new equations of state achieve almost the same high accuracy as the corresponding reference equations of state. The uncertainty of the equations regarding gas phase density and speed of sound is estimated to be (0.03 – 0.05)% over wide ranges of temperature and at pressures up to 30 MPa. State-of-the-art density data are reproduced by the equations with deviations of less than ±0.03%. In the liquid phase, the uncertainty of the equations with regard to density amounts to (0.05 – 0.1)% at pressures up to 30 MPa. The uncertainty in liquid

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[18] In contrast to the reference equation of state for ethane developed by Bücker and Wagner (2006a), who used state-of-the-art density data sets of Claus *et al.* (2003) and Funke *et al.* (2002a,b), preliminary density measurements of Claus *et al.* (1999) were used for the equation of state developed by Klimeck (2000).

[19] The equation was developed individually because the reduced thermodynamic properties of carbon dioxide significantly deviate from those of the simultaneously optimised substances.

phase speed of sound is estimated to be (1 – 2)%. On the vapour-liquid phase boundary, data for the vapour pressure, the saturated liquid density, and the saturated vapour density are represented by the equations to within ±(0.03 – 0.05)%.

- A highly accurate description of the critical region is neither necessary nor intended for the mixture model developed in this work. Nevertheless, the equations achieve a more accurate description of properties in the extended critical region[20] than equations widely applied in practice.
- The extrapolation to temperatures and pressures beyond the range of validity yields reasonable results (see Sec. 4.11.2).

Since methane is the most important natural gas component, which covers more than 80% of the composition of typical natural gases, the characteristics of the equation of state used for this substance are decisive for the accuracy of the new mixture model. Figure 4.1 shows comparisons between selected experimental density data and values calculated from the new equation of state for methane. In the temperature range from 230 K to 350 K, the $p\rho T$ relation of methane is described very accurately by the data of Klimeck *et al.* (2001). The new equation of state represents these data to within their experimental uncertainty, which is approximately 0.02% in density. Other high accuracy data like the experimental results of Jaeschke and Hinze (1991) are reproduced with deviations of less than ±0.05%, which is also in agreement with the uncertainty of the measurements. Since the reference equation of state developed by Setzmann and Wagner (1991) is based on a less accurate data set, the reference equation deviates from the state-of-the-art data of Klimeck *et al.* (2001) by slightly more than +0.02%, especially at elevated pressures between 10 MPa and 30 MPa.

Aside from the improved description of supercritical densities, significant improvements, which are considered to be important for the wide-range equation of state for natural gases as well, are also achieved for caloric properties as shown in Fig. 4.2 for the speed of sound at supercritical temperatures ranging from 250 K to 375 K. All of the state-of-the-art speed of sound data of Trusler and Costa Gomes (1996) are reproduced by the new equation of state to within ±0.03%; the uncertainty of the data is estimated to be (0.01 – 0.02)%. Values calculated from the reference equation of state of Setzmann and Wagner (1991) deviate from the measured data at temperatures below 275 K by more than −0.1% at elevated pressures.

A similar accurate representation is achieved for other caloric properties, such as the isobaric heat capacity and isobaric enthalpy differences.

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[20] The extended critical region is indicated in this work by densities of $0.6\,\rho_\mathrm{c} \le \rho \le 1.4\,\rho_\mathrm{c}$ at temperatures of $0.98\,T_\mathrm{c} \le T \le 1.2\,T_\mathrm{c}$.

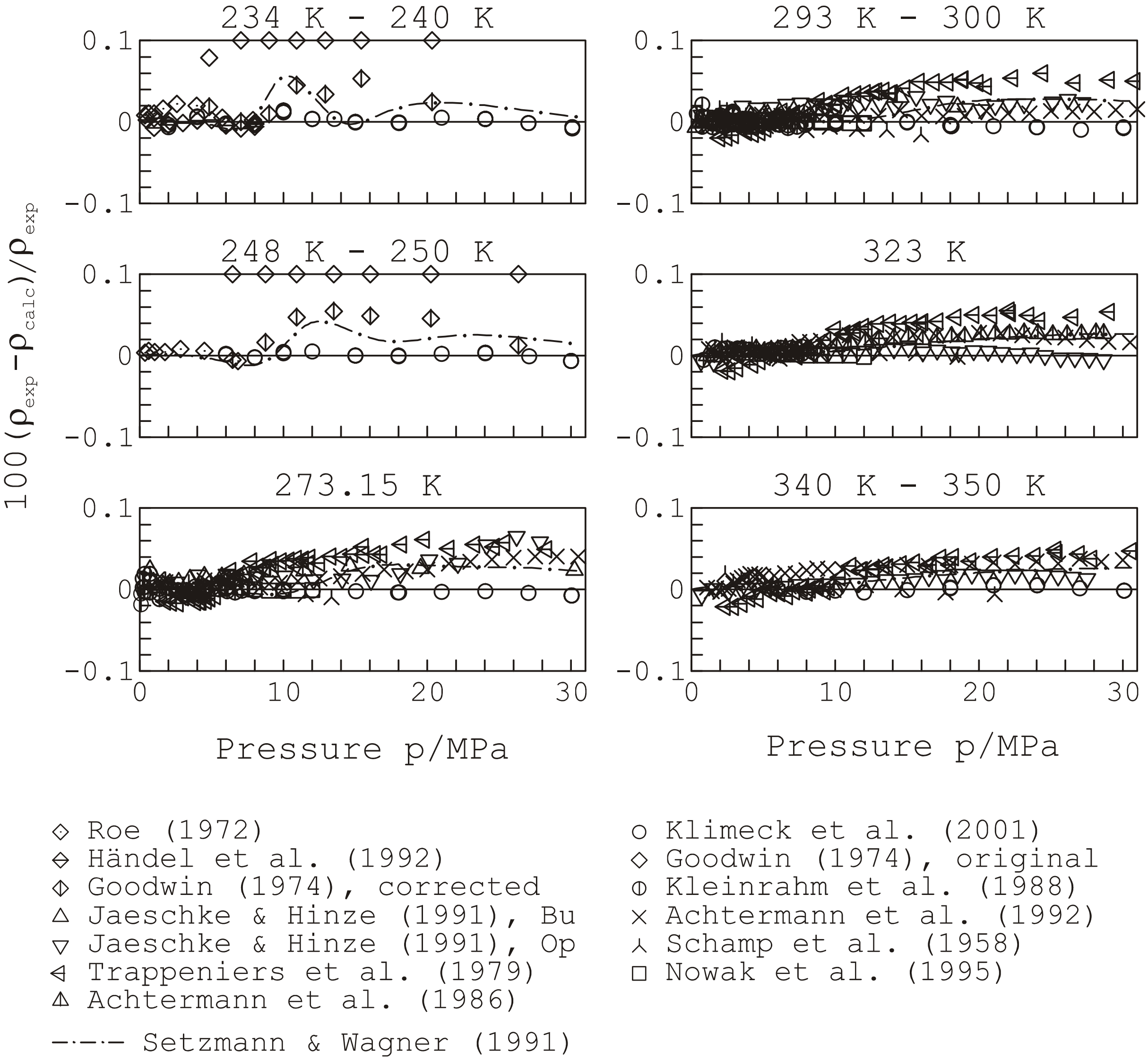

Fig. 4.1 Percentage density deviations of selected experimental *pρT* data for methane from values calculated from the new equation of state, see text. Values calculated from the reference equation of state of Setzmann and Wagner (1991) are plotted for comparison. Bu: Burnett apparatus, Op: optical interferometry method.

Further details concerning the development of the new class of highly accurate equations of state for methane, nitrogen, carbon dioxide and ethane and comprehensive comparisons to experimental data and values calculated from reference equations of state are given in Klimeck (2000) and Klimeck *et al.* (1999). As a result of these comparisons, Figs. A1.1 – A1.8 given in the appendix show conservative estimations of the uncertainty of the new equations with respect to density and speed of sound in the homogeneous gas, liquid, and supercritical regions of the respective substances.

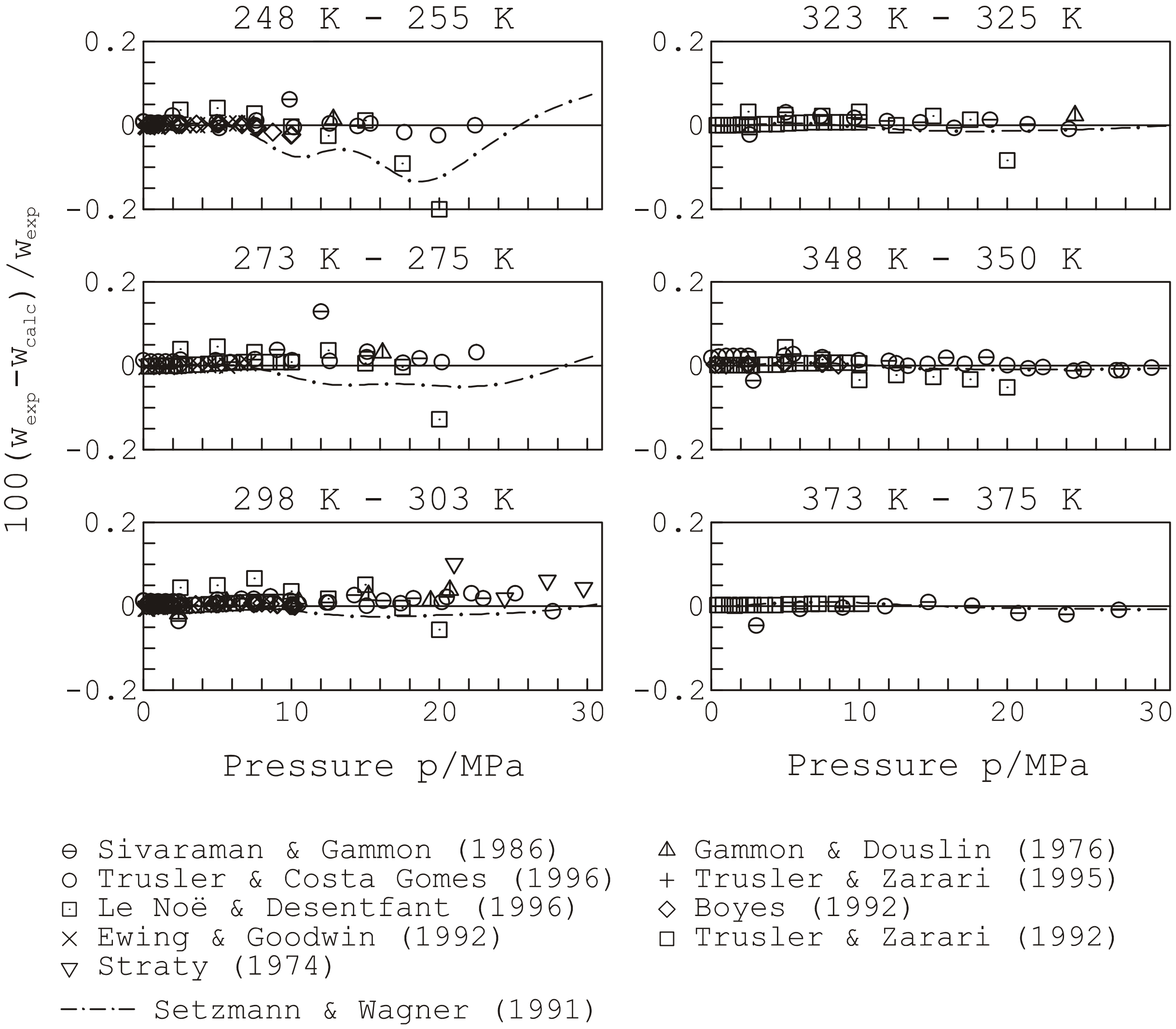

Fig. 4.2 Percentage deviations of selected experimental speed of sound data for methane from values calculated from the new equation of state, see text. Values calculated from the reference equation of state of Setzmann and Wagner (1991) are plotted for comparison.

4.9 The Equations of State for the Secondary Alkanes and Other Secondary Natural Gas Components

A new class of accurate technical equations of state was developed by Span and Wagner (2003a,b) and Span (2000a) for a group of non- and weakly polar substances. These equations are based on a simultaneously optimised structure which consists of 12 functional terms. Although the greatest part of the composition of typical natural gases is covered by the main natural gas components (see Sec. 4.8), the accuracy of the equations used for the secondary natural gas components is not of minor importance as the new mixture model is designed to accurately describe the properties of various natural gases and other mixtures over wide ranges of temperature, pressure and composition. The simultaneously optimised equations fulfil the advanced technical demands on the accuracy of equations of state for the secondary alkanes and further secondary natural gas components considered in the mixture model. Hence, these equations are used for the normal alkanes from propane to n-octane, for isobutane and isopentane, and for oxygen and argon. The uncertainties of the equations regarding different thermodynamic properties are summarised in Table 4.4.

Table 4.4 Uncertainties of the equations of state for propane, n-butane, isobutane, n-pentane, isopentane, n-hexane, n-heptane, n-octane, oxygen, and argon with regard to different thermodynamic properties

Pressure range	Uncertainty in					
	$\rho(T,p)$	$w(T,p)$	$c_p(T,p)$	$p_s(T)$	$\rho'(T)$	$\rho''(T)$
$p \leq 30$ MPa[a]	0.2%[b]	(1 – 2)%[c]	(1 – 2)%[c]	0.2%[d]	0.2%	0.4%[d,e]
$p > 30$ MPa[f]	0.5%	2%	2%	–	–	–

[a] Larger uncertainties are to be expected in the extended critical region.

[b] In the extended critical region, $\Delta p/p$ is used instead of $\Delta\rho/\rho$.

[c] ±1% at gaseous and gas-like supercritical states, ±2% at liquid and liquid-like supercritical states.

[d] Larger relative uncertainties have to be tolerated for small vapour pressures and saturated vapour densities.

[e] Combination of the uncertainties of the gas densities and vapour pressures; experimental data of this accuracy are available for only a few substances.

[f] States at pressures $p > 100$ MPa are not considered due to their limited technical relevance.

The selected data sets for the development of the equations contained all of reliable experimental thermodynamic property data that were available for the corresponding fluids at the time the equations were developed. Data at pressures above 100 MPa were not used due to their limited technical relevance. The equations have the following further characteristics in common:

- On average, the new equations are far superior to older technical equations of state, in many cases their performance comes close to the performance of typical reference equations of state.
- The equations are valid over wide ranges of temperature and at pressures up to 100 MPa (see Table 4.2).
- The extrapolation to temperatures and pressures beyond the range of validity yields reasonable results (see Sec. 4.11.2).

Further details concerning the development of the new class of accurate technical equations of state, which were used in this work for the equations of many secondary natural gas components, are given in Span and Wagner (2003a,b) and Span (2000b).

4.10 Development of the New Equations of State for Hydrogen, Carbon Monoxide, Water, and Helium

To fulfil the demands mentioned above on the structure and accuracy of the new equation of state for natural gases and other mixtures, similar to the equations developed by Klimeck (2000) for the main natural gas components (see Sec. 4.8), new equations of state for hydrogen[21], carbon monoxide, water, and helium[22] were developed prior to the development of the mixture model.

The recommended reference equation of state for water is the IAPWS-95 formulation of Wagner and Pruß (2002) (see Table 4.1). This reference formulation is explicit in the Helmholtz free energy. The equation consists of a complex structure combining 56 terms of four different functional forms. McCarty and Arp (1990) developed a wide ranging equation of state for helium, and McCarty (1989) reported an equation of state for carbon monoxide. Younglove (1982) published an equation for parahydrogen which can easily be transformed to be used for hydrogen as well. These pressure explicit equations for helium, carbon monoxide, and hydrogen are based on the well-known modified BWR (mBWR) equations of state which use 32 terms. This number of terms is significantly larger than desired for the mixture model.

The complex structure of these equations of state is not the only reason for the necessity to develop new equations. Unlike other equations of state, those of Younglove (1982) and McCarty and Arp (1990) for hydrogen and helium show a physically incorrect behaviour in the liquid phase and liquid-like supercritical region at very high densities. As shown in the pressure-density plot for helium in Fig. 4.3, the shapes of the isotherms calculated from the equation of state of McCarty and Arp (1990) pass through maximum values for temperatures $T > T_{\mathrm{t}}$, whereas the isotherms calculated from the new equation for helium developed in this work continuously increase. A similar plot can be shown for hydrogen as well.

In general, a physically correct behaviour, even at the comparatively low absolute temperatures which occur in the sub- and supercritical regions of hydrogen and helium because of their low critical temperatures, is important for the developed mixture model due to the following reasons:

- As explained in Sec. 4.8, the reduced temperature range $1.2 \leq T/T_{\mathrm{c}} \leq 1.8$ corresponds to the region with the highest demands on the accuracy in the description of the thermodynamic

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[21] Under normal conditions hydrogen is a mixture of two different kinds of molecules, namely ortho- and parahydrogen. At room temperature, hydrogen is composed of about 75% of ortho- and 25% of parahydrogen. This is the so-called “normal” hydrogen (n-hydrogen). The equilibrium ratio of these two forms depends on temperature. At low temperatures (around the boiling point), the equilibrium state is comprised almost entirely of parahydrogen. In this work, the term “hydrogen” represents equilibrium hydrogen. The experimental data used for the development of the equation correspond to equilibrium hydrogen and parahydrogen (e.g., for saturated liquid densities).

[22] Represents helium-4.

properties of typical natural gas mixtures. Therefore, in this reduced range, even the equations for the minor and trace components[23] of natural gases have to contribute reasonably to the Helmholtz free energy of the mixture.

- The mixture model should yield accurate results in the extended fluid region. A wrong behaviour in the liquid phase of any pure component would adversely affect the description of the properties of mixtures in this region. The property calculations for mixtures of unusual composition would return false solutions as well.
- Incorrect physical behaviour at high reduced densities would result in a poor extrapolation behaviour of the total mixture model.
- Correct physical behaviour is important for property calculations in any region of the fluid surface, as algorithms for stability analysis and phase equilibrium calculations frequently need calculations in fluid regions and for mixture compositions which are not related to the desired fluid phase.

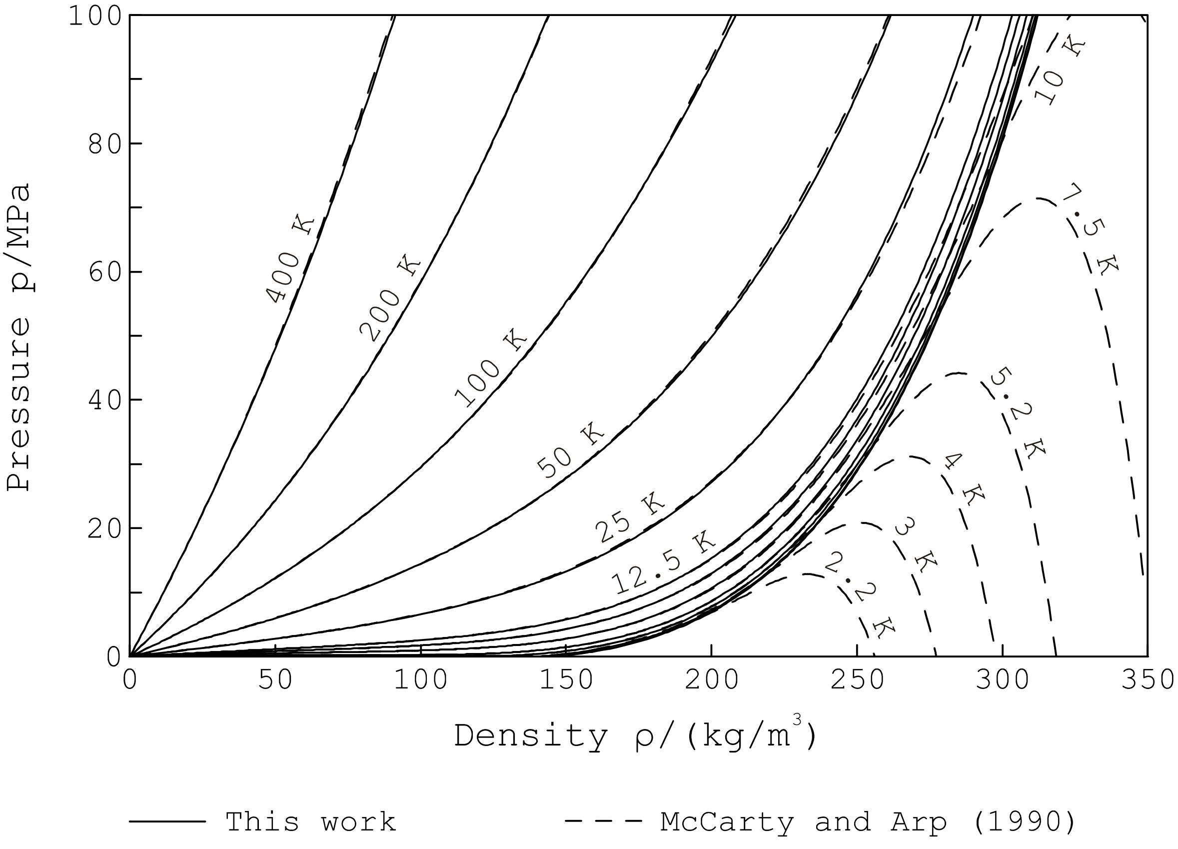

Fig. 4.3 Pressure-density diagram for helium showing isotherms at temperatures ranging from 2.2 K to 400 K calculated from the equation of state developed in this work (see text) and the equation of state of McCarty and Arp (1990).

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[23] For instance, typical natural gases contain less than 0.1 mole-% of helium.

Similar to the simultaneously optimised equations of Span and Wagner (2003b), the development of the new equations of state for hydrogen, carbon monoxide, water, and helium had to fulfil the advanced demands on the accuracy of equations for technical applications.

Unfortunately, for hydrogen and helium, the data situation for reduced temperatures $T/T_\mathrm{c} < 3$ is rather poor as most of the available experimental data were measured at temperatures from 100 K to 400 K, which correspond to comparatively high reduced temperatures of $T/T_\mathrm{c} \geq 3$ for hydrogen and $T/T_\mathrm{c} \geq 20$ for helium[24]. To overcome these additional difficulties, selected experimental data along with physically reasonable data calculated from the existing equations of state and of auxiliary correlation equations for the $p\rho T$ relation in the liquid phase and liquid-like supercritical region were used to optimise the structures of the equations and for fitting the coefficients. For the new equation of state for water, no experimental information was used. Similar to the IAPWS-IF97 formulation of Wagner *et al.* (2000), the new equation for water is based only on data for thermal and caloric properties calculated from the corresponding reference equation of Wagner and Pruß (2002). In contrast to the individually optimised structures of the equations for hydrogen, water, and helium, the new equation for carbon monoxide is based on the simultaneously optimised structure for non- and weakly polar substances developed by Span and Wagner (2003b). Thus, only the coefficients of the equation were fitted to selected experimental data and data calculated from the equation of McCarty (1989). The experimental data sets used for the development and evaluation of the new equations of state are not given here.

In general, the equations for hydrogen, carbon monoxide, water, and helium developed in this work have the following further characteristics in common:

- The new equations of state for hydrogen, water, and helium were developed by using multi-property fitting and optimisation methods described in Secs. 4.4 and 4.5. They have individually optimised structures with 12 to 16 terms. The equation for carbon monoxide is based on the simultaneously optimised structure for non- and weakly polar substances of Span and Wagner (2003b) and consists of 12 terms.
- The equations are valid over wide ranges of temperature and at pressures up to 100 MPa. The equation for hydrogen is valid for pressures up to 300 MPa (see Table 4.2).
- In the supercritical region, the new equations of state for hydrogen, carbon monoxide, and helium achieve a similar or even better description of the thermodynamic properties compared to the existing mBWR equations of state. At supercritical temperatures, the uncertainty of the new equations is, on average and conservatively estimated, 0.2% in density at pressures up to 30 MPa and less than 0.5% at higher pressures. In general, higher uncertainties have to be tolerated in the liquid phase and for other thermodynamic properties. For hydrogen, the uncertainty in density at pressures $p \leq 30$ MPa is less than

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[24] Usually, equations of state cover reduced temperatures $T/T_\mathrm{c} < 3$.

0.2% over the temperature range 65 K ≤ T < 270 K and less than 0.1% at temperatures $T \geq 270$ K. At pressures $p > 30$ MPa, the uncertainty in density is less than (0.2 – 0.3)%.

- The equations behave reasonably in regions characterised solely by poor data.
- The extrapolation to temperatures and pressures beyond the range of validity yields reasonable results (see Sec. 4.11.2).

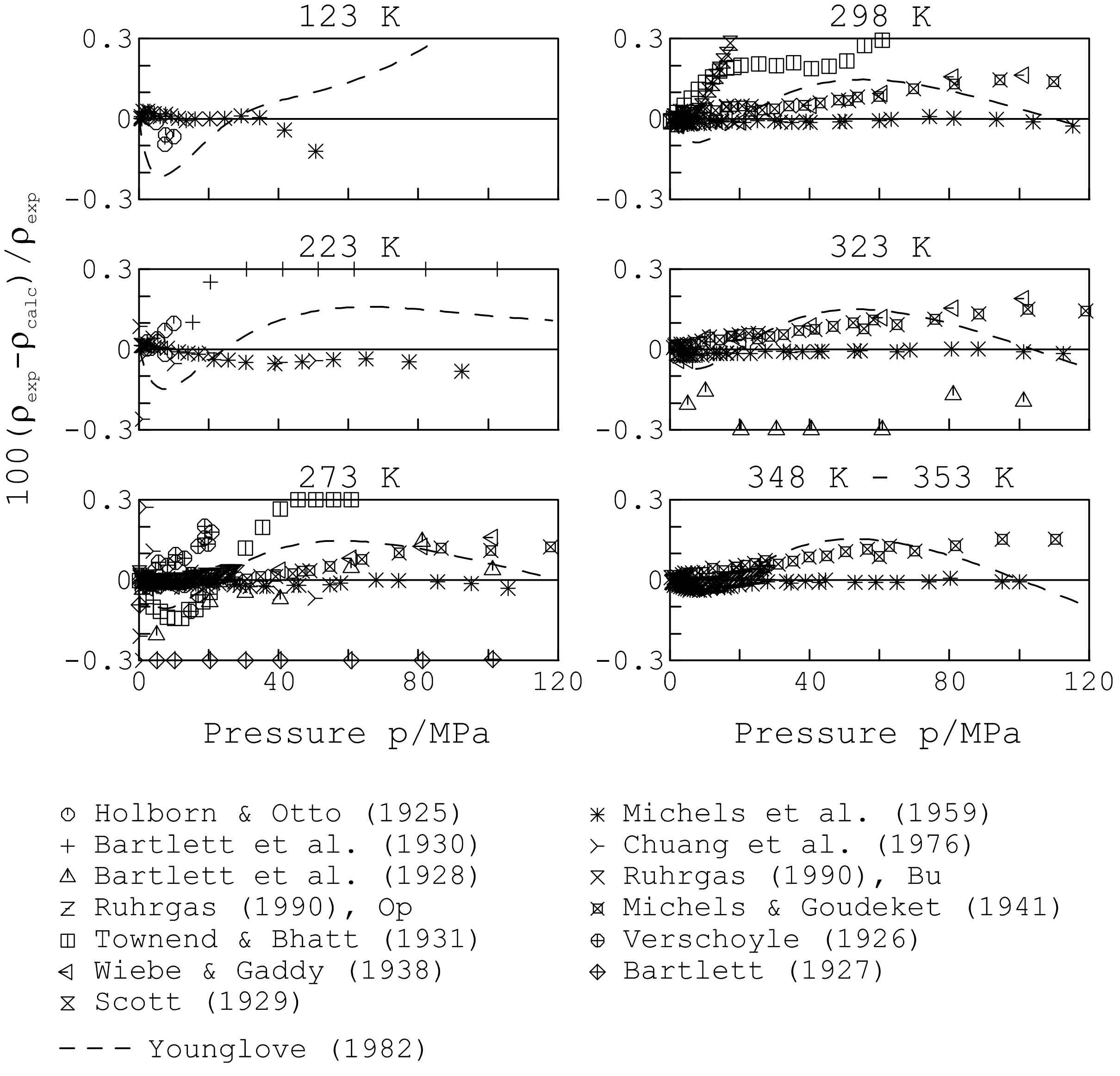

Fig. 4.4 Percentage density deviations of selected experimental $p\rho T$ data for hydrogen from values calculated from the new equation of state, see text. Values calculated from the equation of state of Younglove (1982) are plotted for comparison. Bu: Burnett apparatus, Op: optical interferometry method.

To exemplify the capabilities of the new equations of state, comparisons between selected $p\rho T$ data and values calculated from the new equation of state for hydrogen are shown in Fig. 4.4. The most accurate data are those measured by Jaeschke *et al.* [Ruhrgas (1990), Bu, and Ruhrgas (1990), Op] over the temperature range from 273 K to 353 K and at pressures

$p \leq 28$ MPa. The new equation of state represents these data to within their experimental uncertainty, which is approximately 0.05% in density. All other reliable data are reproduced with deviations of less than ±(0.1 – 0.2)% at pressures up to 120 MPa. The equation of state developed by Younglove (1982) deviates significantly from the measured data by up to −1% in the upper temperature range at pressures above 120 MPa, which is, however, outside the range of validity of this equation. At lower temperatures ($T < 200$ K) and elevated pressures, the equation of Younglove (1982) shows systematically increasing deviations from the new equation of state reaching approximately +3% at 300 MPa and $T = 100$ K. These deviations further increase at temperatures below 100 K. It can be shown that the reason for this behaviour is the physically incorrect description of the liquid-like supercritical phase as described above. A similar behaviour is observed for the equation of McCarty and Arp (1990) for helium.

As a result of the investigations concerning the data situation and the existing equations of state for hydrogen and helium, the development of new reference equations of state along with new measurements using state-of-the-art experimental techniques is strongly recommended for both substances[25].

4.11 Extrapolation Behaviour

The range of validity of an empirical equation of state is typically determined by the overall temperature and pressure ranges of the experimental data used for the development and evaluation of the equation. Usually, when referring to extrapolation, the equation of state should show reasonable behaviour at temperatures and pressures outside of the range of validity (i.e. at temperatures and pressures higher than the maximum limits) (see Sec. 4.11.2).

4.11.1 The Behaviour of the Equation of State for Carbon Dioxide at Reduced Temperatures $(T/T_c) < (T_t/T_c)$

For most equations of state the range of validity covers temperatures from the triple point or melting line of the respective substance up to a certain maximum value (see Table 4.2). With the exception of carbon dioxide, the reduced triple point temperature T_t/T_c ranges from 0.3 to 0.5 for the components considered in the mixture model. This range is in agreement with the minimum reduced temperatures that can occur in mixture calculations[26].

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[25] For example, when considering the use of hydrogen as an alternative energy source, the liquefaction of hydrogen for storage and for easier transportation will play an important role in a future hydrogen economy. The development of improved liquefaction processes will require an accurate description of various thermodynamic properties of hydrogen as well as of helium and mixtures containing helium, which can be used as refrigerants in such processes.

[26] Most of the pure substance equations of state used in the mixture model are based on a simultaneously optimised structure which was established by the use of experimental data covering

Since the triple point temperature of carbon dioxide $T_t = 216.5915$ K [Duschek *et al.* (1990)] is comparatively high, the fluid surface is limited by a reduced temperature $T/T_c \geq 0.712$. In order to be able to calculate thermodynamic properties of natural gases and other mixtures at lower reduced temperatures, reasonable behaviour of the equation for carbon dioxide at reduced temperatures $T/T_c < 0.712$ is required. Therefore, over the temperature range from 90 K to 216 K, artificial data were used for the development of the new equation of state [see Klimeck (2000) and Klimeck *et al.* (1999)]. These data were calculated from the equation of state for the refrigerant R-22 of Marx *et al.* (1992) by means of a simple corresponding states similarity. In this way, the equation for carbon dioxide shows reasonable behaviour of down to a temperature of 90 K[27], which corresponds to a reduced temperature of 0.296.

4.11.2 The Behaviour of the Equations of State at Temperatures and Pressures Beyond the Range of Validity

The range of validity of an empirical equation of state is typically limited by the temperature and pressure ranges which are covered by reliable experimental data used for the development and evaluation of the equation. Modern multi-parameter equations of state are designed to behave reasonably far beyond this range (at higher temperatures and pressures). Investigations on the extrapolation behaviour of empirical equations of state carried out by Span and Wagner (1997) have shown that plots of certain characteristic curves, the so-called "ideal curves", are useful for the assessment of the extrapolation behaviour of an equation of state. Ideal curves are curves along which one property of a real fluid is equal to the corresponding property of the ideal gas at the same temperature and density. These characteristic curves are commonly derived from the compression factor $Z = p/(\rho RT)$ and its derivatives. The characteristic curves are

- the ideal curve $$Z = 1, \tag{4.28}$$
- the Boyle curve $$(\partial Z/\partial \rho)_T = 0, \tag{4.29}$$
- the Joule-Thomson inversion curve $$(\partial Z/\partial T)_p = 0, \tag{4.30}$$
- and the Joule inversion curve $$(\partial Z/\partial T)_\rho = 0. \tag{4.31}$$

Regular shapes of the curves, as shown in Fig. 4.5, and their values at characteristic points[28], e.g. the reduced temperature at which a curve begins (at zero pressure) and the reduced

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reduced temperatures $T/T_c \geq 0.3$. Due to this reason, even substances with a reduced triple point temperature $T_t/T_c > 0.3$ can be extrapolated down to lower temperatures in a reasonable way.

[27] The range of validity of the new equation of state for carbon dioxide is certainly restricted to temperatures $T \geq T_t$. Data calculated in the "pseudo-fluid" region do not have any physical meaning for the pure substance.

[28] The temperature at which the Boyle and ideal curves cross the zero pressure line is known as the Boyle temperature, or the temperature at which the second virial coefficient is zero. The point at

temperature at which a curve passes through a maximum value, are important criteria to obtain reasonable extrapolation behaviour of an equation of state.

Figure 4.5 shows a plot of the ideal curves calculated from the equations of state for methane, n-hexane, and hydrogen, each representing one exemplary equation out of the different classes of equations used for the mixture model. The three equations show reasonable plots of the four ideal curves defined in Eqs. (4.28) – (4.31), indicating that extrapolation beyond their ranges of validity is possible. The characteristic points at which the ideal curves cross the zero pressure line are in agreement with the values determined from universal theories [see Span and Wagner (1997)].

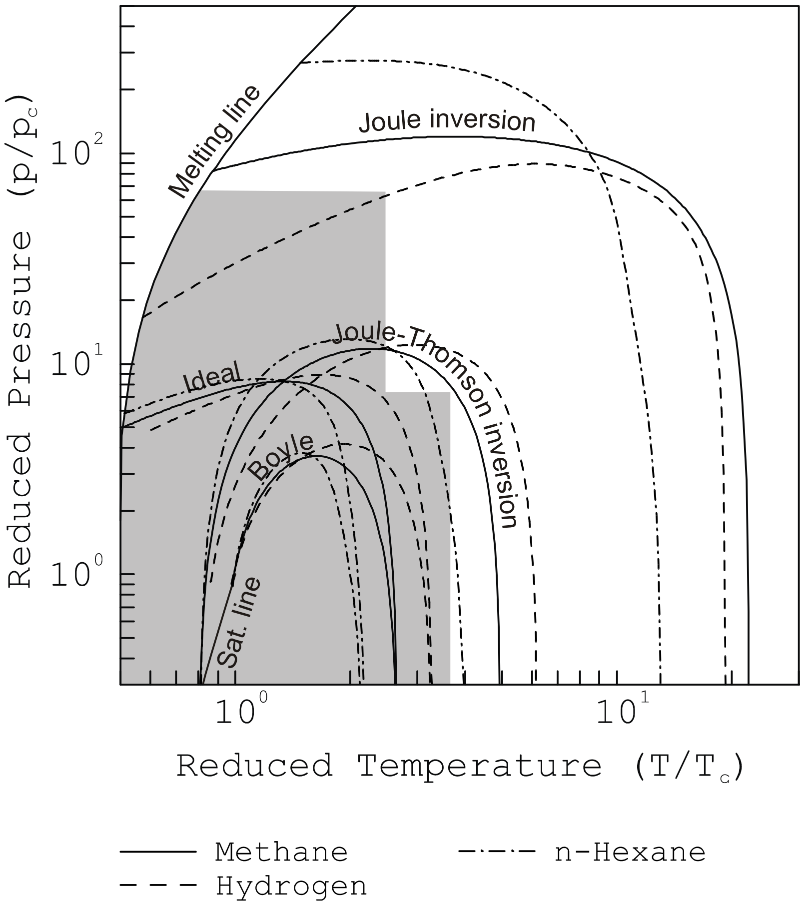

Fig. 4.5 The so-called ideal curves in a double logarithmic p/p_c vs T/T_c diagram as calculated from the equations of state for methane, n-hexane, and hydrogen (see Secs. 4.8 – 4.10), each representing one exemplary equation out of the different classes of equations used for the developed mixture model; for the definition of these curves see Eqs. (4.28) – (4.31). The plotted phase boundaries correspond to those of methane. The area marked in gray corresponds to the region where the equation of state for methane was fitted to experimental data.

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zero pressure along the Joule inversion curve corresponds to the temperature at which the second virial coefficient is at a maximum.

Plots with a similar representation of the ideal curves can also be calculated from the equations of state for the other main and secondary natural gas components. The new equation for carbon dioxide shows similar shapes of the Boyle, the ideal, and the Joule-Thomson inversion curves. For reduced temperatures $T/T_\mathrm{c} \leq 10$, the Joule inversion curve shows a shape that is in accordance with the theoretical predictions, but does not cross the zero pressure line[29]. However, this behaviour does not affect the suitability of the new equation for carbon dioxide, since reduced temperatures $T/T_\mathrm{c} > 10$ are outside the range of interest of the developed mixture model.

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[29] In order for the Joule inversion curve to extend to zero pressure, the second virial coefficient must pass through a maximum value, a criterion which is not followed by all equations of state as proven by Span and Wagner (1997) for several reference equations of state.

5 Equations of State for Mixtures

Recent equations of state for mixtures are based on multi-fluid approximations and are explicit in the Helmholtz free energy. The models use equations of state in the form of fundamental equations for each considered mixture component along with further correlation equations to take into account the residual mixture behaviour. The models enable the accurate description of the thermodynamic properties of mixtures in the extended fluid region for wide ranges of temperature, pressure, and composition. For a pure component the models default to the accurate fundamental equation for the respective substance. The basis for the development and evaluation of such empirical equations of state for mixtures are experimental data (see Chap. 6).

Table 5.1 Overview of existing mixture models based on multi-fluid approximations explicit in the Helmholtz free energy in the order of the year of publication

Reference	Type of mixture	Number of components
Tillner-Roth (1993)	Binary mixture R-152a–R-134a	2
Lemmon (1996)[a]	Mixtures of polar and nonpolar substances[b]	13
Tillner-Roth & Friend (1998)	Binary mixture water–ammonia	2
Tillner-Roth *et al.* (1998)	Hydrofluorocarbon refrigerant mixtures[c]	4
Lemmon *et al.* (2000)	Dry air and similar mixtures	3
Klimeck (2000)	Natural gases and similar mixtures	7
Miyamoto & Watanabe (2003)	Mixtures of hydrocarbon refrigerants[d]	3
Lemmon & Jacobsen (2004)	Hydrofluorocarbon refrigerant mixtures[e]	5
This work	Natural gases, similar gases, and other mixtures	18

[a] Revised by Lemmon & Jacobsen (1999) for mixture components relevant to natural gas.
[b] Considered components include substances relevant to natural gas, dry air, and refrigerants.
[c] Binary and ternary mixtures of R-32, R-125, R-134a, and R-143a.
[d] Binary and ternary mixtures of propane, n-butane, and isobutane.
[e] Binary and ternary mixtures of R-32, R-125, R-134a, R-143a, and R-152a.

The first models of this type were developed independently by Tillner-Roth (1993) for the binary refrigerant mixture R-152a–R-134a and by Lemmon (1996) for mixtures of polar and nonpolar substances including natural gas components. Based on the structures of these models, further equations of state for the binary mixture water–ammonia [Tillner-Roth and Friend (1998)], dry air and similar mixtures [Lemmon *et al.* (2000)], mixtures of hydrocarbon refrigerants [Miyamoto and Watanabe (2003)], and hydrofluorocarbon refrigerant mixtures [Lemmon and Jacobsen (2004), Tillner-Roth *et al.* (1998)] have been reported within the past eight years as shown in Table 5.1. Detailed descriptions of the general structures of these models are given in Tillner-Roth (1998) and Lemmon and Tillner-Roth (1999). Lemmon and

Jacobsen (1999) revised the model of Lemmon (1996) for the mixture components relevant to this work. Hence, the equation of Lemmon and Jacobsen (1999) is used for comparisons.

Tillner-Roth (1993) and Tillner-Roth and Friend (1998) developed equations for individual binary mixtures. Based on the description of the binary subsystems, different models describe the behaviour of ternary mixtures only. Comparisons between ternary data and values calculated from these equations of state are shown by the respective authors [e.g. Lemmon *et al.* (2000), Miyamoto and Watanabe (2003), Lemmon and Jacobsen (2004)]. The nearly identical models of Lemmon (1996) and Lemmon and Jacobsen (1999) enable the description of multi-component mixtures and contain formulations for mixtures of natural gas components.

As mentioned in Chap. 2, the new equation of state for natural gases and other mixtures of natural gas components developed in this work results from the continuation of the preceding work of Klimeck (2000), who established the essential tools required for the development of such multi-fluid mixture models. Based on these tools, a preliminary equation of state for natural gas mixtures consisting of up to seven main and secondary natural gas components, which is also used for comparisons in this work, was developed by Klimeck (2000) to demonstrate the predictive capability of such a mixture approach.

5.1 The General Structure of Multi-Fluid Approximations

The mixture models mentioned above and the new model for natural gases and other mixtures developed in this work are fundamental equations explicit in the Helmholtz free energy a with the independent mixture variables density ρ, temperature T, and molar composition $\bar{x}$. Similar to fundamental equations for pure substances (see Chap. 4), the function $a(\rho,T,\bar{x})$ is split into a part a^{o}, which represents the properties of ideal gas mixtures at a given ρ, T, and $\bar{x}$, and a part a^{r}, which takes into account the residual mixture behaviour:

$$a(\rho,T,\bar{x}) = a^{\mathrm{o}}(\rho,T,\bar{x}) + a^{\mathrm{r}}(\rho,T,\bar{x}). \tag{5.1}$$

Using the Helmholtz free energy in its dimensionless form $\alpha = a/(RT)$, Eq. (5.1) reads[30]

$$\alpha(\delta,\tau,\bar{x}) = \alpha^{\mathrm{o}}(\rho,T,\bar{x}) + \alpha^{\mathrm{r}}(\delta,\tau,\bar{x}), \tag{5.2}$$

where δ is the reduced mixture density and τ is the inverse reduced mixture temperature according to

$$\delta = \rho/\rho_{\mathrm{r}} \quad \text{and} \quad \tau = T_{\mathrm{r}}/T \tag{5.3}$$

with ρ_{r} and T_{r} being the composition-dependent reducing functions for the mixture density and temperature:

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[30] Note that α^{o} does not depend on δ and τ of the mixture, but on ρ and T.

$$\rho_\mathrm{r} = \rho_\mathrm{r}(\bar{x}), \tag{5.4}$$

$$T_\mathrm{r} = T_\mathrm{r}(\bar{x}). \tag{5.5}$$

The dimensionless form of the Helmholtz free energy for the ideal gas mixture α^o is given by

$$\alpha^\mathrm{o}(\rho, T, \bar{x}) = \sum_{i=1}^{N} x_i \left[\alpha_{\mathrm{o}i}^\mathrm{o}(\rho, T) + \ln x_i\right], \tag{5.6}$$

where N is the number of components in the mixture, $\alpha_{\mathrm{o}i}^\mathrm{o}$ is the dimensionless form of the Helmholtz free energy in the ideal-gas state of component i [see Sec. 4.3 and Eq. (7.5)] and the x_i are the mole fractions of the mixture constituents. The term $x_i \ln x_i$ accounts for the entropy of mixing.

In a multi-fluid approximation, the residual part of the reduced Helmholtz free energy of the mixture α^r is given as follows:

$$\alpha^\mathrm{r}(\delta, \tau, \bar{x}) = \sum_{i=1}^{N} x_i\, \alpha_{\mathrm{o}i}^\mathrm{r}(\delta, \tau) + \Delta\alpha^\mathrm{r}(\delta, \tau, \bar{x}), \tag{5.7}$$

where $\alpha_{\mathrm{o}i}^\mathrm{r}$ is the residual part of the reduced Helmholtz free energy of component i [see Sec. 4.7 and Eq. (7.7)] and $\Delta\alpha^\mathrm{r}$ is the so-called departure function. The reduced residual Helmholtz free energy of each component depend on the reduced variables δ and τ of the mixture; the departure function additionally depends on the mixture composition $\bar{x}$.

This general structure is used by the models of Tillner-Roth (1993), Lemmon (1996), and Lemmon and Jacobsen (1999), as well as by all models based on a multi-fluid approximation which intend to achieve an accurate description of the thermodynamic properties of nonideal mixtures.

According to Eq. (5.7), the residual part of the reduced Helmholtz free energy of the mixture α^r is composed of two different parts:

- the linear combination of the residual parts of all considered mixture components and
- the departure function.

In general, the contribution of the departure function to the reduced residual Helmholtz free energy of the mixture is inferior to the contribution of the equations for the pure components.

Summarised, the new equation of state for natural gases and other mixtures based on a multi-fluid approximation consists of

- pure substance equations for all considered mixture components,
- composition-dependent reducing functions $\rho_\mathrm{r}(\bar{x})$ and $T_\mathrm{r}(\bar{x})$ for the mixture density and temperature, and
- a departure function $\Delta\alpha^\mathrm{r}$ depending on the reduced mixture density, the inverse reduced mixture temperature, and the mixture composition.

The reducing functions and the departure function are developed based on experimental mixture data. The following two sections describe the mathematical forms commonly used for the reducing functions and the different existing approaches in the development of departure functions. These sections also present the functions used for the new mixture model.

5.2 Reducing Functions for Density and Temperature

The reducing functions are used to determine the reduced variables for the mixture density and temperature according to Eq. (5.3). The use of correlation equations with adjustable parameters, fitted to mixture data, is recommended for the reducing functions as shown by the investigations of Klimeck (2000) and Kunz (2000). The applicability of a mathematical form for such correlation equations depends on certain conditions, for instance:

- For $x_i \rightarrow 0$ the reducing functions have to smoothly connect to the reducing parameters of the respective substance (i.e. the critical parameters). This is mandatory for the residual parts of the reduced Helmholtz free energy of the pure components.
- The reducing functions have to allow for the description of both binary mixtures and multicomponent mixtures, as the reducing functions of the new equation of state for natural gases and other mixtures are adjusted to data of binary mixtures and, therefore, contain binary parameters.
- The mathematical form of the reducing functions has to be chosen in such a way that a reasonable conversion of the parameters is achieved upon rearranging the indices of the mixture components[31].
- The use of a functional form that is flexible enough to describe both symmetric and asymmetric shapes respecting equimolar composition (see Fig. 5.1) is required.
- The mathematical characteristics of the used reducing functions have to assure physically reasonable values for derived thermodynamic properties and their derivatives with respect to mixture pressure, density, temperature, and composition.

The mathematical structures used for the reducing functions of the models reported in the literature differ. Tillner-Roth (1993) used a quadratic structure for the description of binary mixtures according to

$$Y_{\mathrm{r}}(\bar{x}) = x_1^2\, Y_{\mathrm{c},1} + x_2^2\, Y_{\mathrm{c},2} + 2x_2\left(1 - x_2^{\beta_Y}\right)\zeta_{Y,12}, \tag{5.8}$$

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[31] For instance, a parameter γ_{ij} with $\gamma_{ij} = -\gamma_{ji}$ would be desirable. When rearranging the indices in the reducing functions of Lemmon (1996), the reformulation of the structure of the functions is required. This characteristic is problematical for the user and, furthermore, not reasonable under theoretical aspects.

where Y corresponds to either the molar volume v or the temperature T. Consequently, the reducing function Y_{r} corresponds to either the reciprocal of the reducing function for the mixture density $1/\rho_{\mathrm{r}}$ or the reducing function for the mixture temperature T_{r}. Lemmon (1996) used reducing functions based on a linear structure for the description of multi-component mixtures:

$$Y_{\mathrm{r}}(\bar{x}) = \sum_{i=1}^{N} x_i \, Y_{\mathrm{c},i} + \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} x_i^{\beta_{Y,ij}} x_j \, \zeta_{Y,ij} \,. \tag{5.9}$$

When rearranging the indices of the mixture components, the problems mentioned above occur. Aside from the adjustable parameter ζ, both mathematical forms use an adjustable exponent β, which is the exponent of a mole fraction of a certain mixture component, to realise asymmetric shapes of the functions respecting equimolar composition. In general, the use of noninteger exponents for composition variables (i.e. the mole fractions of the mixture components) of mixing rules is problematic [see Mathias *et al.* (1991)]. To avoid infinite slopes of the reducing functions for $x_i \to 0$ (i.e. small mole fractions of one component in a binary mixture and of one or several components in a multi-component mixture such as natural gas), β must never be smaller than zero for Eq. (5.8) and always be greater than unity for Eq. (5.9). Otherwise, in phase equilibrium calculations, the use of such exponents would lead to, for example, infinite fugacities along with physically wrong derivatives of these with respect to temperature, pressure, and composition. Therefore, reducing functions that contain such exponents should not be used in formulations for multi-component mixtures. Equations (5.8) and (5.9) are equivalent when the parameter β is not used.

The problem described above arises for the binary mixture carbon dioxide–propane in the model of Lemmon (1996). Thus, Lemmon and Jacobsen (1999) introduced a second exponent in Eq. (5.9) which is the exponent of the second mole fraction. In recent models reported for binary and ternary mixtures, no asymmetric behaviour of the reducing functions is considered by the authors [e.g. Lemmon *et al.* (2000), Miyamoto and Watanabe (2003), Lemmon and Jacobsen (2004)]. Such a feature is not necessarily needed for systems with small mixing effects. However, the use of asymmetric shapes significantly improves the accuracy of a fundamental equation in the description of the thermodynamic properties of mixtures, especially for well-measured mixtures.

Therefore, Klimeck (2000) introduced a new class of reducing functions containing an asymmetric expression proposed by Tillner-Roth (1998) which overcomes the dilemma mentioned above. The adjustable parameters of the new reducing functions, which are also used for the mixture model developed in this work, are not restricted to certain ranges of value (i.e. they can be negative or positive). The respective reducing functions for the mixture density and temperature can be written as

$$\frac{1}{\rho_{\mathrm{r}}(\bar{x})} = \sum_{i=1}^{N}\sum_{j=1}^{N} x_i x_j\, \beta_{v,ij}\, \gamma_{v,ij} \frac{x_i + x_j}{\beta_{v,ij}^2\, x_i + x_j} \frac{1}{8}\left(\frac{1}{\rho_{\mathrm{c},i}^{1/3}} + \frac{1}{\rho_{\mathrm{c},j}^{1/3}}\right)^3 \tag{5.10}$$

and

$$T_{\mathrm{r}}(\bar{x}) = \sum_{i=1}^{N}\sum_{j=1}^{N} x_i x_j\, \beta_{T,ij}\, \gamma_{T,ij} \frac{x_i + x_j}{\beta_{T,ij}^2\, x_i + x_j} \left(T_{\mathrm{c},i} \cdot T_{\mathrm{c},j}\right)^{0.5}. \tag{5.11}$$

These functions are based on quadratic mixing rules and with that they are reasonably connected to physically well-founded mixing rules. The two adjustable parameters in the reducing functions consider the deviation between the behaviour of the real mixture and the one resulting from the combining rules for the critical parameters of the pure components. The two binary parameters β and γ [$\beta_{v,ij}$ and $\gamma_{v,ij}$ in Eq. (5.10), and $\beta_{T,ij}$ and $\gamma_{T,ij}$ in Eq. (5.11)] allow for arbitrary symmetric and asymmetric shapes of the reducing functions respecting equimolar composition as exemplified in Fig. 5.1. The asymmetric composition dependence is based on the approach for the excess Gibbs function of van Laar:

$$G^{\mathrm{E}} = x_1 x_2 \frac{A \cdot B}{A\, x_1 + B\, x_2}; \tag{5.12}$$

see Tillner-Roth (1998) for further details. The numerator $x_i + x_j$ in the reducing functions [Eqs. (5.10) and (5.11)] only affects multi-component mixtures and ensures that terms with identical indices smoothly connect to the product $x_i x_i$ for which $\beta_{v,ii} = \beta_{T,ii} = 1$.

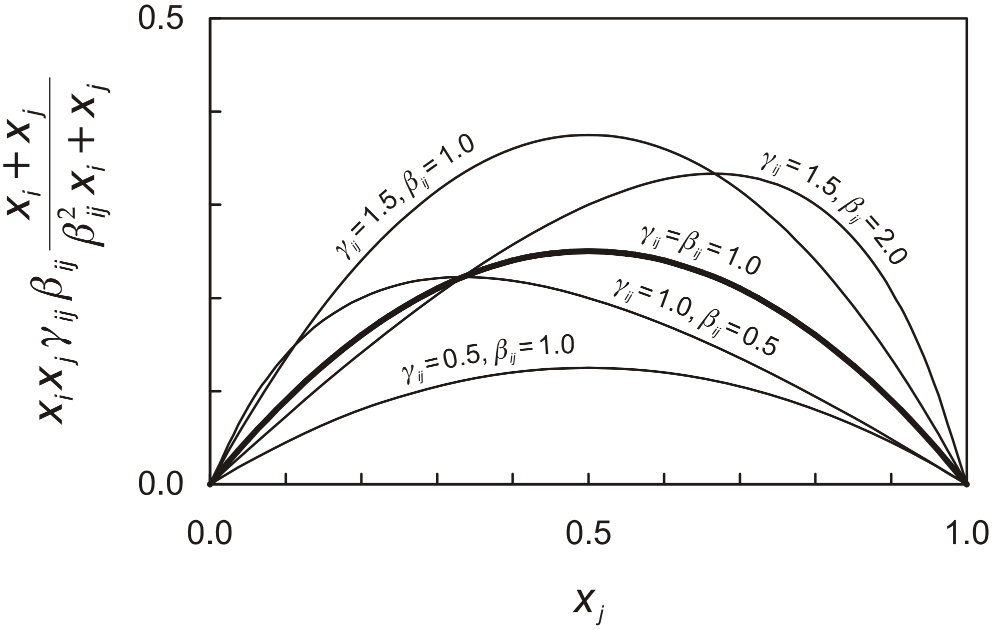

Fig. 5.1 Different symmetric and asymmetric shapes respecting equimolar composition of the reducing functions used for the new mixture model for selected values of the binary parameters β and γ in Eqs. (5.10) and (5.11).

In contrast to Eqs. (5.8) and (5.9), the reducing functions according to Eqs. (5.10) and (5.11) ensure physically reasonable shapes of the functions for any value of their parameters. To ensure that the numbering of mole fractions is symmetric, the following relations have to be obeyed:

$$\gamma_{v,ij} = \gamma_{v,ji},\ \gamma_{T,ij} = \gamma_{T,ji} \quad \text{and} \quad \beta_{v,ij} = 1/\beta_{v,ji},\ \beta_{T,ij} = 1/\beta_{T,ji}. \tag{5.13}$$

When all binary parameters of Eqs. (5.10) and (5.11) are set to unity, the reducing functions with adjustable parameters turn into a quadratic mixing rule using the respective combining rules for the critical parameters of the pure components according to Lorentz and Berthelot:

$$\frac{1}{\rho_{\mathrm{c},ij}} = \frac{1}{8}\left(\frac{1}{\rho_{\mathrm{c},i}^{1/3}} + \frac{1}{\rho_{\mathrm{c},j}^{1/3}}\right)^3, \tag{5.14}$$

$$T_{\mathrm{c},ij} = \left(T_{\mathrm{c},i} \cdot T_{\mathrm{c},j}\right)^{0.5}. \tag{5.15}$$

Therefore, the mixture model developed in this work can easily be extended to components for which poor or even no experimental information is available for fitting the binary parameters of the reducing functions. Moreover, other combining rules can be used instead of Eqs. (5.14) and (5.15) to achieve different shapes of the reducing functions. The use, for example, of the combining rule

$$T_{\mathrm{c},ij} = \frac{1}{2}\left(T_{\mathrm{c},i} + T_{\mathrm{c},j}\right) \tag{5.16}$$

in Eq. (5.11) results in a linear reducing function $T_{\mathrm{r}} = x_1\, T_{\mathrm{c},1} + x_2\, T_{\mathrm{c},2}$ for a binary mixture. Linear combining rules according to Eq. (5.16) are used in the new mixture model for certain binary subsystems which are characterised by poor data[32] (see Sec. 7.10). The linear combining rule is applied for such binary systems through the use of values for the parameters $\gamma_{v,ij}$ and $\gamma_{T,ij}$ calculated from the following conversions:

$$\gamma_{v,ij} = 4\frac{\left(\dfrac{1}{\rho_{\mathrm{c},i}} + \dfrac{1}{\rho_{\mathrm{c},j}}\right)}{\left(\dfrac{1}{\rho_{\mathrm{c},i}^{1/3}} + \dfrac{1}{\rho_{\mathrm{c},j}^{1/3}}\right)^3} \quad \text{and} \quad \gamma_{T,ij} = \frac{1}{2}\frac{\left(T_{\mathrm{c},i} + T_{\mathrm{c},j}\right)}{\left(T_{\mathrm{c},i} \cdot T_{\mathrm{c},j}\right)^{0.5}} \tag{5.17}$$

with $\beta_{v,ij}$ and $\beta_{T,ij}$ set to one. Using the results of Eq. (5.17) instead of unity, no additional numerical effort is required as the structure of Eqs. (5.10) and (5.11) is maintained for all binary subsystems. The use of different combining rules is superfluous when data are used to adjust the binary parameters.

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[32] For example, detailed investigations concerning the use of different combining rules performed in this work showed that linear combining rules are, in general, more suitable for the description of the thermodynamic properties of binary hydrocarbon mixtures than those of Lorentz and Berthelot.

The predictive capability of a multi-fluid approximation based on accurate equations of state in the form of fundamental equations for each mixture component and the new reducing functions given above was investigated in detail for the description of various thermodynamic properties in this work and preceding studies [Klimeck (2000), Kunz (2000)]. These investigations proved the suitability of the new reducing functions according to Eqs. (5.10) and (5.11) for the development of the new equation of state for natural gases and other mixtures.

5.2.1 The Invariance Condition and Alternative Reducing Functions

Aside from the accurate fundamental equations for the mixture components, the new wide-range equation of state for natural gases, similar gases, and other mixtures presented in this work is based on correlation equations developed for binary mixtures. The behaviour of multi-component mixtures depends on the form of the reducing functions for the mixture density and temperature according to Eqs. (5.10) and (5.11) (double summation over all binary subsystems). The restriction to binary reducing equations and the simple extension to multi-component mixtures leads, however, to a loss in accuracy for the prediction of the thermodynamic properties of multi-component mixtures.

The restriction to binary reducing equations is unavoidable due to the comparatively poor data available for ternary, quaternary, and other multi-component mixtures. Consequently, a more accurate description of the properties of multi-component mixtures can only be realised by minimising the loss in accuracy when extending from binary to multi-component mixtures. In mixture models based on multi-fluid approximations, the mathematical structure of the reducing functions has a large influence on this loss in accuracy.

The suitability of a mathematical structure for the extension from binary to multi-component mixtures is connected to certain physically founded conditions. Such a condition, namely the invariance condition, was reported by Michelsen and Kistenmacher (1990)[33] [see also Mathias *et al.* (1991) and Avlonitis *et al.* (1994)]. The authors state that mixture parameters calculated from mixing rules have to be invariant concerning the partitioning of a component into a number of identical subcomponents. This requirement must also be valid for the composition-dependent parameters of equations of state for mixtures. The invariance condition is, however, not fulfilled for the reducing functions used in the new mixture model and those of all other existing models based on multi-fluid approximations which contain expressions for modelling asymmetric shapes with respect to the equimolar composition.

A solution to this problem is based on a mixing rule suggested by Mathias *et al.* (1991) and was proposed by Klimeck (2000) for the reducing functions of multi-fluid approximations.

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[33] Aside from the invariance condition, an additional problem, which is called the "dilution" effect, was investigated by the authors and for the mixture model developed in this work (see Sec. 7.12.2).

Taking into account the structure of this mixing rule, the corresponding reducing functions for density and temperature were introduced in this work for the development of a second (alternative) mixture model according to

$$Y_{\mathrm{r}}(\bar{x}) = \sum_{i=1}^{N}\sum_{j=1}^{N} x_i x_j \, \phi_{Y,ij} \, Y_{\mathrm{c},ij} + \sum_{i=1}^{N} x_i \left(\sum_{j=1}^{N} x_j \, \lambda_{Y,ij}^{1/3} \, Y_{\mathrm{c},ij}^{1/3} \right)^3 , \tag{5.18}$$

where Y corresponds to either the molar volume v or the temperature T, and ϕ and λ are adjustable binary parameters. The very flexible structure of Eq. (5.18) enables asymmetric shapes and the values calculated for $Y_{\mathrm{r}}(\bar{x})$ are invariant when a mixture component is divided in two or more pseudo-components. Further details on the use of these alternative reducing functions and the developed alternative mixture model are provided in Sec. 7.12.

According to Michelsen and Kistenmacher (1990), these theoretical considerations are of practical relevance concerning, for example, mixtures containing very similar components. Therefore, detailed investigations of the problem of invariance regarding the new mixture model along with the suitability of the alternative reducing functions with respect to their use in mixture models based on multi-fluid approximations were performed in this work. The ideas and conclusions of these investigations are given in Sec. 7.12.4.

5.3 Departure Functions

The concept of a departure function $\Delta\alpha^{\mathrm{r}}(\delta,\tau,\bar{x})$ for the description of the behaviour of nonideal mixtures according to Eq. (5.7) was independently developed by Tillner-Roth (1993) and Lemmon (1996). The purpose of this function is to further improve the accuracy of the multi-fluid mixture model in the description of thermodynamic properties when fitting the parameters of the reducing functions to accurate experimental data is not sufficient.

As mentioned above, the departure function is in general of minor importance for the residual behaviour of the mixture as it only describes an additional small residual deviation to the real mixture behaviour. The development of such a function is associated with considerable effort which is, however, necessary to fulfil the high demands on the accuracy of the new mixture model in the description of the thermodynamic properties of natural gases and other mixtures.

5.3.1 Binary Specific Departure Functions

Originally, the departure function developed by Tillner-Roth (1993) was designed to describe the behaviour of individual binary mixtures for which a large amount of accurate experimental data are available. Such a binary specific departure function can be written in the form

$$\Delta\alpha^{\mathrm{r}}(\delta,\tau,\bar{x}) = f^{\Delta}(x_1,x_2)\cdot\alpha_{12}^{\mathrm{r}}(\delta,\tau). \tag{5.19}$$

In Eq. (5.19) the composition dependence in the form of the factor f^{Δ} is clearly separated from a function only depending on the reduced mixture density δ and the inverse reduced mixture temperature τ. For a given composition dependence, the structure of the function $\alpha_{12}^{\mathrm{r}}(\delta,\tau)$ which yields the best representation of the thermodynamic properties of the mixture can be determined through the use of suitable structure optimisation procedures (see Sec. 4.4.2). The composition-dependent factor f^{Δ} has to equal zero for a pure component.

5.3.2 Generalised Departure Functions

The model of Lemmon and Jacobsen (1999) was developed to describe the thermodynamic properties of multi-component mixtures. To achieve a sufficiently accurate representation, Lemmon and Jacobsen (1999) also used a departure function. The structure of this function is similar to the one of the binary specific function of Tillner-Roth (1993), but generalised for all considered binary systems in order to achieve an accurate description for a number of well-measured mixtures along with mixtures with limited data sets. Such a generalised departure function is given by

$$\Delta\alpha^{\mathrm{r}}(\delta,\tau,\bar{x}) = \sum_{i=1}^{N-1}\sum_{j=i+1}^{N} x_i x_j F_{ij}\,\alpha_{\mathrm{gen}}^{\mathrm{r}}(\delta,\tau)\,. \tag{5.20}$$

Similar to Eq. (5.19), the composition dependence in Eq. (5.20) is separated from a function which only depends on reduced mixture density δ and inverse reduced mixture temperature τ. This structure can also be determined by using structure-optimisation methods. This structure is identical for all binary mixtures according to Eq. (5.20), only the parameter F_{ij} is binary specific. The structure of the composition-dependent factor

$$f^{\Delta} = x_i x_j F_{ij} \tag{5.21}$$

does not necessarily have to be a quadratic composition dependence. Under a smooth connection to the pure components, any arbitrary structure can be used which may, for example, result in asymmetric shapes with respect to the equimolar composition.

5.3.3 The Departure Functions of the New Mixture Model

Binary specific and generalised departure functions have their respective advantages and disadvantages. In general, binary specific departure functions enable a more accurate description of the thermodynamic properties of mixtures than generalised formulations, which is an important feature concerning the high demands on the accuracy of the new equation of state for natural gases and other mixtures. To develop a binary specific departure function a large amount of accurate experimental data of thermal and caloric properties is required. On the other hand, generalised departure functions can be used for binary mixtures characterised by poor or limited data. Experimental information for a number of binary mixtures can be used for the development of generalised formulations.

The ideas mentioned above were taken into account for the development of departure functions for the new mixture model. The accurate description of binary mixtures consisting of the main natural gas components (see Table 4.2) is of fundamental importance for the accuracy in the description of thermal and caloric properties of natural gases and similar mixtures. Therefore, accurate binary specific departure functions for mixtures of these components were developed.

The data situation for many binary systems does not allow the development of binary specific departure functions for these systems. Hence, a generalised departure function was developed. Binary mixtures characterised by very limited data or of minor importance regarding the composition of natural gases due to the small mole fractions of the respective components can be considered without a departure function, i.e. $\Delta\alpha_{ij}^{\mathrm{r}} = 0$.

In the new mixture model for natural gases, similar gases, and other mixtures developed in this work, the departure function $\Delta\alpha^{\mathrm{r}}$ of multi-component mixtures is the sum of all binary specific and generalised departure functions of the involved binary subsystems:

$$\Delta\alpha^{\mathrm{r}}(\delta,\tau,\bar{x}) = \sum_{i=1}^{N-1}\sum_{j=i+1}^{N}\Delta\alpha_{ij}^{\mathrm{r}}(\delta,\tau,\bar{x}) \tag{5.22}$$

with

$$\Delta\alpha_{ij}^{\mathrm{r}}(\delta,\tau,\bar{x}) = x_i x_j F_{ij}\,\alpha_{ij}^{\mathrm{r}}(\delta,\tau). \tag{5.23}$$

The parameter F_{ij} equals unity for binary specific departure functions and is fitted for binary mixtures using a generalised departure function, where $\Delta\alpha_{ij}^{\mathrm{r}} = \Delta\alpha_{\mathrm{gen}}^{\mathrm{r}}$. This structure of the departure function for the multi-component mixture was firstly used by Klimeck (2000) for the preliminary equation of state for natural gases.

The new equation of state contains a total of seven binary specific departure functions and one generalised departure function for eight binary hydrocarbon mixtures (see Table 7.16). The functions $\alpha_{ij}^{\mathrm{r}}(\delta,\tau)$ were developed using procedures based on the fitting and structure-optimisation methods described in Chap. 4, see also Sec. 5.5. As the mixture model is not limited to the number of binary specific and generalised formulations available here, the extension of the model by developing further departure functions for, for example, binary mixtures of air components and mixtures containing carbon dioxide, is considered for the near future (see also Chap. 9). Moreover, the extension of the developed generalised formulation for important binary hydrocarbon mixtures by adding further hydrocarbons seems to be reasonable. Nevertheless, for natural gases and similar mixtures this will lead to only minor revisions as the accuracy of the mixture model presented in this work already fulfils the defined requirements (see Chap. 3, Sec. 7.13, and Chap. 8).

The considerations presented in this section led to the basic structure of the new equation of state for natural gases, similar gases, and other mixtures as a multi-fluid approximation. In Sec. 7.1, the exact structure resulting from the investigations of this work is introduced ahead of the detailed description of the development of the different binary equations (see Sec. 7.10).

The basic structure of the new mixture model agrees with the one for seven natural gas components used by Klimeck (2000). But due to physically incorrect behaviour in calculated vapour-liquid equilibrium states, a new functional form for α_{ij}^{r} was introduced in this work and all of the binary equations containing a departure function had to be redeveloped (see Secs. 7.10 and 7.11) resulting in a completely revised, fundamentally improved formulation.

5.3.4 Functional Forms for α_{ij}^{r}

Similar to the structure of the residual part of the Helmholtz free energy of a pure substance equation of state, the structure of the equation for $\alpha_{ij}^{\mathrm{r}}(\delta,\tau)$ of a binary specific or generalised departure function [see Eq. (5.23)] can be determined by using modern structure-optimisation methods (see Chap. 4). A survey of the type of terms used for the departure functions of mixture models reported in the literature is given in Table 5.2, see also Table 5.1.

The departure functions of the mixture models reported in the literature are mostly composed of the two basic functional forms, namely the polynomial terms and polynomial terms in combination with exponential terms according to Eqs. (4.24) and (4.25), as shown in Table 5.2. These functional forms are used in many formulations for the residual Helmholtz free energy of modern wide-range pure substance equations of state as described in Sec. 4.6. For example, the generalised departure functions developed by Lemmon and Jacobsen (1999) and Lemmon *et al.* (2000) only consist of pure polynomial terms. Lemmon and Jacobsen (2004) only used polynomial terms in combination with exponential terms and the departure functions developed by Tillner-Roth and Friend (1998) and Klimeck (2000) are composed of both functional forms according to

$$\alpha_{ij}^{\mathrm{r}}(\delta,\tau) = \sum_{k=1}^{K_{\mathrm{Pol},ij}} n_{ij,k}\,\delta^{d_{ij,k}}\,\tau^{t_{ij,k}} + \sum_{k=K_{\mathrm{Pol},ij}+1}^{K_{\mathrm{Pol},ij}+K_{\mathrm{Exp},ij}} n_{ij,k}\,\delta^{d_{ij,k}}\,\tau^{t_{ij,k}}\,e^{-\delta^{c_{ij,k}}}\,. \qquad (5.24)$$

Equation (5.24) is of the same structure as the residual part of the dimensionless Helmholtz free energy of all pure substance equations of state used for the components considered in the developed mixture model [see Eq. (4.27)]. The number of terms used in the reported mixture formulations varies from two to 14 (see Table 5.2). Usually, values for the density exponent $c_{ij,k}$ of the exponential expression in Eq. (5.24) range from $c_{ij,k} = 1$ to $c_{ij,k} = 3$. In the preliminary mixture model for natural gases, Klimeck (2000) used density exponents up to $c_{ij,k} = 6$ along with a bank of terms very similar to the one used for optimising the structure of the new class of pure substance equations of state for the main natural gas components (see Sec. 4.8).

The use of such banks of terms for determining the structures of the residual part of the Helmholtz free energy of multi-parameter equations of state for pure substances has proven worthly for the development of such formulations. Aside from the ordinary polynomial terms, the polynomial terms in combination with exponential terms in the extended form (see Sec. 4.6.2) are considered to be the standard functional forms of modern wide-range pure substance equations of state since Schmidt and Wagner (1985) introduced such exponential functions.

Table 5.2 Survey of the type of terms used for the departure functions of existing mixture models based on multi-fluid approximations explicit in the Helmholtz free energy

Reference	Type of departure function[a]	Number of terms used for the departure functions			Range of exponent $c_{ij,k}$ [d]
		total	polynomial[b]	exponential[c]	
Tillner-Roth (1993)	B	5[e]	3	–	–
Tillner-Roth & Friend (1998)	B	14	1	13	1 – 2
Tillner-Roth *et al.* (1998)	B	6 – 8	1 – 2	4 – 6	1 – 2
Lemmon & Jacobsen (1999)	G	10	10	–	–
Lemmon *et al.* (2000)	G	2	2	–	–
Klimeck (2000)	B, G	5 – 9	1 – 3	2 – 7	1 – 6
Miyamoto & Watanabe (2003)	G	4	2	2	1
Lemmon & Jacobsen (2004)	B, G	4 – 8	–	4 – 8	1 – 3

[a] "B" and "G" indicate binary specific and generalised departure functions.

[b] Number of polynomial terms according to Eq. (4.24).

[c] Number of polynomial terms in combination with exponential terms according to Eq. (4.25).

[d] Range of values used for the density exponent $c_{ij,k}$ of the exponential expression in Eq. (5.24), i.e. of the exponential term $\exp(-\delta^{c_{ij,k}})$ [see also Eq. (4.25)].

[e] Two terms of the total number of terms contain logarithmic functions in δ and τ.

Nevertheless, no investigations have been reported yet concerning the suitability of these functional forms for mixture models based on multi-fluid approximations. However, it can be imagined that a functional form which describes the difference between the ideal and real behaviour of a pure fluid, i.e. the residual behaviour including, for example, the vapour-liquid equilibrium, is not appropriate for the description of an additional residual deviation in the real mixture behaviour as needed for a departure function. Driven by the need for a functional term which enables both the accurate description of the thermal and caloric properties of binary and multi-component mixtures within the uncertainty of the best measured data and a reasonable behaviour of the mixture model in regions characterised by poor data, a comprehensive investigation regarding the suitability of exponential functions was performed for the first time in this work. As a result of these investigations, a new functional form for use in the bank of terms for the development of departure functions of binary mixtures was introduced. This term can be written as

$$\alpha^{\mathrm{r}}_{ij,k} = n_{ij,k}\, \delta^{d_{ij,k}}\, \tau^{t_{ij,k}}\, e^{-\eta_{ij,k}\left(\delta-\varepsilon_{ij,k}\right)^2 - \beta_{ij,k}\left(\delta-\gamma_{ij,k}\right)}, \tag{5.25}$$

where $\eta_{ij,k}$, $\varepsilon_{ij,k}$, $\beta_{ij,k}$, and $\gamma_{ij,k}$ are adjustable parameters used to model the shape of the term. Further details and results of the investigations and the manner of use of the new term for the mixture model are given in Sec. 7.11.

5.4 The Calculation of Thermodynamic Properties Derived from the Helmholtz Free Energy of Mixture Models Based on Multi-Fluid Approximations

The Helmholtz free energy of a mixture as a function of density, temperature, and the mixture composition is one of the four fundamental forms of an equation of state. Similar to fundamental equations for pure substances, all thermodynamic properties of a mixture can be obtained by combining various derivatives of Eq. (5.2). The thermodynamic properties in the homogeneous gas, liquid, and supercritical regions of a mixture are related only to derivatives with respect to density and temperature. Thus, in the homogeneous region, the same basic relations can be applied to both pure substance equations and equations of state for mixtures explicit in the Helmholtz free energy (see also Sec. 4.2). The respective derivatives of Eq. (5.2) with respect to the reduced variables δ and τ are, however, much more complex than those of Eq. (4.2) for a pure substance, as the mixture model is composed of several different correlation equations [see Eqs. (5.3) – (5.7), (5.10), and (5.11)]. In addition, very sophisticated derivatives with respect to mixture composition, namely mole numbers n_i and mole fractions x_i, have to be taken into account for phase equilibrium calculations (see Secs. 5.4.1 and 7.3).

For example, in the homogeneous gas, liquid, and supercritical regions, the pressure p, the enthalpy h, and the entropy s can be determined from the following equations:

$$\frac{p(\delta,\tau,\bar{x})}{\rho R T} = 1 + \delta\alpha^{\mathrm{r}}_{\delta}, \tag{5.26}$$

$$\frac{h(\delta,\tau,\bar{x})}{R T} = 1 + \tau\left(\alpha^{\mathrm{o}}_{\tau} + \alpha^{\mathrm{r}}_{\tau}\right) + \delta\alpha^{\mathrm{r}}_{\delta}, \tag{5.27}$$

$$\frac{s(\delta,\tau,\bar{x})}{R} = \tau\left(\alpha^{\mathrm{o}}_{\tau} + \alpha^{\mathrm{r}}_{\tau}\right) - \alpha^{\mathrm{o}} - \alpha^{\mathrm{r}} \tag{5.28}$$

with α^{o} and α^{r} according to Eqs. (5.6) and (5.7), and

$$\alpha^{\mathrm{r}}_{\delta} = \left(\frac{\partial \alpha^{\mathrm{r}}}{\partial \delta}\right)_{\tau,\bar{x}} = \sum_{i=1}^{N} x_i \left(\frac{\partial \alpha^{\mathrm{r}}_{\mathrm{o}i}(\delta,\tau)}{\partial \delta}\right)_{\tau} + \left(\frac{\partial \Delta\alpha^{\mathrm{r}}(\delta,\tau,\bar{x})}{\partial \delta}\right)_{\tau,\bar{x}}, \tag{5.29}$$

$$\alpha_\tau^{\mathrm{r}} = \left(\frac{\partial \alpha^{\mathrm{r}}}{\partial \tau}\right)_{\delta,\bar{x}} = \sum_{i=1}^{N} x_i \left(\frac{\partial \alpha_{\mathrm{o}i}^{\mathrm{r}}(\delta,\tau)}{\partial \tau}\right)_{\delta} + \left(\frac{\partial \Delta\alpha^{\mathrm{r}}(\delta,\tau,\bar{x})}{\partial \tau}\right)_{\delta,\bar{x}}, \tag{5.30}$$

$$\alpha_\tau^{\mathrm{o}} = \left(\frac{\partial \alpha^{\mathrm{o}}}{\partial \tau}\right)_{\delta,\bar{x}} = \left(\frac{\partial T}{\partial \tau}\right)_{\bar{x}} \cdot \sum_{i=1}^{N} x_i \left(\frac{\partial \alpha_{\mathrm{o}i}^{\mathrm{o}}(\rho,T)}{\partial T}\right)_{\rho}; \tag{5.31}$$

see Table 7.5 for the derivatives of α^{o} and α^{r} with respect to the reduced mixture variables δ and τ for the new mixture model. Further relations between Eq. (5.2) (and its derivatives) and the thermodynamic properties considered in many technical applications are listed in Tables 7.1 – 7.3.

To ensure that the mixture is homogeneous, a stability investigation by means of, for example, the tangent-plane-distance method [e.g. Michelsen (1982a)], has to be performed. A description of the stability analysis procedure applied in this work is given in Sec. 7.5.1. This procedure is in general not necessary for the calculation of the thermodynamic properties of pure substances due to the existing accurate auxiliary equations for properties on the phase boundary (see Sec. 4.2).

As mentioned before, the calculation of phase equilibrium properties of mixtures requires a considerably more complex and time-consuming effort compared to pure substances. This happens because of the larger number of variables along with the larger number of phase equilibrium conditions resulting from this, and because of the very sophisticated derivatives with respect to mixture composition. Furthermore, the number of equilibrium phases is usually not known in advance. Aside from the ordinary vapour-liquid equilibrium, further phase equilibria, such as liquid-liquid, vapour-liquid-liquid, and other multi-phase equilibria, may occur when dealing with mixtures. In contrast to the pure substances, in general, no accurate auxiliary equations are available to determine the initial estimates required for the iterative solution of the resulting set of equations. To verify that the solution for an equilibrium mixture is stable, the thermodynamic state function involved in the calculation, e.g. the total (or molar) Gibbs free energy of the overall system for a pT flash calculation, has to be at its global minimum[34]. Thus, to ascertain that the derived minimum is the global minimum, a stability analysis has to be performed as well.

5.4.1 The Calculation of Vapour-Liquid Equilibrium Properties

Thermodynamic equilibrium between two or more coexisting phases exists when neither the net flux of heat, momentum, nor material is exchanged across the phase boundary. Consequently, temperature, pressure, and the chemical potentials μ_i of all components i have to be equal in all phases. For the common two-phase vapour-liquid equilibrium of a non-

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[34] In this context, for instance, the total Gibbs free energy is just the energy of a state point, and the overall Gibbs free energy would be the total energy of all the states (phases) in a system.

reacting mixture consisting of N components, the following phase equilibrium conditions must be satisfied:

- equality of temperature $$T' = T'' = T\,, \tag{5.32}$$
- equality of pressure $$p' = p'' = p_{\mathrm{s}}\,, \tag{5.33}$$
- equality of chemical potentials $$\mu_i' = \mu_i''\,, \quad i = 1, 2, ..., N. \tag{5.34}$$

The chemical potential μ_i equals the partial molar Gibbs free energy $\hat{g}_i$ of component i and is related to the Helmholtz free energy of a mixture according to

$$\mu_i = \left(\frac{\partial A}{\partial n_i}\right)_{T,V,n_j}, \tag{5.35}$$

where V is the total volume, neither the molar nor the specific volume, and n_j signifies that all mole numbers are held constant except n_i. Substituting $A = nRT\alpha$ and $\alpha = \alpha^{\mathrm{o}} + \alpha^{\mathrm{r}}$ [see Eq. (5.2)] in Eq. (5.35) results in

$$\frac{\mu_i}{RT} = \frac{1}{RT}\left(\frac{\partial A}{\partial n_i}\right)_{T,V,n_j} = \left(\frac{\partial n\alpha^{\mathrm{o}}}{\partial n_i}\right)_{T,V,n_j} + \left(\frac{\partial n\alpha^{\mathrm{r}}}{\partial n_i}\right)_{T,V,n_j}. \tag{5.36}$$

The partial derivative of $n\alpha^{\mathrm{o}}$ with respect to the mole number n_i of component i can be determined from Eq. (5.6) resulting in

$$\left(\frac{\partial n\alpha^{\mathrm{o}}}{\partial n_i}\right)_{T,V,n_j} = \alpha_{\mathrm{o}i}^{\mathrm{o}}(\rho, T) + 1 + \ln x_i, \tag{5.37}$$

where $\alpha_{\mathrm{o}i}^{\mathrm{o}} = a_{\mathrm{o}i}^{\mathrm{o}}/(RT)$ with $a_{\mathrm{o}i}^{\mathrm{o}}(\rho, T)$ similar to Eq. (4.13). By successively inserting Eqs. (5.37) and (5.36) in Eq. (5.34), it finally leads to

$$\ln(x_i'\rho') + \left(\frac{\partial n\alpha^{\mathrm{r}}(\delta', \tau', \bar{x}')}{\partial n_i}\right)_{T,V,n_j} = \ln(x_i''\rho'') + \left(\frac{\partial n\alpha^{\mathrm{r}}(\delta'', \tau'', \bar{x}'')}{\partial n_i}\right)_{T,V,n_j}, \quad i = 1, 2, ..., N, \tag{5.38}$$

where x_i' is the mole fraction of component i in the liquid phase and x_i'' is the mole fraction of component i in the vapour phase.

For the calculation of phase equilibria, the fugacity f_i and the fugacity coefficient φ_i of component i are often used instead of the chemical potential. Equation (5.34) can then be replaced with one of the following equations:

$$f_i' = f_i''\,, \quad i = 1, 2, ..., N, \tag{5.39}$$

$$\varphi_i'/\varphi_i'' = x_i''/x_i'\,, \quad i = 1, 2, ..., N. \tag{5.40}$$

The ratio of x_i'' over x_i' is defined as the K-factor of component i:

$$K_i = x_i''/x_i'\,. \tag{5.41}$$

The fugacity f_i and fugacity coefficient φ_i of component i are related to Eq. (5.2) by

$$f_i = x_i \rho RT \exp\left(\frac{\partial n\alpha^{\mathrm{r}}}{\partial n_i}\right)_{T,V,n_j} \tag{5.42}$$

and

$$\ln \varphi_i = \left(\frac{\partial n\alpha^{\mathrm{r}}}{\partial n_i}\right)_{T,V,n_j} - \ln Z. \tag{5.43}$$

For each of the equations describing the material equilibrium [Eqs. (5.34) and (5.38) – (5.40)], the determination of the partial derivative

$$\left(\frac{\partial n\alpha^{\mathrm{r}}}{\partial n_i}\right)_{T,V,n_j} = \alpha^{\mathrm{r}} + n\left(\frac{\partial \alpha^{\mathrm{r}}}{\partial n_i}\right)_{T,V,n_j} \tag{5.44}$$

is required. From Eq. (5.44) follows that the derivative of α^{r} [see Eq. (5.7)] with respect to the mole number n_i of component i has to be calculated at constant temperature T, constant volume V, and constant n_j with $j \neq i$. Although this relation appears to be simple, it is difficult to apply as the reduced mixture variables $\delta = \delta(\bar{x})$ and $\tau = \tau(\bar{x})$ of α^{r} also depend on the mixture composition. The differential of $\alpha^{\mathrm{r}}(\delta,\tau,\bar{x})$ with respect to n_i can be transposed into the following equation:

$$n\left(\frac{\partial \alpha^{\mathrm{r}}}{\partial n_i}\right)_{T,V,n_j} = \left(\frac{\partial \alpha^{\mathrm{r}}}{\partial \delta}\right)_{\tau,\bar{x}} \cdot n\left(\frac{\partial \delta}{\partial n_i}\right)_{T,V,n_j} + \left(\frac{\partial \alpha^{\mathrm{r}}}{\partial \tau}\right)_{\delta,\bar{x}} \cdot n\left(\frac{\partial \tau}{\partial n_i}\right)_{T,V,n_j} + n\left(\frac{\partial \alpha^{\mathrm{r}}}{\partial n_i}\right)_{\delta,\tau,n_j}, \tag{5.45}$$

where

$$n\left(\frac{\partial \alpha^{\mathrm{r}}}{\partial n_i}\right)_{\delta,\tau,n_j} = \sum_{k=1}^{N}\left(\frac{\partial \alpha^{\mathrm{r}}}{\partial x_k}\right)_{\delta,\tau,x_j} \cdot n\left(\frac{\partial x_k}{\partial n_i}\right)_{T,V,n_j} = \left(\frac{\partial \alpha^{\mathrm{r}}}{\partial x_i}\right)_{\delta,\tau,x_j} - \sum_{k=1}^{N} x_k \left(\frac{\partial \alpha^{\mathrm{r}}}{\partial x_k}\right)_{\delta,\tau,x_j}, \tag{5.46}$$

$$n\left(\frac{\partial \delta}{\partial n_i}\right)_{T,V,n_j} = \delta - \frac{\delta}{\rho_{\mathrm{r}}} \cdot n\left(\frac{\partial \rho_{\mathrm{r}}}{\partial n_i}\right)_{n_j} = \delta - \frac{\delta}{\rho_{\mathrm{r}}}\left[\left(\frac{\partial \rho_{\mathrm{r}}}{\partial x_i}\right)_{x_j} - \sum_{k=1}^{N} x_k \left(\frac{\partial \rho_{\mathrm{r}}}{\partial x_k}\right)_{x_j}\right], \tag{5.47}$$

$$n\left(\frac{\partial \tau}{\partial n_i}\right)_{T,V,n_j} = \frac{\tau}{T_{\mathrm{r}}} \cdot n\left(\frac{\partial T_{\mathrm{r}}}{\partial n_i}\right)_{n_j} = \frac{\tau}{T_{\mathrm{r}}}\left[\left(\frac{\partial T_{\mathrm{r}}}{\partial x_i}\right)_{x_j} - \sum_{k=1}^{N} x_k \left(\frac{\partial T_{\mathrm{r}}}{\partial x_k}\right)_{x_j}\right] \tag{5.48}$$

with $\rho_{\mathrm{r}} = \rho_{\mathrm{r}}(\bar{x})$ and $T_{\mathrm{r}} = T_{\mathrm{r}}(\bar{x})$ according to, for example, Eqs. (5.10) and (5.11). Introducing $\alpha_{\delta}^{\mathrm{r}}$ and $\alpha_{\tau}^{\mathrm{r}}$ according to Eqs. (5.29) and (5.30), and

$$\alpha_{x_i}^{\mathrm{r}} = \left(\frac{\partial \alpha^{\mathrm{r}}}{\partial x_i}\right)_{\delta,\tau,x_j} = \alpha_{\mathrm{o}i}^{\mathrm{r}}(\delta,\tau) + \left(\frac{\partial \Delta\alpha^{\mathrm{r}}(\delta,\tau,\bar{x})}{\partial x_i}\right)_{\delta,\tau,x_j}, \tag{5.49}$$

Eq. (5.45) can be rewritten as

$$n\left(\frac{\partial\alpha^{\mathrm{r}}}{\partial n_i}\right)_{T,V,n_j} = \delta\alpha_\delta^{\mathrm{r}}\left[1-\frac{1}{\rho_{\mathrm{r}}}\left[\left(\frac{\partial\rho_{\mathrm{r}}}{\partial x_i}\right)_{x_j}-\sum_{k=1}^{N}x_k\left(\frac{\partial\rho_{\mathrm{r}}}{\partial x_k}\right)_{x_j}\right]\right]$$
$$+\ \tau\alpha_\tau^{\mathrm{r}}\frac{1}{T_{\mathrm{r}}}\left[\left(\frac{\partial T_{\mathrm{r}}}{\partial x_i}\right)_{x_j}-\sum_{k=1}^{N}x_k\left(\frac{\partial T_{\mathrm{r}}}{\partial x_k}\right)_{x_j}\right]$$
$$+\ \alpha_{x_i}^{\mathrm{r}}-\sum_{k=1}^{N}x_k\,\alpha_{x_k}^{\mathrm{r}}\,. \tag{5.50}$$

The respective derivatives of α^{r} [see Eq. (5.7)] with respect to δ, τ, and x_i are given in Table 7.5; those of the reducing functions ρ_{r} and T_{r} used for the new mixture model [see Eqs. (5.10) and (5.11)] are listed in Table 7.10. Even more complex and sophisticated derivatives of Eq. (5.50) with respect to temperature, total volume, composition (n_i and x_i), and the reduced variables δ and τ are required for the iterative solution of the phase equilibrium conditions for flash, phase envelope, and other advanced phase equilibrium calculations (see Sec. 7.3). To enable the development of computing-time saving algorithms, all of the derivatives needed for such applications of the mixture model, even the second derivatives of α^{r} with respect to composition, were determined analytically in this work; for further details see Chap. 7.

Similar to the calculation of phase equilibrium properties of fundamental equations for pure substances, the following equations can be obtained from the equality of temperature and pressure [Eqs. (5.32) and (5.33)]:

$$\frac{p_{\mathrm{s}}}{\rho' RT}=1+\delta'\alpha_\delta^{\mathrm{r}}(\delta',\tau',\bar{x}'), \tag{5.51}$$

$$\frac{p_{\mathrm{s}}}{\rho'' RT}=1+\delta''\alpha_\delta^{\mathrm{r}}(\delta'',\tau'',\bar{x}''). \tag{5.52}$$

Since the two phases of a non-critical mixture are characterised by different compositions resulting in different values for the reducing functions and the corresponding reduced variables, a simple integral criterion which connects all phase equilibrium properties in a single relation such as Eq. (4.11) does not exist for mixtures[35]. Aside from the equality of temperature, pressure, and chemical potentials, further equations resulting from the material balances between the molar amounts of the components in the overall system and the coexisting phases have to be satisfied as secondary conditions according to

$$x_i=(1-\beta)x_i'+\beta x_i'',\quad i=1,2,...,N, \tag{5.53}$$

where the overall vapour fraction is

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[35] The equations that correspond to the Maxwell criterion for pure substances [Eq. (4.11)] for fitting the different correlation equations of multi-fluid mixture models to VLE data of binary mixtures are described in Sec. 5.5.2.

$$\beta = \frac{n''}{n} = \frac{n''}{n' + n''} \tag{5.54}$$

with

$$\sum_{i=1}^{N} x_i = 1, \quad \sum_{i=1}^{N} x_i' = 1, \quad \text{and} \quad \sum_{i=1}^{N} x_i'' = 1. \tag{5.55}$$

Substituting Eq. (5.41) into the material balance equations [Eq. (5.53)] yields

$$x_i' = \frac{x_i}{1 - \beta + \beta K_i} \quad \text{and} \quad x_i'' = \frac{K_i\, x_i}{1 - \beta + \beta K_i}. \tag{5.56}$$

Thus, the phase mole fractions $\bar{x}'$ and $\bar{x}''$ can be calculated from the K-factors, the overall vapour fraction β, and the overall composition $\bar{x}$.

Formulation of a Set of Equations

As described in the sections above, all of the basic relations required for vapour-liquid equilibrium calculations using a mixture model based on a multi-fluid approximation have been derived. A general formulation of the vapour-liquid equilibrium of a non-reacting mixture of N components can be expressed by the following set of nonlinear equations:

$$T' - T_\mathrm{s} = 0, \tag{5.57a}$$

$$T'' - T_\mathrm{s} = 0, \tag{5.57b}$$

$$RT'\rho_\mathrm{r}'(\bar{x}')\delta'\left[1 + \delta'\alpha_\delta^\mathrm{r}(\delta', \tau', \bar{x}')\right] - p_\mathrm{s} = 0, \tag{5.57c}$$

$$RT''\rho_\mathrm{r}''(\bar{x}'')\delta''\left[1 + \delta''\alpha_\delta^\mathrm{r}(\delta'', \tau'', \bar{x}'')\right] - p_\mathrm{s} = 0, \tag{5.57d}$$

$$\ln(x_i'\rho') + \left(\frac{\partial n\alpha^\mathrm{r}(\delta', \tau', \bar{x}')}{\partial n_i}\right)_{T,V,n_j} - \ln(x_i''\rho'') - \left(\frac{\partial n\alpha^\mathrm{r}(\delta'', \tau'', \bar{x}'')}{\partial n_i}\right)_{T,V,n_j} = 0, \quad i = 1, 2, \ldots, N, \tag{5.57e}$$

$$1 - \sum_{i=1}^{N} x_i' = 0, \tag{5.57f}$$

$$1 - \sum_{i=1}^{N} x_i'' = 0, \tag{5.57g}$$

$$(1 - \beta)\, x_i' + \beta\, x_i'' - x_i = 0, \quad i = 1, 2, \ldots, N. \tag{5.57h}$$

With T_s, T', T'', p_s, δ', δ'', $\bar{x}'$, $\bar{x}''$, β, and $\bar{x}$, the set of equations contains $3N + 7$ variables, but only $2N + 6$ equations. Thus, $N + 1$ variables have to be specified.

The above set of equations can be reduced to a smaller set by using the fugacity coefficient equilibrium equations [Eq. (5.40)] along with the equilibrium factors [Eq. (5.41)] according to

$$K_i = \frac{\varphi_i'}{\varphi_i''}, \quad i = 1, 2, ..., N, \tag{5.58}$$

and the following summation of mole fraction relations, the Rachford-Rice equation [Rachford and Rice (1952)]:

$$\sum_{i=1}^{N}(x_i'' - x_i') = \sum_{i=1}^{N} \frac{x_i (K_i - 1)}{1 - \beta + \beta K_i} = 0. \tag{5.59}$$

In combination with the two specification equations used to define the phase equilibrium problem and written in the general form

$$q_1(\bar{x}', \bar{x}'', T, p, \beta) = 0 \quad \text{and} \quad q_2(\bar{x}', \bar{x}'', T, p, \beta) = 0, \tag{5.60}$$

one obtains $N + 3$ equations for the $N + 3$ variables, namely the N K-factors, the vapour fraction β, the temperature T $(= T_s)$, and the pressure p $(= p_s)$. The fugacity coefficients of Eq. (5.58) depend on temperature, pressure, and the phase compositions $\bar{x}'$ and $\bar{x}''$ [see Eq. (5.43)]. The phase compositions are given in terms of the K-factors and β according to Eq. (5.56). Equation (5.60) typically corresponds to fixing two of the independent variables T, p, and β, or, alternatively, fixing one of these variables, e.g. the pressure p, and in addition specifying an overall property of the mixture, such as the total enthalpy H, the total entropy S, or the total volume V (see also Sec. 5.4.3). Since the calculated values of the K-factors frequently span a range of several orders of magnitude and in order to obtain a suitable scaling, it is common to use the logarithm of the K-factors as the independent variables.

Initial Estimates

The iterative solution of Eqs. (5.57a) – (5.57h) requires initial estimates for the variables to be calculated (see Sec. 5.4.3 for brief information on commonly applied numerical procedures). At low pressures ($p < 1$ MPa), where the gas phase of a mixtures behaves nearly ideally, suitable initial estimates for unknown quantities, such as the phase compositions, saturation temperature, and vapour pressure, can be obtained by solving Raoult's law. For higher pressures these initial estimates are not applicable. A customary method employed when no information about the solution is available in advance is the use of the Wilson K-factor expression[36] to generate approximate values of phase properties according to

$$\ln K_i = \ln\left(\frac{p_{c,i}}{p}\right) + 5.373(1 + \omega_i)\left(1 - \frac{T_{c,i}}{T}\right), \tag{5.61}$$

where K_i is the K-factor of component i [see Eq. (5.41)], and $T_{c,i}$, $p_{c,i}$, and ω_i are the critical temperature, the critical pressure, and the acentric factor of component i. The Wilson

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[36] The Wilson K-factor approximation is actually a generalised correlation equation for the vapour pressure of the form $\ln p_s = A - B/T$, fixed at the pure component critical point and at a reduced temperature of $T/T_c = 0.7$, where $\log_{10}(p_s/p_c) = -1 - \omega$.

approximation is usually adequate for calculations of hydrocarbon mixtures, although the *K*-values predicted for components at supercritical conditions can be quite erroneous [see Michelsen and Mollerup (2004)].

For the development and evaluation of the new mixture model, the available experimental data were used as initial estimates. In general, experimental results do not contain the complete information for the required variables in the set of equations. Thus, the remaining quantities have to be estimated.

Approximate values for the saturated liquid and saturated vapour densities are of essential importance. At a given temperature, for a known composition and a given vapour pressure, the corresponding liquid phase or gas phase density can be calculated iteratively from an equation of state analogous to the density calculations in the homogeneous region. The resulting liquid phase density is a suitable initial estimate for the saturated liquid density, and the calculated gas phase density can be used as an estimate for the saturated vapour density.

The Trivial Solution

An important problem associated with the iterative calculation of phase equilibrium properties from equations of state is the potential existence of a solution with identical phase compositions and properties in all phases. Such a trivial solution automatically satisfies Eqs. (5.57a) – (5.57h). The problem is frequently encountered when inadequate initial estimates are used and are particularly magnified for calculations in the critical region. At the critical point of a mixture the vapour and liquid phases have identical compositions, and the equilibrium compositions are nearly equal in the vicinity of the critical point, i.e.

$$x_i' \approx x_i'' \approx x_i . \tag{5.62}$$

Iterative phase equilibrium calculations in this region tend to converge to the trivial solution unless initial estimates of high quality are used.

5.4.2 The Calculation of Liquid-Liquid and Multi-Phase Equilibrium Properties

Since mixture models based on multi-fluid approximations are valid in the extended fluid region, they allow the calculation of fugacity coefficients in the liquid phase. Therefore, they should in principle be suitable to describe equilibria between two liquid phases and also between several vapour and liquid phases. Although (almost) only vapour-liquid equilibrium data were used for the development of the new mixture model for phase equilibrium, the first investigations performed in this work showed that the model is capable of predicting liquid-liquid equilibria (LLE) as well as vapour-liquid-liquid equilibria (VLLE), similar to other commonly applied equations of state such as cubic equations (see also Sec. 7.7.3).

Similar to Eqs. (5.32) – (5.34) the following basic set of equations has to be solved to calculate the multi-phase equilibrium of P coexisting phases of a non-reacting mixture consisting of N components:

- equality of temperature $T^{(1)} = T^{(2)} = ... = T^{(P)}$, (5.63)
- equality of pressure $p^{(1)} = p^{(2)} = ... = p^{(P)}$, (5.64)
- equality of chemical potentials $\mu_i^{(1)} = \mu_i^{(2)} = ... = \mu_i^{(P)}, \quad i = 1, 2, ..., N.$ (5.65)

The iterative solution of these basic equilibrium conditions can be rather complicated for both liquid-liquid and multi-phase equilibrium calculations due to several reasons [see, for example, Michelsen (1986), Michelsen and Mollerup (2004)]. The main difficulties of such calculations are the lack of "natural" initial estimates and the presence of two or more liquid phases with different compositions where more than one component is present in significant amounts. Due to the lack of "natural" initial estimates, the verification of stability may require repeated calculations using different initial estimates. The presence of two or more liquid phases which are composed of several components in substantial amounts requires extensive stability analysis calculations for which it may be difficult to obtain convergence.

5.4.3 Numerical Procedures for Iterative Phase Equilibrium Calculations

As described in the previous sections, the phase equilibrium conditions form a nonlinear set of equations which has to be solved iteratively. For the corresponding iterative procedures, different types of phase equilibrium calculations can be defined which depend on the quantities specified and those to be calculated. The number of variables that can be specified independently is in accordance with the number of degrees of freedom which can be expressed, according to the phase rule of Gibbs, as

$$F = N + 2 - P, \tag{5.66}$$

where F is the number of degrees of freedom, N is the number of components in the system, and P is the number of coexisting phases in the system. The number of degrees of freedom equals the difference between the total number of variables and the number of equilibrium conditions. For the vapour-liquid equilibrium, five common types of VLE calculations typically encountered in technical applications are specified as shown in Table 5.3.

The bubble and dew point calculation types listed in Table 5.3 have in common the respective composition of either the vapour or liquid phase. With the pT flash calculation the equilibrium compositions of both phases are determined for given values of temperature T, pressure p, and overall composition $\bar{x}$. In addition to the phase equilibrium calculation at a specified temperature and pressure, which is the well-known isothermal flash calculation, a number of other flash specifications are of practical importance. Examples of technical relevance are the isenthalpic flash (specification of pressure and enthalpy) and the isentropic flash (specification of pressure and entropy). Additionally, specification of temperature and volume (e.g. storage vessels and pipeline shutdown), and specification of volume and internal energy (e.g. unsteady state operations), are of increasing interest [see Michelsen (1999)].

Table 5.3 Five common types of vapour-liquid equilibrium calculations

Calculation type	Specified quantities	Calculated quantities
1 Bubble point pressure at a given temperature	$T, \bar{x}'$	$\rho', \rho'', p, \bar{x}''$
2 Dew point pressure at a given temperature	$T, \bar{x}''$	$\rho', \rho'', p, \bar{x}'$
3 Bubble point temperature at a given pressure	$p, \bar{x}'$	$\rho', \rho'', T, \bar{x}''$
4 Dew point temperature at a given pressure	$p, \bar{x}''$	$\rho', \rho'', T, \bar{x}'$
5 pT flash	$p, T, \bar{x}$	$\rho', \rho'', \bar{x}', \bar{x}''$

Over the last several decades, a numerous amount of procedures were reported which are suitable to solve the phase equilibrium conditions based on equations of state for mixtures. A survey of such procedures is given by Heidemann (1983). The computational aspects of a number of iterative procedures to solve two-phase and multi-phase equilibrium conditions are presented by Michelsen and Mollerup (2004).

Successive Substitution

A simple and commonly applied numerical method is the successive substitution. A detailed description of this procedure is given by Prausnitz and Chueh (1968) and Lemmon (1991). For the successive substitution the solution to all quantities to be calculated is not determined simultaneously. Starting, for example, with an estimated value for the vapour pressure, the corresponding phase compositions and densities are calculated to satisfy the remaining phase equilibrium conditions. Based on this iterative solution, a new value for the vapour pressure is calculated and the iterative process is successively continued until the solution to all variables and equations is determined. The main advantages of this approach are the comparatively simple structure of the corresponding algorithm and a less sensitive behaviour in the quality of the initial estimates than are frequently observed for methods which simultaneously solve all phase equilibrium conditions. On the other hand, the sequence of iterations converges only linearly to the solution resulting in a comparatively low speed of convergence.

The Newton-Raphson Method

Another well-established numerical method used for solving nonlinear algebraic equations is the Newton-Raphson method [e.g. Press *et al.* (1986)]. Algorithms based on this approach solve the phase equilibrium conditions simultaneously and were successfully used and optimised by numerous authors [e.g. Asselineau *et al.* (1979), Michelsen (1980), Deiters (1985), Wendland (1994)]. A corresponding algorithm was developed by Klimeck (2000) and is used for the development of the new mixture model in this work. Starting from initial estimates for all involved variables, the nonlinear set of equations composed of the phase equilibrium conditions and the secondary conditions is linearised and the resulting linear set of equations is solved. The resulting solution vector is inserted in the nonlinear set of equations, which is then linearised and solved again. These steps are repeated until convergence occurs. An essential advantage of the Newton-Raphson method is the quadratic convergence of the iterations. Machine accuracy can be obtained with very little additional effort. The main drawback of the Newton-Raphson method is that the convergence is only assured when "good" initial estimates are available. In general, it is very difficult to ascertain that initial estimates are of adequate quality since experimental data for the phase equilibrium are often of poor quality (see Chap. 6) and no accurate auxiliary equations are available to determine the initial estimates for calculations under nonideal conditions (e.g. high pressure phase equilibria, critical point calculations, etc.). Therefore, the use of alternative convergence methods for phase equilibrium calculations is advantageous for the initial iterations to enhance the stability of the iterative process. Such an alternative method is the successive substitution approach described above. Further details concerning the Newton-Raphson method and the algorithm used, which is based on a full Newton-Raphson approach, are given by Klimeck (2000).

5.4.4 Minimisation of a Thermodynamic State Function

Frequently, the set of nonlinear equations to be solved for phase equilibrium calculations can be formulated as an optimisation problem. Thus, the solution corresponds to an extremum of an objective function. For instance, the flash specifications of practical importance mentioned above can be formulated as a minimisation of a thermodynamic state function. The solution for the isothermal flash as the classical and most frequent example yields the global minimum of the Gibbs free energy of the mixture. In addition, specifications of composition in combination with pressure and enthalpy, pressure and entropy, temperature and volume (the "natural" choice of independent variables for mixture models explicit in the Helmholtz free energy), internal energy and volume, and entropy and volume all permit the application of a corresponding thermodynamic state function for which a global minimum must be located. Table 5.4 lists the state functions to be minimised with the corresponding flash specifications.

Table 5.4 State functions to be minimised for given specifications

Specification	$p, T, \bar{n}$	$p, H, \bar{n}$	$p, S, \bar{n}$	$T, V, \bar{n}$	$U, V, \bar{n}$	$S, V, \bar{n}$
State function	G	$-S$	H	A	$-S$	U

The essential difference between solving a general set of algebraic equations and determining a local minimum is that for minimisation problems procedures which guarantee convergence from arbitrary initial estimates can be constructed. There are two important advantages of the approach based on minimisation. Firstly, the minimisation problems for most cases have a unique solution, and secondly, stability analysis can be used to verify its correctness and to determine the number of equilibrium phases. Details regarding different state function based optimisation approaches are given by Michelsen (1999) and Michelsen and Mollerup (2004). The following paragraphs provide a brief introduction to the basic principles of the minimisation of thermodynamic state functions.

In equilibrium calculations which can be formulated as minimisation problems, it is often advantageous to use molar amounts (per unit feed) instead of mole fractions as the independent variables. The liquid and vapour amounts are related to the corresponding mole fractions by

$$l_i = (1-\beta)\,x_i' \quad \text{and} \quad v_i = \beta\, x_i''. \tag{5.67}$$

Hence, the material balance equation, Eq. (5.53), can be simplified to

$$l_i + v_i = x_i, \quad i = 1, 2, ..., N. \tag{5.68}$$

For the two-phase isothermal flash (at specified T, p, and $\bar{x}$), the equilibrium calculation can then be formulated as

$$\min G\left(T, p, \bar{v}, \bar{l}\right) \tag{5.69}$$

subject to $T = T_{\text{spec}}$, $p = p_{\text{spec}}$, and the set of linear constraints $\bar{l} + \bar{v} = \bar{x}$, or as the unconstrained minimisation by treating the mole numbers in the liquid phase as dependent variables (see also Sec. 7.6.1):

$$\min G\left(T_{\text{spec}}, p_{\text{spec}}, \bar{v}, \bar{x} - \bar{v}\right). \tag{5.70}$$

The phase equilibrium calculation for other specifications (see Table 5.4) is, however, not as straightforward as for the pT flash since the specification of, for example, the total enthalpy or total entropy (of the overall system), is nonlinear in the independent variables and thus the constraint cannot be eliminated explicitly. For example, the minimisation formulation of the two-phase isenthalpic flash is

$$\min\left\{-S\left(T, p, \bar{v}, \bar{l}\right)\right\} \tag{5.71}$$

subject to the constraints

$$p = p_{\text{spec}}, \quad \bar{l} + \bar{v} = \bar{x}, \quad \text{and} \quad H\left(T, p, \bar{v}, \bar{l}\right) - H_{\text{spec}} = 0. \tag{5.72}$$

Eliminating the linear material balance constraint similar to the pT flash results in:

$$\min\left\{-S\left(T, p_{\text{spec}}, \bar{v}, \bar{x} - \bar{v}\right)\right\} \quad \text{subject to} \quad H\left(T, p_{\text{spec}}, \bar{v}, \bar{x} - \bar{v}\right) - H_{\text{spec}} = 0, \tag{5.73}$$

where the constraint of specified total enthalpy is nonlinear in its independent variables. In order to formally eliminate the remaining constraint, the objective function can be modified by forming the function Q defined by

$$Q\left(T, p_{\text{spec}}, \bar{v}, \bar{x}-\bar{v}\right)=\frac{1}{T}\left(G-H_{\text{spec}}\right) \tag{5.74}$$

with the independent variables T and $\bar{v}$; see Michelsen (1999) for further characteristics of this approach. Similar Q-functions for state function based specifications with the Gibbs free energy as the "core function" can be formulated for the other specifications listed in Table 5.4.

With regard to mixture models based on multi-fluid approximations explicit in the reduced Helmholtz free energy, it should be mentioned that flash calculations for all of the different specifications listed in Table 5.4 can also be formulated as minimisation (or maximisation) problems using the Helmholtz free energy as the core function (see Sec. 7.9).

5.5 Basics of the Development of the Binary Correlation Equations in Mixture Models Based on Multi-Fluid Approximations

The basic principles for the development of mixture models based on multi-fluid approximations are strongly related to the development of empirical equations of state for pure substances (see Chap. 4). In contrast to the development of an equation for the residual part of the Helmholtz free energy of a pure substance equation of state (see Sec. 4.4), several correlation equations characterised by mathematically different structures have to be developed to take into account the residual behaviour of a mixture. As already mentioned, the respective tools used for the development of the new multi-fluid mixture model were developed and reported in a preceding study by Klimeck (2000). Some of the basic and important principles of the development of multi-fluid mixture models are briefly summarised in the following sections. Further details are given by Klimeck (2000).

As described in Chap. 4, the minimisation of the sum of squares according to Eq. (4.16) is the essential criterion for optimising the structure of modern multi-parameter equations of state and fitting their coefficients to data. The same is true for the development of the different correlation equations in mixture models based on multi-fluid approximations. The sum of squares of all data used for the development of the equations is calculated by the summation over all weighted residua $\chi_{j,m}$ of each of the M_j measured data points for the J considered properties according to

$$\chi^2=\sum_{j=1}^{J}\sum_{m=1}^{M_j}\chi_{j,m}^2 . \tag{5.75}$$

The weighted residuum $\chi_{j,m}$ of any property z can be expressed as

$$\chi_{j,m} = \left[z_{\text{exp}} - z_{\text{calc}}(\overline{a})\right]_{j,m} \cdot \sigma_{\text{tot},m}^{-1}. \tag{5.76}$$

Similar to the relations for property calculations, the residua of thermodynamic properties in the homogeneous region are basically the same for both pure substances and mixtures. Thus, the same basic relations can be applied for the development of mixture models based on multi-fluid approximations (see Table 4.3). For example, the weighted formulation of the residuum $\Delta z = z_{\text{exp}} - z_{\text{calc}}(\overline{a})$ of a measured speed of sound data point, i.e. $z = w$, is given by

$$\chi = \left[\frac{w^2 M}{RT} - 1 - 2\delta\alpha_\delta^{\text{r}} - \delta^2\alpha_{\delta\delta}^{\text{r}} + \frac{\left(1 + \delta\alpha_\delta^{\text{r}} - \delta\tau\alpha_{\delta\tau}^{\text{r}}\right)^2}{\tau^2\left(\alpha_{\tau\tau}^{\text{o}} + \alpha_{\tau\tau}^{\text{r}}\right)}\right] \cdot \sigma_{\text{tot}}^{-1}. \tag{5.77}$$

A list of the residua of other thermodynamic properties used for the development of the equations presented in this work is provided by the selected sums of squares of the linear and nonlinear data given in Table 4.3.

To minimise the sum of squares by a variation of the parameter vector $\overline{a}$ of the correlation equation to be developed, the procedures used require the derivatives of each residuum with respect to all parameters a_i. The calculation of the partial derivative

$$\left(\frac{\partial \chi_{j,m}}{\partial a_i}\right)_{a_k} = \left(\frac{\partial\left[z_{\text{exp}} - z_{\text{calc}}(\overline{a})\right]_{j,m}}{\partial a_i}\right)_{a_k} \cdot \sigma_{\text{tot},m}^{-1} \tag{5.78}$$

can be reduced to the derivative of the calculated property z_{calc} with respect to the parameters:

$$\left(\frac{\partial \chi_{j,m}}{\partial a_i}\right)_{a_k} = -\left(\frac{\partial\left[z_{\text{calc}}(\overline{a})\right]_{j,m}}{\partial a_i}\right)_{a_k} \cdot \sigma_{\text{tot},m}^{-1}. \tag{5.79}$$

To allow the development of computing-time saving algorithms, the derivatives of the various considered thermodynamic properties were analytically determined in the tools developed by Klimeck (2000).

5.5.1 The Calculation of the Derivatives of the Residua with Respect to the Parameters a_i

For fitting the coefficients and parameters of the used mixture model to experimental data for thermal and caloric properties of binary mixtures, the evaluation of the required derivatives with respect to the different coefficients and parameters requires a comparatively large effort. For a binary mixture, the residual part of the reduced Helmholtz free energy of a multi-fluid mixture model can be expressed in the following general form:

$$\alpha^{\text{r}}(\delta,\tau,\overline{x}) = \alpha^{\text{r,lin}}(\delta,\tau,\overline{x}) + f^{\Delta}(\overline{x}) \cdot \alpha^{\text{r},\Delta}(\delta,\tau), \tag{5.80}$$

where $\alpha^{\mathrm{r,lin}}$ is the contribution of the linearly combined residual parts of the pure substance equations of state [see Eq. (5.7)] and δ and τ are the reduced mixture variables according to Eq. (5.3). The fitting of the coefficients and parameters of such an approach requires the distinction whether the parameter a_i is a parameter of

- the reducing function for mixture density ρ_{r} [e.g. Eq. (5.10)],
- the reducing function for mixture temperature T_{r} [e.g. Eq. (5.11)],
- the composition-dependent factor f^{Δ} [e.g. Eq. (5.21)], or
- the function $\alpha^{\mathrm{r},\Delta}$, which is the part of the departure function depending only on the reduced mixture variables δ and τ [e.g. Eq. (5.24)].

For fitting an equation of state for mixtures to, for example, speed of sound data $w(T,p,\bar{x})$, the following cases have to be distinguished[37]. When the parameter a_i is a parameter of the reducing function for the mixture density, the derivative of Eq. (5.77) with respect to a_i is given by

$$\left(\frac{\partial \chi}{\partial a_i}\right)_{T,p,\bar{x},a_k} = \frac{\partial \chi}{\partial \delta} \frac{\delta\left(1+\delta\alpha_{\delta}^{\mathrm{r}}\right)}{1+2\delta\alpha_{\delta}^{\mathrm{r}}+\delta^2\alpha_{\delta\delta}^{\mathrm{r}}} \cdot \frac{1}{\rho_{\mathrm{r}}} \frac{\partial \rho_{\mathrm{r}}}{\partial a_i}. \tag{5.81}$$

For a_i as a parameter of the reducing function for mixture temperature, the derivative can be written as

$$\left(\frac{\partial \chi}{\partial a_i}\right)_{T,p,\bar{x},a_k} = \left(-\frac{\partial \chi}{\partial \tau} + \frac{\partial \chi}{\partial \delta} \frac{\delta^2\alpha_{\delta\tau}^{\mathrm{r}}}{1+2\delta\alpha_{\delta}^{\mathrm{r}}+\delta^2\alpha_{\delta\delta}^{\mathrm{r}}}\right) \cdot \frac{1}{T} \frac{\partial T_{\mathrm{r}}}{\partial a_i}. \tag{5.82}$$

In case a_i represents a parameter of the composition-dependent factor f^{Δ} of the departure function, it is obtained as

$$\begin{aligned}\left(\frac{\partial \chi}{\partial a_i}\right)_{T,p,\bar{x},a_k} &= \left(-2\delta\alpha_{\delta}^{\mathrm{r},\Delta} - \delta^2\alpha_{\delta\delta}^{\mathrm{r}}\right)\frac{\partial f^{\Delta}}{\partial a_i} \\ &+ \frac{1}{\tau^2\alpha_{\tau\tau}}\left(2\left(1+\delta\alpha_{\delta}^{\mathrm{r}}-\delta\tau\alpha_{\delta\tau}^{\mathrm{r}}\right)\left(\delta\alpha_{\delta}^{\mathrm{r},\Delta}-\delta\tau\alpha_{\delta\tau}^{\mathrm{r},\Delta}\right) - \frac{\left(1+\delta\alpha_{\delta}^{\mathrm{r}}-\delta\tau\alpha_{\delta\tau}^{\mathrm{r}}\right)^2}{\alpha_{\tau\tau}}\alpha_{\tau\tau}^{\mathrm{r},\Delta}\right)\frac{\partial f^{\Delta}}{\partial a_i} \\ &+ \frac{\partial \chi}{\partial \delta}\frac{\delta^2}{1+2\delta\alpha_{\delta}^{\mathrm{r}}+\delta^2\alpha_{\delta\delta}^{\mathrm{r}}}\alpha_{\delta}^{\mathrm{r},\Delta}\frac{\partial f^{\Delta}}{\partial a_i}.\end{aligned} \tag{5.83}$$

Whereas for a parameter of the function $\alpha^{\mathrm{r},\Delta}$, which only depends on the reduced mixture variables δ and τ, the derivative results in

$$\left(\frac{\partial \chi}{\partial a_i}\right)_{T,p,\bar{x},a_k} = -2\delta f^{\Delta}\alpha_{\delta a_i}^{\mathrm{r},\Delta} - \delta^2 f^{\Delta}\alpha_{\delta\delta a_i}^{\mathrm{r},\Delta}$$

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[37] For simplicity, the factor σ_{tot} [see Eq. (4.18)] is set to unity.

$$+\frac{1}{\tau^2\alpha_{\tau\tau}}\left(2\left(1+\delta\alpha_\delta^{\mathrm{r}}-\delta\tau\alpha_{\delta\tau}^{\mathrm{r}}\right)\left(\delta f^\Delta\alpha_{\delta a_i}^{\mathrm{r},\Delta}-\delta\tau f^\Delta\alpha_{\delta\tau a_i}^{\mathrm{r},\Delta}\right)-\frac{\left(1+\delta\alpha_\delta^{\mathrm{r}}-\delta\tau\alpha_{\delta\tau}^{\mathrm{r}}\right)^2}{\alpha_{\tau\tau}}f^\Delta\alpha_{\tau\tau a_i}^{\mathrm{r},\Delta}\right)$$

$$+\frac{\partial\chi}{\partial\delta}\frac{\delta^2}{1+2\delta\alpha_\delta^{\mathrm{r}}+\delta^2\alpha_{\delta\delta}^{\mathrm{r}}}f^\Delta\alpha_{\delta a_i}^{\mathrm{r},\Delta}. \tag{5.84}$$

The respective derivatives required for fitting all other thermodynamic properties in the homogeneous region can be derived in the same way. For nonlinear data the tools of Klimeck (2000) for the development of mixture models based on a multi-fluid approximation enable either the direct fitting, or for the use in the linearised form with precorrelated values for the density and the required precorrelation coefficients.

5.5.2 The Consideration of VLE Properties of Binary Mixtures

The new mixture model for natural gases and other mixtures is based, aside from many other thermodynamic properties, on data of thermal properties for the vapour-liquid equilibrium of binary mixtures. Similar to the calculation of phase equilibrium properties, the fitting of VLE data of mixtures requires much more complex and sophisticated procedures compared to pure substances.

For a binary mixture, the set of nonlinear equations for phase equilibrium calculations [Eqs. (5.57a) – (5.57h)] can be reduced to the following four relations:

$$\frac{p_{\mathrm{s}}}{\rho' RT}=1+\delta'\alpha_\delta^{\mathrm{r}\,\prime}, \tag{5.85}$$

$$\frac{p_{\mathrm{s}}}{\rho'' RT}=1+\delta''\alpha_\delta^{\mathrm{r}\,\prime\prime}, \tag{5.86}$$

$$\ln\left(\frac{x_1'\rho'}{x_1''\rho''}\right)-\frac{p_{\mathrm{s}}}{RT}\left(\frac{1}{\rho''}-\frac{1}{\rho'}\right)=\alpha^{\mathrm{r}\,\prime\prime}-\alpha^{\mathrm{r}\,\prime}$$
$$-(1-x_1')\left[-\frac{\delta'}{\rho_{\mathrm{r}}'}\alpha_\delta^{\mathrm{r}\,\prime}\left(\frac{\mathrm{d}\rho_{\mathrm{r}}}{\mathrm{d}x_1}\right)'+\frac{1}{T}\alpha_\tau^{\mathrm{r}\,\prime}\left(\frac{\mathrm{d}T_{\mathrm{r}}}{\mathrm{d}x_1}\right)'+\left(\frac{\partial\alpha^{\mathrm{r}}}{\partial x_1}\right)_{\delta,\tau}'\right]$$
$$+(1-x_1'')\left[-\frac{\delta''}{\rho_{\mathrm{r}}''}\alpha_\delta^{\mathrm{r}\,\prime\prime}\left(\frac{\mathrm{d}\rho_{\mathrm{r}}}{\mathrm{d}x_1}\right)''+\frac{1}{T}\alpha_\tau^{\mathrm{r}\,\prime\prime}\left(\frac{\mathrm{d}T_{\mathrm{r}}}{\mathrm{d}x_1}\right)''+\left(\frac{\partial\alpha^{\mathrm{r}}}{\partial x_1}\right)_{\delta,\tau}''\right], \tag{5.87}$$

$$\ln\left(\frac{(1-x_1')\rho'}{(1-x_1'')\rho''}\right)-\frac{p_{\mathrm{s}}}{RT}\left(\frac{1}{\rho''}-\frac{1}{\rho'}\right)=\alpha^{\mathrm{r}\,\prime\prime}-\alpha^{\mathrm{r}\,\prime}$$
$$+x_1'\left[-\frac{\delta'}{\rho_{\mathrm{r}}'}\alpha_\delta^{\mathrm{r}\,\prime}\left(\frac{\mathrm{d}\rho_{\mathrm{r}}}{\mathrm{d}x_1}\right)'+\frac{1}{T}\alpha_\tau^{\mathrm{r}\,\prime}\left(\frac{\mathrm{d}T_{\mathrm{r}}}{\mathrm{d}x_1}\right)'+\left(\frac{\partial\alpha^{\mathrm{r}}}{\partial x_1}\right)_{\delta,\tau}'\right]$$

$$-x_1''\left[-\frac{\delta''}{\rho_\mathrm{r}''}\alpha_\delta^{\mathrm{r}\,''}\left(\frac{\mathrm{d}\rho_\mathrm{r}}{\mathrm{d}x_1}\right)'' + \frac{1}{T}\alpha_\tau^{\mathrm{r}\,''}\left(\frac{\mathrm{d}T_\mathrm{r}}{\mathrm{d}x_1}\right)'' + \left(\frac{\partial\alpha^\mathrm{r}}{\partial x_1}\right)''_{\delta,\tau}\right]. \tag{5.88}$$

5.5.3 Linearised VLE Data for Optimising the Structure of the Departure Function and for Fitting the Nonlinear Elements of a Multi-Fluid Approximation

Since the structure-optimisation method only works with linear data (see Sec. 4.4), the VLE data have to be linearised for optimising the structure of the departure function, i.e. the function $\alpha^{\mathrm{r},\Delta}$ of Eq. (5.80). Similar to the linear fitting of a pure substance equation of state to thermal properties on the vapour-liquid phase boundary [see Wagner (1970), (1972), Bender (1970), (1971), and McCarty (1970)], each equation in the set of nonlinear equations representing the mixture equilibrium conditions is isolated. Instead of iteratively solving Eqs. (5.85) – (5.88) for the independent variables, a data type $(T, p_\mathrm{s}, \rho', \rho'', x_1', x_1'')_\mathrm{exp}$ is considered, which contains data for all equilibrium properties of a binary mixture. This approach enables the use of the thermodynamic information on the phase equilibrium for the linear structure optimisation of the part of the departure function which only depends on the reduced mixture variables δ and τ. The contributions of the residua to the sum of squares resulting from Eqs. (5.85) – (5.88) are given by:

$$\chi_{\mathrm{s},1,m}^2 = \left[\frac{p_\mathrm{s} - \rho' RT}{\rho' RT} - \delta'\alpha_\delta^{\mathrm{r}\,'}\right]_m^2 \cdot \sigma_m^{-2}, \tag{5.89}$$

$$\chi_{\mathrm{s},2,m}^2 = \left[\frac{p_\mathrm{s} - \rho'' RT}{\rho'' RT} - \delta''\alpha_\delta^{\mathrm{r}\,''}\right]_m^2 \cdot \sigma_m^{-2}, \tag{5.90}$$

$$\begin{aligned}\chi_{\mathrm{s},3,m}^2 = \Bigg[& \ln\left(\frac{x_1'\rho'}{x_1''\rho''}\right) - \frac{p_\mathrm{s}}{RT}\left(\frac{1}{\rho''} - \frac{1}{\rho'}\right) - \alpha^{\mathrm{r}\,''} + \alpha^{\mathrm{r}\,'} \\ & + (1 - x_1')\left[-\frac{1}{\rho_\mathrm{r}'}\left(\frac{p_\mathrm{s}}{\rho' RT} - 1\right)\left(\frac{\mathrm{d}\rho_\mathrm{r}}{\mathrm{d}x_1}\right)' + \frac{1}{T}\alpha_\tau^{\mathrm{r}\,'}\left(\frac{\mathrm{d}T_\mathrm{r}}{\mathrm{d}x_1}\right)' + \left(\frac{\partial\alpha^\mathrm{r}}{\partial x_1}\right)'_{\delta,\tau}\right] \\ & - (1 - x_1'')\left[-\frac{1}{\rho_\mathrm{r}''}\left(\frac{p_\mathrm{s}}{\rho'' RT} - 1\right)\left(\frac{\mathrm{d}\rho_\mathrm{r}}{\mathrm{d}x_1}\right)'' + \frac{1}{T}\alpha_\tau^{\mathrm{r}\,''}\left(\frac{\mathrm{d}T_\mathrm{r}}{\mathrm{d}x_1}\right)'' + \left(\frac{\partial\alpha^\mathrm{r}}{\partial x_1}\right)''_{\delta,\tau}\right]\Bigg]_m^2 \cdot \sigma_m^{-2},\end{aligned} \tag{5.91}$$

$$\begin{aligned}\chi_{\mathrm{s},4,m}^2 = \Bigg[& \ln\left(\frac{(1 - x_1')\rho'}{(1 - x_1'')\rho''}\right) - \frac{p_\mathrm{s}}{RT}\left(\frac{1}{\rho''} - \frac{1}{\rho'}\right) - \alpha^{\mathrm{r}\,''} + \alpha^{\mathrm{r}\,'} \\ & - x_1'\left[-\frac{1}{\rho_\mathrm{r}'}\left(\frac{p_\mathrm{s}}{\rho' RT} - 1\right)\left(\frac{\mathrm{d}\rho_\mathrm{r}}{\mathrm{d}x_1}\right)' + \frac{1}{T}\alpha_\tau^{\mathrm{r}\,'}\left(\frac{\mathrm{d}T_\mathrm{r}}{\mathrm{d}x_1}\right)' + \left(\frac{\partial\alpha^\mathrm{r}}{\partial x_1}\right)'_{\delta,\tau}\right]\end{aligned}$$

$$\left. + x_1'' \left[-\frac{1}{\rho_\mathrm{r}''} \left(\frac{p_\mathrm{s}}{\rho'' RT} - 1 \right) \left(\frac{\mathrm{d}\rho_\mathrm{r}}{\mathrm{d}x_1} \right)'' + \frac{1}{T} \alpha_\tau^{\mathrm{r}''} \left(\frac{\mathrm{d}T_\mathrm{r}}{\mathrm{d}x_1} \right)'' + \left(\frac{\partial \alpha^\mathrm{r}}{\partial x_1} \right)_{\delta,\tau}'' \right] \right]_m^2 \cdot \sigma_m^{-2} . \tag{5.92}$$

The derivatives of the weighted residua $\chi_{\mathrm{s},1,m}$, $\chi_{\mathrm{s},2,m}$, $\chi_{\mathrm{s},3,m}$, and $\chi_{\mathrm{s},4,m}$ with respect to the parameters of the function $\alpha^{\mathrm{r},\Delta}(\delta,\tau,\bar{a})$ can be calculated from Eq. (5.79) as described by Klimeck (2000).

As the linearised data for the thermal VLE properties of binary mixtures are directly connected to the reduced residual Helmholtz free energy of the mixture, Eqs. (5.89) – (5.92) can be similarly used for the linear fitting of the parameters of the nonlinear elements of the multi-fluid approximation, namely the reducing functions for mixture density and temperature and the composition-dependent factor f^Δ of the departure function. Hence, the fitting of the parameters of the different correlation equations of a multi-fluid mixture model can be performed without iteratively solving the phase equilibrium conditions. For calculating the respective derivatives it is certainly decisive whether the parameter is part of the reducing function for the mixture density, the reducing function for the mixture temperature, or the composition-dependent factor.

The use of data types which require the iterative solution of equations is problematic due to the considerably higher demand of computing time. Moreover, such iterations may fail for unsuitable initial estimates resulting from, for example, poor data. Under these conditions, the direct fitting of VLE properties may lead to an instable fitting process[38]. Therefore, Klimeck (2000) developed routines which enabled the parameters of the nonlinear elements of a multi-fluid approximation to be fitted to linearised VLE data aside from routines which allow the direct fitting of the parameters to VLE data. The linearised fitting procedures were used in this work for fitting VLE data of poor quality, and also at the beginning of a fitting process to establish a first set of parameters that are then further optimised by using the direct fitting routines described in the next section.

5.5.4 Direct Fitting to VLE Data

As demonstrated in the previous section, the linearisation of the phase equilibrium conditions is applicable to take into account the experimental information of VLE data for optimising the structure of the departure function and for the linear and computing-time saving fitting of the nonlinear elements of a multi-fluid approximation. The direct fitting of, for example,

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[38] For instance, a failure of the iteration in the first step of the nonlinear fitting process occurs when, for given values of temperature and composition, no phase equilibrium exists for the initial parameter vector $\bar{a}$. Consequently, the respective data point will be excluded from this step and the contribution of this point to the sum of squares vanishes. If the next iteration for the varied parameter vector $\bar{a}$ is successful, the same data point would now contribute to the sum of squares. This ends up in a higher sum of squares although the equation yields a better result.

saturated liquid densities, vapour pressures, and saturated vapour phase compositions, can only be achieved by nonlinear procedures. Therefore, similar to pure substances [see Ahrendts and Baehr (1979), (1981)], Klimeck (2000) isolated the phase equilibrium conditions for binary mixtures.

There are a number of options to form residua to fit the parameters of equations of state for mixtures to data of thermodynamic properties for the vapour-liquid equilibrium. When considering the data type $(p_\mathrm{s}, T_\mathrm{s}, x_1', x_1'')_\mathrm{exp}$, which is the most measured type in the literature (see Chap. 6), the experimental information can be used for fitting in several ways. Measured pressures can be used for fitting the bubble point pressure at a given temperature and composition of the saturated liquid phase

$$\chi_m^2 = \left[p_\mathrm{s} - p_\mathrm{s,calc}(T, x_1')\right]_m^2 \cdot \sigma_m^{-2} \tag{5.93}$$

or for the dew point pressure at a given temperature and composition of the saturated vapour phase

$$\chi_m^2 = \left[p_\mathrm{s} - p_\mathrm{s,calc}(T, x_1'')\right]_m^2 \cdot \sigma_m^{-2}. \tag{5.94}$$

Similarly, the measured temperature can be used as a bubble point temperature or dew point temperature at a given pressure and at a given saturated liquid or saturated vapour phase composition:

$$\chi_m^2 = \left[T_\mathrm{s} - T_\mathrm{s,calc}(p, x_1')\right]_m^2 \cdot \sigma_m^{-2}, \tag{5.95}$$

$$\chi_m^2 = \left[T_\mathrm{s} - T_\mathrm{s,calc}(p, x_1'')\right]_m^2 \cdot \sigma_m^{-2}. \tag{5.96}$$

Similar combinations are obtained for the phase equilibrium compositions.

Based on the experiences of Klimeck (2000) and those reported in the literature by other authors regarding the sensitivity of the parameters of equations of state while fitting different phase equilibrium properties, only the fitting of bubble point pressures, saturated liquid densities, and saturated vapour phase compositions was performed for the new mixture model. The contributions to the sum of squares for fitting these properties can be formulated for a binary mixture as follows:

$$\chi_{\mathrm{s},5,m}^2 = \left[p_\mathrm{s} - p_\mathrm{s,calc}(T, x_1', \bar{a})\right]_m^2 \cdot \sigma_m^{-2}, \tag{5.97}$$

$$\chi_{\mathrm{s},6,m}^2 = \left[\rho' - \rho'_\mathrm{calc}(T, x_1', \bar{a})\right]_m^2 \cdot \sigma_m^{-2}, \tag{5.98}$$

$$\chi_{\mathrm{s},7,m}^2 = \left[x_1'' - x''_\mathrm{1,calc}(T, x_1', \bar{a})\right]_m^2 \cdot \sigma_m^{-2}. \tag{5.99}$$

Equations (5.97) – (5.99) depend on the temperature T and the composition of the saturated liquid phase x_1'. For the nonlinear fitting procedure, the derivatives of the residua with respect to the parameters of the respective correlation equation are required. Therefore, the derivatives $\partial p_{\mathrm{s,calc}}/\partial a_i$, $\partial \rho'_{\mathrm{calc}}/\partial a_i$, and $\partial x''_{1,\mathrm{calc}}/\partial a_i$ have to be determined. For the analytic evaluation of these derivatives the phase equilibrium conditions have to be isolated:

$$p_{\mathrm{s}} = -a'_v, \tag{5.100}$$

$$p_{\mathrm{s}} = -a''_v, \tag{5.101}$$

$$p_{\mathrm{s}} = \frac{(a' - a'') + \left[(1 - x'_1) \left(\frac{\partial a}{\partial x_1} \right)'_{T,v} - (1 - x''_1) \left(\frac{\partial a}{\partial x_1} \right)''_{T,v} \right]}{v'' - v'}, \tag{5.102}$$

$$p_{\mathrm{s}} = \frac{(a' - a'') + \left[-x'_1 \left(\frac{\partial a}{\partial x_1} \right)'_{T,v} + x''_1 \left(\frac{\partial a}{\partial x_1} \right)''_{T,v} \right]}{v'' - v'}. \tag{5.103}$$

By means of suitable transformations the results for the derivatives of the three properties considered for fitting are obtained:

$$\left(\frac{\partial p_{\mathrm{s,calc}}}{\partial a_i} \right)_{T,x'_1,a_j} = \frac{1}{v'' - v'} \frac{a'_{a_i} - a''_{a_i} - (x''_1 - x'_1) \frac{a'_{xv}}{a'_{vv}} a'_{va_i} + (x''_1 - x'_1) a'_{xa_i}}{1 + \frac{x''_1 - x'}{v'' - v'} \frac{a'_{xv}}{a'_{vv}}}, \tag{5.104}$$

$$\left(\frac{\partial \rho'_{\mathrm{calc}}}{\partial a_i} \right)_{T,x'_1,a_j} = \frac{\rho^2}{a'_{vv}} \left[a'_{va_i} + \frac{1}{v'' - v'} \frac{a'_{a_i} - a''_{a_i} - (x''_1 - x'_1) \frac{a'_{xv}}{a'_{vv}} a'_{va_i} + (x''_1 - x'_1) a'_{xa_i}}{1 + \frac{x''_1 - x'}{v'' - v'} \frac{a'_{xv}}{a'_{vv}}} \right], \tag{5.105}$$

$$\begin{aligned} \left(\frac{\partial x''_{1,\mathrm{calc}}}{\partial a_i} \right)_{T,x'_1,a_j} &= \frac{1}{a'_{xx} - \frac{a''_{xv}}{a''_{vv}}} \left[a'_{xa_i} - a''_{xa_i} - \frac{a'_{xv}}{a'_{vv}} a'_{va_i} + \frac{a''_{xv}}{a''_{vv}} a''_{va_i} \right. \\ &\left. + \left(\frac{a''_{xv}}{a''_{vv}} - \frac{a'_{xv}}{a'_{vv}} \right) \frac{1}{v'' - v'} \frac{a'_{a_i} - a''_{a_i} - (x''_1 - x'_1) \frac{a'_{xv}}{a'_{vv}} a'_{va_i} + (x''_1 - x'_1) a'_{xa_i}}{1 + \frac{x''_1 - x'}{v'' - v'} \frac{a'_{xv}}{a'_{vv}}} \right], \end{aligned} \tag{5.106}$$

where

$$a_{a_i} = \left(\frac{\partial a}{\partial a_i} \right)_{T,v,a_j}, \tag{5.107}$$

$$a_{va_i} = \left(\frac{\partial a_v}{\partial a_i} \right)_{T,v,a_j}, \tag{5.108}$$

$$a_{xa_i} = \left(\frac{\partial a_x}{\partial a_i} \right)_{T,v,a_j}. \tag{5.109}$$

Table 5.5 Derivatives of a, a_v, and a_x with respect to the parameters of the elements of a multi-fluid approximation required for the direct fitting of data for the vapour pressure, saturated liquid density, and vapour phase composition[a]

a_i is parameter of	$a_{a_i} = \left(\frac{\partial a}{\partial a_i}\right)_{T,v,a_j}$	$a_{va_i} = \left(\frac{\partial a_v}{\partial a_i}\right)_{T,v,a_j}$	$a_{xa_i} = \left(\frac{\partial a_x}{\partial a_i}\right)_{T,v,a_j}$
$\alpha^{\mathrm{r},\Delta}(\delta,\tau,\bar{a})$	$a_{a_i} = RT\,f^{\Delta}\alpha^{\mathrm{r},\Delta}_{a_i}$	$a_{va_i} = -RT\,f^{\Delta}\frac{\delta}{\rho_\mathrm{r}}\alpha^{\mathrm{r},\Delta}_{\delta a_i}$	$a_{xa_i} = RT\left[\frac{df^{\Delta}}{dx_1}\alpha^{\mathrm{r},\Delta}_{a_i} - \frac{\delta}{\rho_\mathrm{r}}\frac{\mathrm{d}\rho_\mathrm{r}}{\mathrm{d}x_1}f^{\Delta}\alpha^{\mathrm{r},\Delta}_{\delta a_i} + \frac{1}{T}\frac{\mathrm{d}T_\mathrm{r}}{\mathrm{d}x_1}f^{\Delta}\alpha^{\mathrm{r},\Delta}_{\tau a_i}\right]$
$f^{\Delta}(\bar{x},\bar{a})$	$a_{a_i} = RT\,\alpha^{\mathrm{r},\Delta}_{a_i}\frac{\partial f^{\Delta}}{\partial a_i}$	$a_{va_i} = -RT\,\alpha^{\mathrm{r},\Delta}_{\delta}\frac{\delta}{\rho_\mathrm{r}}\frac{\partial f^{\Delta}}{\partial a_i}$	$a_{xa_i} = RT\left[\alpha^{\mathrm{r},\Delta}\frac{\partial}{\partial a_i}\frac{\mathrm{d}f^{\Delta}}{\mathrm{d}x_1} - \left(\frac{\delta}{\rho_\mathrm{r}}\frac{\mathrm{d}\rho_\mathrm{r}}{\mathrm{d}x_1}\alpha^{\mathrm{r},\Delta}_{\delta} - \frac{1}{T}\frac{\mathrm{d}T_\mathrm{r}}{\mathrm{d}x_1}\alpha^{\mathrm{r},\Delta}_{\tau}\right)\frac{\partial f^{\Delta}}{\partial a_i}\right]$
$\rho_\mathrm{r}(\bar{x},\bar{a})$	$a_{a_i} = -RT\,\alpha^{\mathrm{r}}_{\delta}\frac{\delta}{\rho_\mathrm{r}}\frac{\partial\rho_\mathrm{r}}{\partial a_i}$	$a_{va_i} = RT\,\delta^2\left(\delta\alpha^{\mathrm{r}}_{\delta\delta} + \alpha^{\mathrm{r}}_{\delta}\right)\frac{\partial\rho_\mathrm{r}}{\partial a_i}$	$a_{xa_i} = RT\left[-\frac{\delta}{\rho_\mathrm{r}}\frac{\partial\rho_\mathrm{r}}{\partial a_i}\left[\frac{\partial\alpha^{\mathrm{r}}_{\delta}}{\partial x_1} - \frac{\delta}{\rho_\mathrm{r}}\alpha^{\mathrm{r}}_{\delta\delta} - \frac{2}{\rho_\mathrm{r}}\alpha^{\mathrm{r}}_{\delta} + \frac{1}{T}\alpha^{\mathrm{r}}_{\delta\tau}\frac{\mathrm{d}T_\mathrm{r}}{\mathrm{d}x_1}\right] - \frac{\delta}{\rho_\mathrm{r}}\alpha^{\mathrm{r}}_{\delta}\frac{\partial}{\partial a_i}\frac{\mathrm{d}\rho_\mathrm{r}}{\mathrm{d}x_1}\right]$
$T_\mathrm{r}(\bar{x},\bar{a})$	$a_{a_i} = -R\alpha^{\mathrm{r}}_{\tau}\frac{\partial T_\mathrm{r}}{\partial a_i}$	$a_{va_i} = -R\rho\,\delta\alpha^{\mathrm{r}}_{\delta\tau}\frac{\partial T_\mathrm{r}}{\partial a_i}$	$a_{xa_i} = RT\left[\frac{1}{T}\frac{\partial T_\mathrm{r}}{\partial a_i}\left[\frac{\partial\alpha^{\mathrm{r}}_{\tau}}{\partial x_1} - \frac{\delta}{\rho_\mathrm{r}}\alpha^{\mathrm{r}}_{\delta\tau}\frac{\mathrm{d}\rho_\mathrm{r}}{\mathrm{d}x_1} + \frac{1}{T}\alpha^{\mathrm{r}}_{\tau\tau}\frac{\mathrm{d}T_\mathrm{r}}{\mathrm{d}x_1}\right] + \frac{1}{T}\alpha^{\mathrm{r}}_{\tau}\frac{\partial}{\partial a_i}\frac{\mathrm{d}T_\mathrm{r}}{\mathrm{d}x_1}\right]$

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[a] See Eq. (5.80) for the definition of f^{Δ} and $\alpha^{\mathrm{r},\Delta}$.

From Eqs. (5.104) – (5.106) the required derivatives of the corresponding residua can be derived. The fitting routines developed by Klimeck (2000) depend on reduced variables. Therefore, the equations above have to be transformed according to $a = RT\left(\alpha^{\mathrm{o}} + \alpha^{\mathrm{r}}\right)$ [see Eqs. (5.1) and (5.2)]. Equations (5.107) – (5.109) differ depending on the affiliation of the respective parameter to the elements of a multi-fluid mixture model. An overview of all of these derivatives is given in Table 5.5.

6 Experimental Data for Binary and Multi-Component Mixtures of Natural Gas Components

The new wide-range equation of state for natural gases and other mixtures is based on pure substance equations of state for each considered mixture component (see Chap. 4) and correlation equations for binary mixtures consisting of these components (see Chaps. 5 and 7). This allows a suitable predictive description of multi-component mixtures over a wide range of compositions, which means it is able to predict the properties of a variety of different natural gases and other multi-component mixtures. The basis for the development of such an empirical equation of state are experimental data of several thermodynamic properties. These data are used to determine the structures, coefficients, and parameters of the correlation equations and to evaluate the behaviour of the equation of state in different fluid regions. The quality and the extent of the available data limit the achievable accuracy of the equation. Therefore, a comprehensive database of binary and multi-component mixture data has been built up and continuously updated since the beginning of this project[39].

The database contains more than 100,000 experimental data for the thermal and caloric properties of binary mixtures, natural gases, and other multi-component mixtures, measured by more than 500 different authors. The collected data cover the homogeneous gas, liquid, and supercritical regions as well as vapour-liquid equilibrium (VLE) states at temperatures ranging from 16 K to 800 K and pressures up to 2,000 MPa. The different types of thermodynamic properties are as follows:

- $p\rho T$
- Isochoric heat capacity c_v
- Speed of sound w
- Isobaric heat capacity c_p
- Enthalpy differences Δh
- Excess molar enthalpy h^{E}
- Second acoustic virial coefficient β_{a}
- Saturated liquid density ρ'
- VLE data

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[39] The database also contains very recently obtained data that were not available at the time the new equation of state was developed. To evaluate the accuracy of the new equation of state in the description of thermodynamic properties, the new measurements were used for comparisons as well.

Almost 70% of the available mixture data describe the $p\rho T$ relation. More than 20% of the data are vapour-liquid equilibrium state points and less than 10% account for caloric properties. More than 79,000 data for thermal and caloric properties are available for a total of 98 binary mixtures consisting of the 18 considered natural gas components listed in Table 4.2. The number of binary data selected for the development of the new equation of state amounts to approximately 40,000. Thus, about 50% of all the available binary mixture data were used for fitting the coefficients and parameters and for optimising the structure of the new wide-range equation of state. All of the remaining data were used for comparisons. For multi-component mixtures, about 27,000 data for thermal and caloric properties are accessible. This enabled a comprehensive validation of the new equation of state with data for natural gases and other multi-component mixtures.

Table 6.1 Overview of all binary and multi-component mixture data collected for the development and evaluation of the new wide-range equation of state for natural gases and other mixtures

Data type	Number of data points			
	Binary mixtures		Multi-component	Sum[d]
	total[a]	used[b]	mixtures[c]	
$p\rho T$ data	51442	30252	21769	73211
Isochoric heat capacity	1236	625	–	1236
Speed of sound	2819	1805	1337	4156
Isobaric heat capacity	1072	490	325	1397
Enthalpy differences	1804	198	1166	2970
Excess molar enthalpy	177	20	–	177
Second acoustic virial coeff.	21	–	–	21
Saturated liquid density[e]	460	119	124	584
VLE data[f]	20161	6350	2284	22445
Total	**79192**	**39859**	**27005**	**106197**

[a] Number of all available data points.
[b] Number of data points used for the development of the new wide-range equation of state.
[c] Number of all available natural gas and other multi-component mixture data.
[d] Sum of all available binary and multi-component mixture data.
[e] Listed separately due to a different data format. Saturated liquid (and vapour) densities may also be tabulated as ordinary $p\rho T$ or VLE data.
[f] The total number of VLE data comprises 15,225 $pTxy$ data, 3,386 pTx data, and 3,834 pTy data.

Table 6.1 gives an overview of all binary and multi-component mixture data compiled in the database. More detailed descriptions of the data are given in the following sections (see Tables 6.3 – 6.5). Nevertheless, due to the extensive amount of data for a large number of different binary and multi-component mixtures, only basic remarks on the data situation are given in this chapter. Further summaries and comprehensive listings of all binary and multi-component mixture data along with detailed statistical comparisons of each data set by means of the new equation of state, the AGA8-DC92 equation of Starling and Savidge (1992), and the cubic equation of state of Peng and Robinson (1976) are provided in the appendix of this work (see Tables A2.1 – A2.8). Full bibliographical information on the references of the data is given in the “References” section at the end of this work.

All available data were assessed by means of comparisons with other data and values calculated from different equations of state. The data classified as “reliable” were used for the development of the new equation of state. Other data were only used for comparisons. Many of the collected data do not meet present quality standards. However, for several binary mixtures these data represent the only available experimental information.

Table 6.2 Estimated relative experimental uncertainties of the most accurate binary and multi-component mixture data

Data type	Property	Relative uncertainty
$p\rho T$ data	$\Delta\rho/\rho$	≤ (0.05 – 0.1)%
Isochoric heat capacity	$\Delta c_v/c_v$	≤ (1 – 2)%
Speed of sound (gas phase)	$\Delta w/w$	≤ (0.05 – 0.1)%
Isobaric heat capacity	$\Delta c_p/c_p$	≤ (1 – 2)%
Enthalpy differences	$\Delta(\Delta h)/\Delta h$	≤ (0.2 – 0.5)%
Saturated liquid density	$\Delta\rho'/\rho'$	≤ (0.1 – 0.2)%
VLE data	$\Delta p_\mathrm{s}/p_\mathrm{s}$	≤ (1 – 3)%

The total uncertainties of the most accurate experimental binary and multi-component mixture data with respect to selected thermodynamic properties are listed in Table 6.2. The tabulated values represent the lowest uncertainties achieved by the new mixture model. The corresponding experimental results are based on modern measurement techniques which fulfil present quality standards. For density measurements, these include, for example, the results that were determined by using a two-sinker or single-sinker densimeter [e.g. Glos *et al.* (2000) and Chamorro *et al.* (2006)]. Highly accurate speed of sound data were, in general, measured by means of spherical-resonators [e.g. Costa Gomes and Trusler (1998), Estela-Uribe (1999), Trusler (2000)]. Data measured using methods based on these particular techniques are characterised by uncertainties equal to or below the lowest values listed in Table 6.2. In contrast to the experimental uncertainties given for pure fluid properties measured using state-of-the-art techniques, the experimental uncertainties estimated for the properties of mixtures measured with the same apparatuses are, in general, higher due to the significant contribution of the uncertainty in the mixture composition.

Aside from the data taken from the literature, about 28% of all $p\rho T$ data were taken from the “GERG Databank of High-Accuracy Compression Factor Measurements – GERG TM7 1996” [Jaeschke *et al.* (1997)], which comprises a total of about 12,000 binary data and above

16,000 data of more than 110 natural gases and other related multi-component mixtures. Many of these density data were measured at the Ruhrgas using two different methods of measurement, namely the Burnett method and an optical interferometry method. The uncertainty of these measurements is claimed by the authors to be $\Delta\rho/\rho \leq (0.07 - 0.1)\%$, which agrees with the results of the investigations of Klimeck (2000) and those carried out in this work. Although, the experimental data assembled in the GERG TM7 provide, on average, a very reliable basis for the development and evaluation of the new mixture model, the major drawback of these data is their limited temperature range. Most of the data were measured in the gas phase at temperatures from 270 K to 350 K and pressures $p \leq 30$ MPa[40].

As shown in Table 6.4, data for vapour-liquid equilibrium states provide an essential amount of experimental information on the mixture behaviour for many of the considered binary systems. Moreover, for several binary mixtures there are no data available in the homogeneous region. In general, the collected VLE data are very useful as they cover large composition ranges. This feature is important for fitting the parameters of the composition-dependent elements of the multi-fluid approximation (namely the reducing functions) to experimental data. However, the quality of these data is comparatively poor and in several cases not suitable for the development of an accurate equation of state. In contrast to the available thermodynamic properties for mixtures in the homogeneous region which almost achieve the accuracy of the corresponding properties for pure fluids, the experimental uncertainty in vapour pressure differs by several orders of magnitude. Usually, the uncertainty in vapour pressure of binary and multi-component mixtures amounts to (3 – 5)% and more. Similarly high experimental uncertainties occur for measured bubble and dew point compositions, dew point temperatures, and saturated vapour densities. These weaknesses in the VLE data sets limit the achievable accuracy in the description of such properties by the developed mixture model; for further investigations regarding the quality of VLE data see Klimeck (2000).

The type of VLE measurements depends on the experimental equipment used by the authors. There are basically three different types of VLE data. Most of the available VLE data are comprised of experimental values for the temperature T, the pressure p, and the compositions $\bar{x}$ and $\bar{y}$ ($\bar{x}'$ and $\bar{x}''$, respectively) of the two equilibrium phases. These data are referred to in this work as $pTxy$ data. This type was essentially used for the developed mixture model. Other measurements only consider the composition of either the saturated liquid phase (pTx data) or saturated vapour phase (pTy data). Only few VLE data consider the saturated vapour and saturated liquid densities in addition to temperature, pressure, and the compositions of both phases. Such data provide complete experimental information on the VLE state, which would be advantageous for the development of the new equation of state. However, most of the few existing data are of the same poor quality as observed for the other VLE data types.

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[40] The GERG TM7 database covers temperatures from 218 K to 425 K and pressures up to 60 MPa.

The most accurate VLE data are those measured by Haynes *et al.* [Hiza *et al.* (1977), Hiza and Haynes (1980), Haynes (1982), Haynes (1983)] for saturated liquid densities of binary and multi-component mixtures of liquefied natural gas (LNG) components. The uncertainty in density of these data is less than (0.1 – 0.2)%. Resulting from the chosen measuring technique, the measured pressures are considered as only approximate vapour pressures and cannot be used. As the vapour pressures are very strong functions of composition, errors concerning the composition affect vapour pressure data considerably more than saturated liquid density data [Hiza *et al.* (1977)].

For caloric properties of binary and multi-component mixtures in the homogeneous region, a total of about 10,000 data are available. The most accurate caloric data are speeds of sound and enthalpy differences as shown in Table 6.2. Usually, a substantial amount of these data were measured in the gas phase at temperatures ranging from 250 K to 350 K and pressures up to 12 MPa. Comparatively few accurate measurements exist for higher pressures. In contrast to the collected $p\rho T$ data, caloric data are only present for a limited number of binary mixtures and cover, in general, limited composition ranges.

6.1 Data for Binary Mixtures

An extensive amount of data for the thermal and caloric properties of binary mixtures has been collected and assessed within the framework of this project. As shown in Table 6.4, out of the 153 possible combinations of binary mixtures consisting of the 18 considered natural gas components, data for a total of 98 binary mixtures is available for the development and evaluation of the new wide-range equation of state for natural gases and other mixtures. Compared to the preceding study of Klimeck (2000), who developed a preliminary equation of state for natural gases consisting of seven main and secondary natural gas components, the total number of binary data was more than doubled and with that the number of considered binary mixtures was nearly quintupled in this work.

The data situation differs with respect to certain thermodynamic properties and the type of binary mixtures. Most of the binary data account for the $p\rho T$ relation followed by data for vapour-liquid equilibrium states as shown in Table 6.3. Since methane is the most important natural gas component, the data situation for mixtures containing methane is of primary interest for the development of the new equation of state. The most extensive data sets are those for the binary systems methane–nitrogen and methane–ethane, followed by the data for the binary mixtures methane–carbon dioxide and methane–propane. For these mixtures, data for the $p\rho T$ relation as well as for speeds of sound are available in the homogeneous region. These data are supplemented by an extensive number of thermal properties at vapour-liquid equilibrium. The data situation deteriorates for the methane–n-butane and methane–isobutane mixtures and for mixtures of methane with heavier hydrocarbons or further secondary components as well (see Table 6.4). Data for caloric properties are not available for most of these systems and the number of $p\rho T$ data is also comparatively low. In general, comparatively poor data are available for many mixtures of secondary components. For some binary mixtures, the development is based only on $p\rho T$ or VLE data.

Liquid phase densities of comparatively high quality and measured over wide ranges of pressure ($p \leq 40$ MPa) exist for the binary mixtures methane–nitrogen, methane–ethane, and some other mixtures, such as binary mixtures consisting of the heavier hydrocarbons n-pentane, n-hexane, and n-heptane. In contrast to the data sets for gas phase densities, many of the liquid phase densities were measured for a limited number of compositions, or at only one constant temperature (e.g. 298.15 K) or pressure (e.g. 0.1 MPa).

Table 6.3 Summary of the available data for thermal and caloric properties of binary mixtures

Data type	Number of data points total[a]	Number of data points used[b]	Covered ranges Temperature T/K	Covered ranges Pressure p/MPa	Covered ranges Composition[c,d] x
$p\rho T$ data	51442	30252	66.9 – 800	0.00 – 1027	0.00 – 1.00
Isochoric heat capacity	1236	625	101 – 345	67.1^{ρ} – 902^{ρ}	0.01 – 0.84
Speed of sound	2819	1805	157 – 450	0.00 – 1971	0.01 – 0.96
Isobaric heat capacity	1072	490	100 – 424	0.00 – 52.9	0.09 – 0.93
Enthalpy differences	1804	198	107 – 525	0.00 – 18.4	0.05 – 0.90
Excess molar enthalpy	177	20	221 – 373	0.8 – 15.0	0.01 – 0.98
Second acoustic virial coeff.	21	–	200 – 375		0.15 – 0.20
Saturated liquid density[e]	460	119	95.0 – 394	0.03 – 22.1	0.00 – 1.00
VLE data[f]	20161	6350	15.5 – 700	0.00 – 422	0.00 – 1.00
Total	**79192**	**39859**	**15.5 – 800**	**0.00 – 1971**	**0.00 – 1.00**

[a] Number of all available data points.

[b] Number of data points used for the development of the new wide-range equation of state.

[c] Mole fractions of the second component of the binary mixture, i.e. component B of mixture A–B. Values of 0.00 and 1.00 result from a mixture composition close to a pure component.

[d] The composition range for VLE data corresponds to bubble point compositions.

[e] Listed separately due to a different data format. Saturated liquid (and vapour) densities may also be tabulated as ordinary $p\rho T$ or VLE data.

[f] The total number of VLE data comprises 12,991 $pTxy$ data, 3,369 pTx data, and 3,801 pTy data.

[ρ] Density in $\mathrm{kg \cdot m^{-3}}$ instead of pressure.

Only about 9% of the data account for caloric properties (see Table 6.3), dispersed on 17 out of the 98 considered binary mixtures, whereas $p\rho T$ and VLE data are present for most of the considered binary mixtures. Nevertheless, the available caloric data provide a suitable basis for the development of the new equation of state for natural gases as most of these data are for binary mixtures consisting of the main natural gas components, which already cover about 97% of the composition of typical natural gas mixtures (see also Sec. 4.8).

The data situation was significantly improved within the past five to seven years as new data for several binary mixtures were measured as part of the GERG project "Reference Equation of State for Thermal and Caloric Properties of Natural Gases" [see Klimeck (2000)] and by numerous other independent authors. These include, for example, the very accurate measurements for gas phase densities and speeds of sound of the binary mixtures methane–nitrogen [Estela-Uribe (1999), Trusler (2000), Chamorro *et al.* (2006)], methane–carbon dioxide [Estela-Uribe (1999), Glos *et al.* (2000), Wöll and El Hawary (2003)], methane–ethane [Costa Gomes and Trusler (1998), Wöll and El Hawary (2003)], and nitrogen–ethane [Trusler (2000)]. For the vapour-liquid equilibrium, comparatively accurate data were reported, for example, for methane–ethane and nitrogen–ethane [Raabe *et al.* (2001)], methane–carbon dioxide and methane–propane [Webster and Kidnay (2001)], propane–n-butane [VonNiederhausern and Giles (2001)], and propane–isobutane [VonNiederhausern and Giles (2001), Lim *et al.* (2004)]; for further details see Table A2.1 of the appendix.

With regard to the requirements on the new wide-range equation of state for natural gases, which demand a very accurate description of gas phase properties at supercritical temperatures, the present data situation is satisfactory for the $p\rho T$ relation in the homogeneous region of binary mixtures of important natural gas components as some of the weaknesses described by Klimeck (2000) were eliminated within the past five years. Nevertheless, the development of the new equation revealed several weaknesses in the data sets concerning mixtures containing secondary and minor components. For example, only comparatively few data exist for mixtures consisting of the secondary natural gas components as well as for mixtures containing one of the main natural gas components and a secondary component (see Table 6.4). In many cases only data in the liquid phase at limited temperatures or pressures (e.g. at atmospheric pressure) are available for the $p\rho T$ relation of mixtures consisting of heavier hydrocarbons. No suitable data are available for many mixtures containing oxygen, argon, and helium.

Data for liquid phase densities for many binary mixtures of important natural gas components only exist as values for the saturated liquid density[41] and densities located near to the saturation boundary. Most of these data cover temperatures from 100 K to 140 K, thus, enabling the development of an equation of state for the accurate description of the range important for custody transfer of LNG and natural gas liquefaction processes. When describing larger ranges in the liquid region, additional measurements over wide temperature and pressure ranges are necessary.

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[41] Those of the few saturated liquid densities of binary mixtures present in the literature where the respective pressures were additionally measured were also considered as ordinary $p\rho T$ data. For most of the binary mixtures, no other information concerning the volumetric behaviour of the liquid phase is available.

Within the framework of the GERG project mentioned above, new measurements were performed for speeds of sound of methane–nitrogen and nitrogen–ethane which eliminated some of the weaknesses in these data sets. However, further measurements are still worthwhile in order to improve the data situation with regard to caloric properties:

- For binary mixtures of methane–propane and methane–carbon dioxide, further speed of sound data should be measured at pressures above 10 MPa.
- As the heavier alkanes have a significant influence on the speed of sound of multi-component mixtures at lower temperatures, speed of sound data at supercritical temperatures should be measured for the binary mixtures methane–n-butane[42] and methane–isobutane.
- For mixtures of important natural gas components, such as nitrogen–carbon dioxide and carbon dioxide–propane, only few data are available for caloric properties. There is no caloric information available for most of the considered binary mixtures consisting of secondary natural gas components.

Nevertheless, with the measurements carried out in the past five years, the data situation was improved in a way that the demands on the accuracy in the description of thermal and caloric properties of the new equation of state for natural gases can be fulfilled (see Chap. 3).

Aside from the recently reported binary mixture data, other data were collected, which were also used only for comparisons as they were not present at the time the new equation of state was developed (see also Table A2.1). Some of these data will probably be used for further improvements in the equation of state in the near future, which will lead to minor revisions. This concerns, for example, the binary mixtures nitrogen–helium, carbon dioxide–propane, carbon dioxide–n-hexane, carbon dioxide–carbon monoxide, ethane–n-pentane, propane–hydrogen, helium–argon, and some binary mixtures consisting of the heavier hydrocarbons from n-pentane to n-octane (see also Chap. 9). Nevertheless, for most of these systems, the description of the new data by the developed equation of state is already quite satisfactory.

Table 6.4 presents a summary of the available data for thermal and caloric properties of all considered binary mixtures. For each mixture, the table provides information on the temperature, pressure, and composition ranges covered by the data as well as the number of data points available and used for the development of the new wide-range equation of state. A detailed listing of all binary data sets is provided in the appendix of this work (see Table A2.1).

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[42] Recently, Plantier et al. (2005) reported speed of sound data for methane–n-butane with a particular focus on the critical state. These are the only available caloric properties for this system.

Table 6.4 Summary of the available data for the 98 considered binary mixtures

Binary mixture	Number of data points		Covered ranges		
	total[a]	used[b]	Temperature T/K	Pressure p/MPa	Composition[c,d] x
CH_4–N_2					
$p\rho T$ data	3619	1465	82.0 – 673	0.04 – 507	0.02 – 0.90
Speed of sound	693	456	170 – 400	0.1 – 750	0.05 – 0.54
Isobaric heat capacity	111	–	110 – 275	3.0 – 10.0	0.47 – 0.70
Enthalpy differences	247	–	107 – 367	0.1 – 10.0	0.10 – 0.75
Saturated liquid density[e]	197	21	95.0 – 183	0.1 – 4.9	0.00 – 1.00
VLE data	1237	439	78.4 – 190	0.02 – 5.1	0.00 – 1.00
Total	**6104**	**2381**	**78.4 – 673**	**0.02 – 750**	**0.00 – 1.00**
CH_4–CO_2					
$p\rho T$ data	2392	1107	220 – 673	0.03 – 99.9	0.06 – 0.98
Speed of sound	324	324	200 – 450	0.1 – 17.3	0.05 – 0.30
Isobaric heat capacity	249	–	313 – 424	0.2 – 15.5	0.58 – 0.86
VLE data	616	156	143 – 301	0.9 – 8.5	0.00 – 0.99
Total	**3581**	**1587**	**143 – 673**	**0.03 – 99.9**	**0.00 – 0.99**
CH_4–C_2H_6					
$p\rho T$ data	3759	2001	91.0 – 394	0.00 – 35.9	0.04 – 0.81
Isochoric heat capacity	785	625	101 – 335	67.1^{ρ} – 588^{ρ}	0.10 – 0.84
Speed of sound	810	411	200 – 375	0.00 – 20.1	0.05 – 0.65
Isobaric heat capacity	98	72	110 – 350	0.6 – 30.0	0.15 – 0.29
Enthalpy differences	896	22	110 – 525	0.2 – 16.5	0.06 – 0.75
Second acoustic virial coeff.	9	–	200 – 375		0.20
Saturated liquid density[e]	45	20	105 – 250	0.03 – 6.3	0.10 – 0.95
VLE data	901	183	111 – 302	0.01 – 6.9	0.00 – 0.99
Total	**7303**	**3334**	**91.0 – 525**	**0.00 – 35.9**	**0.00 – 0.99**
CH_4–C_3H_8					
$p\rho T$ data	2901	1889	91.0 – 511	0.03 – 68.9	0.01 – 0.90
Speed of sound	225	222	213 – 375	0.05 – 17.0	0.10 – 0.15
Isobaric heat capacity	280	215	100 – 422	1.7 – 13.8	0.09 – 0.77
Enthalpy differences	238	99	110 – 366	0.00 – 14.0	0.05 – 0.32
Second acoustic virial coeff.	12	–	225 – 375		0.15
Saturated liquid density[e]	20	20	105 – 130	0.03 – 0.3	0.14 – 0.70
VLE data	558	266	91.7 – 363	0.00 – 10.2	0.00 – 1.00
Total	**4234**	**2711**	**91.0 – 511**	**0.00 – 68.9**	**0.00 – 1.00**
CH_4–n-C_4H_{10}					
$p\rho T$ data	1681	879	108 – 573	0.1 – 68.9	0.01 – 1.00
Speed of sound	43	–	311	2.1 – 17.2	0.11 – 0.84
Saturated liquid density[e]	31	31	105 – 140	0.1 – 0.6	0.07 – 0.41

Table 6.4 (continued)

Binary mixture	Number of data points total[a]	Number of data points used[b]	Temperature T/K	Covered ranges Pressure p/MPa	Composition[c,d] x
CH_4–n-C_4H_{10} (continued)					
VLE data	603	117	144 – 411	0.1 – 13.3	0.02 – 1.00
Total	**2358**	**1027**	**105 – 573**	**0.1 – 68.9**	**0.01 – 1.00**
CH_4–i-C_4H_{10}					
$p\rho T$ data	593	582	95.0 – 511	0.04 – 34.5	0.04 – 0.84
Saturated liquid density[e]	17	17	110 – 140	0.1 – 0.6	0.08 – 0.51
VLE data	171	110	198 – 378	0.5 – 11.8	0.02 – 1.00
Total	**781**	**709**	**95.0 – 511**	**0.04 – 34.5**	**0.02 – 1.00**
CH_4–n-C_5H_{12}					
$p\rho T$ data	1106	699	293 – 511	0.1 – 34.5	0.00 – 1.00
VLE data	812	40	173 – 461	0.1 – 17.1	0.03 – 1.00
Total	**1918**	**739**	**173 – 511**	**0.1 – 34.5**	**0.00 – 1.00**
CH_4–i-C_5H_{12}					
$p\rho T$ data	332	256	257 – 478	1.4 – 10.3	0.21 – 0.85
VLE data	29	13	344 – 450	2.8 – 6.9	0.70 – 1.00
Total	**361**	**269**	**257 – 478**	**1.4 – 10.3**	**0.21 – 1.00**
CH_4–n-C_6H_{14}					
$p\rho T$ data	971	244	183 – 423	0.5 – 41.4	0.01 – 0.99
VLE data	472	52	182 – 444	0.1 – 19.8	0.00 – 0.99
Total	**1443**	**296**	**182 – 444**	**0.1 – 41.4**	**0.00 – 0.99**
CH_4–n-C_7H_{16}					
$p\rho T$ data	1038	292	278 – 511	0.3 – 69.8	0.00 – 0.99
VLE data	218	44	200 – 511	0.01 – 24.9	0.10 – 0.99
Total	**1256**	**336**	**200 – 511**	**0.01 – 69.8**	**0.00 – 0.99**
CH_4–n-C_8H_{18}					
$p\rho T$ data	89	89	223 – 423	1.0 – 7.1	0.00 – 0.97
Speed of sound	144	71	293 – 373	25.0 – 100	0.02
VLE data	35	28	298 – 423	1.0 – 7.1	0.71 – 0.97
Total	**268**	**188**	**223 – 423**	**1.0 – 100**	**0.00 – 0.97**
CH_4–H_2					
$p\rho T$ data	1696	1427	130 – 600	0.2 – 107	0.05 – 0.91
VLE data	110	90	90.3 – 174	1.0 – 27.6	0.00 – 0.35
Total	**1806**	**1517**	**90.3 – 600**	**0.2 – 107**	**0.00 – 0.91**

Table 6.4 (continued)

Binary mixture	Number of data points total[a]	Number of data points used[b]	Covered ranges Temperature T/K	Covered ranges Pressure p/MPa	Covered ranges Composition[c,d] x
CH_4–O_2					
VLE data	3	–	93.2 – 107	0.1 – 0.4	0.9989 – 0.9990
Total	**3**	**–**	**93.2 – 107**	**0.1 – 0.4**	**0.9989 – 0.9990**
CH_4–CO					
$p\rho T$ data	456	447	116 – 353	0.4 – 160	0.03 – 0.80
VLE data	55	54	91.4 – 178	0.03 – 4.7	0.03 – 0.97
Total	**511**	**501**	**91.4 – 353**	**0.03 – 160**	**0.03 – 0.97**
CH_4–H_2O					
$p\rho T$ data	384	253	398 – 699	0.1 – 63.2	0.08 – 0.96
Total	**384**	**253**	**398 – 699**	**0.1 – 63.2**	**0.08 – 0.96**
CH_4–He					
VLE data	520	489	93.2 – 194	0.1 – 26.2	0.00 – 0.34
Total	**520**	**489**	**93.2 – 194**	**0.1 – 26.2**	**0.00 – 0.34**
CH_4–Ar					
$p\rho T$ data	36	36	91.0 – 143	0.1 – 122	0.15 – 0.84
VLE data	163	51	105 – 178	0.2 – 5.1	0.02 – 0.96
Total	**199**	**87**	**91.0 – 178**	**0.1 – 122**	**0.02 – 0.96**
N_2–CO_2					
$p\rho T$ data	2856	823	209 – 673	0.1 – 274	0.10 – 0.98
Speed of sound	65	65	250 – 350	0.5 – 10.3	0.50
Isobaric heat capacity	203	203	313 – 363	0.2 – 16.5	0.68 – 0.93
Saturated liquid density[e]	23	–	209 – 268	10.8 – 21.4	0.40 – 0.50
VLE data	380	115	209 – 303	1.0 – 21.4	0.40 – 1.00
Total	**3527**	**1206**	**209 – 673**	**0.1 – 274**	**0.10 – 1.00**
N_2–C_2H_6					
$p\rho T$ data	812	564	105 – 478	0.2 – 62.1	0.00 – 0.96
Speed of sound	112	112	250 – 400	0.05 – 30.2	0.30 – 0.70
Isobaric heat capacity	36	–	110 – 270	3.0 – 5.1	0.41
Enthalpy differences	188	77	110 – 343	0.2 – 14.2	0.41 – 0.75
Saturated liquid density[e]	11	4	105 – 138	0.4 – 2.8	0.73 – 0.96
VLE data	901	79	92.8 – 302	0.02 – 13.5	0.00 – 1.00
Total	**2060**	**836**	**92.8 – 478**	**0.02 – 62.1**	**0.00 – 1.00**
N_2–C_3H_8					
$p\rho T$ data	363	294	100 – 422	0.3 – 42.1	0.00 – 0.98
Saturated liquid density[e]	6	6	100 – 115	0.4 – 0.9	0.93 – 0.98

Table 6.4 (continued)

Binary mixture	Number of data points		Covered ranges		
	total[a]	used[b]	Temperature T/K	Pressure p/MPa	Composition[c,d] x
N_2–C_3H_8 (continued)					
VLE data	349	117	78.0 – 353	0.03 – 21.9	0.47 – 1.00
Total	**718**	**417**	**78.0 – 422**	**0.03 – 42.1**	**0.00 – 1.00**
N_2–n-C_4H_{10}					
$p\rho T$ data	942	925	270 – 478	0.2 – 68.9	0.02 – 0.91
Saturated liquid density[e]	30	–	339 – 380	1.2 – 22.1	0.50 – 0.98
VLE data	292	108	153 – 422	0.2 – 29.1	0.39 – 1.00
Total	**1264**	**1033**	**153 – 478**	**0.2 – 68.9**	**0.02 – 1.00**
N_2–i-C_4H_{10}					
$p\rho T$ data	64	46	255 – 311	0.2 – 20.8	0.03 – 0.99
VLE data	98	31	120 – 394	0.2 – 20.8	0.54 – 1.00
Total	**162**	**77**	**120 – 394**	**0.2 – 20.8**	**0.03 – 1.00**
N_2–n-C_5H_{12}					
$p\rho T$ data	84	78	277 – 378	0.3 – 20.8	0.01 – 1.00
VLE data	42	37	277 – 378	0.3 – 20.8	0.60 – 1.00
Total	**126**	**115**	**277 – 378**	**0.3 – 20.8**	**0.01 – 1.00**
N_2–i-C_5H_{12}					
$p\rho T$ data	94	88	278 – 377	0.2 – 20.8	0.01 – 1.00
VLE data	47	46	278 – 377	0.2 – 20.8	0.56 – 1.00
Total	**141**	**134**	**278 – 377**	**0.2 – 20.8**	**0.01 – 1.00**
N_2–n-C_6H_{14}					
VLE data	52	25	311 – 444	1.7 – 34.5	0.40 – 0.98
Total	**52**	**25**	**311 – 444**	**1.7 – 34.5**	**0.40 – 0.98**
N_2–n-C_7H_{16}					
VLE data	114	41	305 – 497	1.2 – 69.1	0.28 – 0.99
Total	**114**	**41**	**305 – 497**	**1.2 – 69.1**	**0.28 – 0.99**
N_2–n-C_8H_{18}					
$p\rho T$ data	144	143	293 – 373	25.0 – 100	0.79
Speed of sound	144	144	293 – 373	25.0 – 100	0.79
VLE data	26	–	293 – 373	3.2 – 35.0	0.65 – 1.00
Total	**314**	**287**	**293 – 373**	**3.2 – 100**	**0.65 – 1.00**
N_2–H_2					
$p\rho T$ data	1488	1479	270 – 573	0.1 – 307	0.15 – 0.87
VLE data	45	19	77.4 – 113	0.5 – 15.2	0.01 – 0.39
Total	**1533**	**1498**	**77.4 – 573**	**0.1 – 307**	**0.01 – 0.87**

Table 6.4 (continued)

Binary mixture	Number of data points		Covered ranges		
	total[a]	used[b]	Temperature T/K	Pressure p/MPa	Composition[c,d] x
N_2–O_2					
$p\rho T$ data	79	–	66.9 – 333	0.1 – 15.7	0.20 – 0.89
VLE data	526	475	63.0 – 136	0.00 – 3.0	0.01 – 1.00
Total	**605**	**475**	**63.0 – 333**	**0.00 – 15.7**	**0.01 – 1.00**
N_2–CO					
$p\rho T$ data	343	343	273 – 353	0.3 – 30.1	0.03 – 0.03
VLE data	117	106	70.0 – 123	0.02 – 2.7	0.07 – 1.00
Total	**460**	**449**	**70.0 – 353**	**0.02 – 30.1**	**0.03 – 1.00**
N_2–H_2O					
$p\rho T$ data	275	212	429 – 707	2.1 – 286	0.05 – 0.95
Total	**275**	**212**	**429 – 707**	**2.1 – 286**	**0.05 – 0.95**
N_2–He					
$p\rho T$ data	2669	1259	77.2 – 423	0.1 – 1027	0.06 – 0.99
Speed of sound	112	–	157 – 298	200 – 1000	0.50
VLE data	585	–	64.9 – 126	1.2 – 83.1	0.00 – 0.58
Total	**3366**	**1259**	**64.9 – 423**	**0.1 – 1027**	**0.00 – 0.99**
N_2–Ar					
$p\rho T$ data	767	652	73.8 – 423	0.01 – 800	0.16 – 0.84
VLE data	487	399	72.2 – 134	0.1 – 2.8	0.00 – 0.98
Total	**1254**	**1051**	**72.2 – 423**	**0.01 – 800**	**0.00 – 0.98**
CO_2–C_2H_6					
$p\rho T$ data	2522	1266	220 – 478	0.03 – 68.9	0.01 – 0.90
Isochoric heat capacity	259	–	218 – 341	67.6^{ρ} – 902^{ρ}	0.26 – 0.75
Speed of sound	69	–	220 – 450	0.1 – 1.3	0.40
Isobaric heat capacity	56	–	303 – 393	0.00 – 52.9	0.50
Enthalpy differences	79	–	230 – 350	15.2 – 18.4	0.10 – 0.90
VLE data	492	216	207 – 298	0.3 – 6.6	0.01 – 0.99
Total	**3477**	**1482**	**207 – 478**	**0.00 – 68.9**	**0.01 – 0.99**
CO_2–C_3H_8					
$p\rho T$ data	1421	862	278 – 511	0.1 – 70.6	0.07 – 0.97
Saturated liquid density[e]	51	–	278 – 311	0.7 – 6.7	0.06 – 0.98
VLE data	619	89	211 – 361	0.1 – 6.9	0.02 – 0.99
Total	**2091**	**951**	**211 – 511**	**0.1 – 70.6**	**0.02 – 0.99**
CO_2–n-C_4H_{10}					
$p\rho T$ data	125	–	311 – 360	1.1 – 10.6	0.03 – 0.20
Excess molar enthalpy	20	20	221 – 242	0.8 – 4.4	0.17 – 0.85

Table 6.4 (continued)

Binary mixture	Number of data points total[a]	used[b]	Covered ranges Temperature T/K	Pressure p/MPa	Composition[c,d] x
CO_2–n-C_4H_{10} (continued)					
VLE data	438	223	228 – 418	0.03 – 8.2	0.06 – 1.00
Total	**583**	**243**	**221 – 418**	**0.03 – 10.6**	**0.03 – 1.00**
CO_2–i-C_4H_{10}					
$p\rho T$ data	126	–	311 – 360	1.0 – 10.5	0.03 – 0.20
Saturated liquid density[e]	29	–	311 – 394	0.7 – 7.2	0.12 – 0.97
VLE data	94	73	311 – 394	0.6 – 7.4	0.10 – 0.99
Total	**249**	**73**	**311 – 394**	**0.6 – 10.5**	**0.03 – 0.99**
CO_2–n-C_5H_{12}					
$p\rho T$ data	804	366	278 – 423	0.2 – 65.0	0.01 – 0.99
VLE data	214	72	253 – 459	0.2 – 9.9	0.02 – 0.99
Total	**1018**	**438**	**253 – 459**	**0.2 – 65.0**	**0.01 – 0.99**
CO_2–i-C_5H_{12}					
$p\rho T$ data	106	91	278 – 378	0.2 – 9.4	0.00 – 0.99
VLE data	53	36	278 – 378	0.2 – 9.4	0.03 – 0.99
Total	**159**	**127**	**278 – 378**	**0.2 – 9.4**	**0.00 – 0.99**
CO_2–n-C_6H_{14}					
VLE data	20	20	298 – 313	0.4 – 7.7	0.08 – 0.95
Total	**20**	**20**	**298 – 313**	**0.4 – 7.7**	**0.08 – 0.95**
CO_2–n-C_7H_{16}					
$p\rho T$ data	141	101	299 – 459	0.1 – 55.5	0.01 – 0.98
VLE data	64	44	311 – 477	0.2 – 13.3	0.05 – 0.98
Total	**205**	**145**	**299 – 477**	**0.1 – 55.5**	**0.01 – 0.98**
CO_2–n-C_8H_{18}					
VLE data	20	16	313 – 348	1.5 – 11.4	0.11 – 0.86
Total	**20**	**16**	**313 – 348**	**1.5 – 11.4**	**0.11 – 0.86**
CO_2–H_2					
$p\rho T$ data	413	316	273 – 473	0.2 – 50.7	0.01 – 0.75
VLE data	138	68	220 – 298	1.1 – 20.3	0.00 – 0.16
Total	**551**	**384**	**220 – 473**	**0.2 – 50.7**	**0.00 – 0.75**
CO_2–O_2					
VLE data	144	–	223 – 283	1.0 – 13.2	0.00 – 0.78
Total	**144**	**–**	**223 – 283**	**1.0 – 13.2**	**0.00 – 0.78**

Table 6.4 (continued)

Binary mixture	Number of data points		Covered ranges		
	total[a]	used[b]	Temperature T/K	Pressure p/MPa	Composition[c,d] x
CO_2–CO					
$p\rho T$ data	75	–	323 – 423	0.1 – 6.5	0.43
Total	**75**	**–**	**323 – 423**	**0.1 – 6.5**	**0.43**
CO_2–H_2O					
$p\rho T$ data	448	446	323 – 699	0.1 – 34.6	0.02 – 0.79
VLE data	201	–	383 – 623	10.0 – 350	0.57 – 1.00
Total	**649**	**446**	**323 – 699**	**0.1 – 350**	**0.02 – 1.00**
CO_2–He					
$p\rho T$ data	1401	1278	253 – 800	0.2 – 58.8	0.06 – 0.96
VLE data	30	–	253 – 293	3.0 – 14.1	0.00 – 0.05
Total	**1431**	**1278**	**253 – 800**	**0.2 – 58.8**	**0.00 – 0.96**
CO_2–Ar					
$p\rho T$ data	572	496	288 – 373	0.3 – 101	0.06 – 0.87
VLE data	31	10	233 – 288	2.6 – 13.2	0.03 – 0.35
Total	**603**	**506**	**233 – 373**	**0.3 – 101**	**0.03 – 0.87**
C_2H_6–C_3H_8					
$p\rho T$ data	697	360	108 – 322	0.00 – 13.8	0.00 – 0.89
Isobaric heat capacity	16	–	120 – 270	5.1	0.39
Enthalpy differences	156	–	110 – 343	0.1 – 14.2	0.20 – 0.39
Excess molar enthalpy	157	–	323 – 373	5.0 – 15.0	0.01 – 0.98
VLE data	494	286	128 – 369	0.00 – 5.2	0.00 – 1.00
Total	**1520**	**646**	**108 – 373**	**0.00 – 15.0**	**0.00 – 1.00**
C_2H_6–n-C_4H_{10}					
$p\rho T$ data	269	223	269 – 414	0.5 – 13.8	0.05 – 0.83
VLE data	379	114	235 – 419	0.2 – 5.8	0.05 – 0.98
Total	**648**	**337**	**235 – 419**	**0.2 – 13.8**	**0.05 – 0.98**
C_2H_6–i-C_4H_{10}					
VLE data	99	34	203 – 394	0.00 – 5.4	0.04 – 0.98
Total	**99**	**34**	**203 – 394**	**0.00 – 5.4**	**0.04 – 0.98**
C_2H_6–n-C_5H_{12}					
$p\rho T$ data	1508	1422	278 – 511	0.1 – 68.9	0.01 – 0.90
Isochoric heat capacity	57	–	309	231^{ρ} – 491^{ρ}	0.01 – 0.32
VLE data	67	59	278 – 444	0.3 – 6.8	0.02 – 1.00
Total	**1632**	**1481**	**278 – 511**	**0.1 – 68.9**	**0.01 – 1.00**

Table 6.4 (continued)

Binary mixture	Number of data points total[a]	used[b]	Temperature T/K	Covered ranges Pressure p/MPa	Composition[c,d] x
C_2H_6–n-C_6H_{14}					
VLE data	46	43	298 – 450	0.2 – 7.9	0.08 – 0.99
Total	**46**	**43**	**298 – 450**	**0.2 – 7.9**	**0.08 – 0.99**
C_2H_6–n-C_7H_{16}					
$p\rho T$ data	212	170	275 – 521	0.3 – 8.6	0.02 – 0.73
VLE data	533	–	235 – 540	0.3 – 8.8	0.02 – 1.00
Total	**745**	**170**	**235 – 540**	**0.3 – 8.8**	**0.02 – 1.00**
C_2H_6–n-C_8H_{18}					
$p\rho T$ data	64	51	273 – 373	0.4 – 5.3	0.02 – 0.95
VLE data	82	47	273 – 373	0.4 – 6.8	0.02 – 0.95
Total	**146**	**98**	**273 – 373**	**0.4 – 6.8**	**0.02 – 0.95**
C_2H_6–H_2					
$p\rho T$ data	552	382	275 – 422	0.2 – 26.2	0.10 – 0.80
VLE data	117	61	139 – 283	0.7 – 53.3	0.00 – 0.40
Total	**669**	**443**	**139 – 422**	**0.2 – 53.3**	**0.00 – 0.80**
C_2H_6–CO					
VLE data	22	21	173 – 273	0.9 – 11.7	0.01 – 0.83
Total	**22**	**21**	**173 – 273**	**0.9 – 11.7**	**0.01 – 0.83**
C_3H_8–n-C_4H_{10}					
$p\rho T$ data	899	545	239 – 411	0.1 – 13.8	0.15 – 0.90
VLE data	459	60	237 – 420	0.03 – 11.0	0.05 – 0.99
Total	**1358**	**605**	**237 – 420**	**0.03 – 13.8**	**0.05 – 0.99**
C_3H_8–i-C_4H_{10}					
$p\rho T$ data	788	495	200 – 400	0.1 – 35.4	0.15 – 0.86
Isochoric heat capacity	135	–	203 – 345	484^{ρ} – 649^{ρ}	0.30 – 0.70
Isobaric heat capacity	23	–	293 – 353	0.1 – 1.2	0.50
VLE data	288	148	237 – 394	0.04 – 4.2	0.00 – 1.00
Total	**1234**	**643**	**200 – 400**	**0.04 – 35.4**	**0.00 – 1.00**
C_3H_8–n-C_5H_{12}					
$p\rho T$ data	283	267	321 – 461	0.1 – 4.6	0.12 – 0.86
VLE data	258	–	321 – 468	0.4 – 4.5	0.04 – 1.00
Total	**541**	**267**	**321 – 468**	**0.1 – 4.6**	**0.04 – 1.00**
C_3H_8–i-C_5H_{12}					
$p\rho T$ data	640	628	273 – 573	0.1 – 8.1	0.10 – 0.90

Table 6.4 (continued)

Binary mixture	Number of data points total[a]	Number of data points used[b]	Covered ranges Temperature T/K	Covered ranges Pressure p/MPa	Covered ranges Composition[c,d] x
C_3H_8–i-C_5H_{12} (continued)					
VLE data	89	78	273 – 453	0.1 – 4.6	0.02 – 0.97
Total	**729**	**706**	**273 – 573**	**0.1 – 8.1**	**0.02 – 0.97**
C_3H_8–n-C_6H_{14}					
$p\rho T$ data	235	203	325 – 497	0.1 – 5.0	0.08 – 0.86
VLE data	401	–	288 – 497	0.1 – 5.0	0.02 – 0.96
Total	**636**	**203**	**288 – 497**	**0.1 – 5.0**	**0.02 – 0.96**
C_3H_8–n-C_7H_{16}					
VLE data	197	40	333 – 533	2.1 – 5.2	0.02 – 0.98
Total	**197**	**40**	**333 – 533**	**2.1 – 5.2**	**0.02 – 0.98**
C_3H_8–n-C_8H_{18}					
$p\rho T$ data	155	136	313 – 550	0.7 – 5.9	0.04 – 0.79
Total	**155**	**136**	**313 – 550**	**0.7 – 5.9**	**0.04 – 0.79**
C_3H_8–H_2					
$p\rho T$ data	73	–	298 – 348	0.3 – 5.1	0.73 – 0.84
VLE data	215	140	172 – 361	1.4 – 55.2	0.01 – 0.67
Total	**288**	**140**	**172 – 361**	**0.3 – 55.2**	**0.01 – 0.84**
C_3H_8–CO					
VLE data	37	37	148 – 323	1.4 – 15.2	0.02 – 0.43
Total	**37**	**37**	**148 – 323**	**1.4 – 15.2**	**0.02 – 0.43**
C_3H_8–H_2O					
$p\rho T$ data	55	47	529 – 663	20.0 – 330	0.29 – 0.98
Total	**55**	**47**	**529 – 663**	**20.0 – 330**	**0.29 – 0.98**
n-C_4H_{10}–i-C_4H_{10}					
$p\rho T$ data	352	16	240 – 380	0.03 – 7.1	0.21 – 0.80
VLE data	228	197	273 – 374	0.1 – 2.0	0.02 – 0.98
Total	**580**	**213**	**240 – 380**	**0.03 – 7.1**	**0.02 – 0.98**
n-C_4H_{10}–n-C_5H_{12}					
$p\rho T$ data	73	65	358 – 464	1.0 – 3.7	0.13 – 0.86
VLE data	195	–	298 – 464	0.1 – 3.7	0.10 – 0.98
Total	**268**	**65**	**298 – 464**	**0.1 – 3.7**	**0.10 – 0.98**
n-C_4H_{10}–n-C_6H_{14}					
$p\rho T$ data	157	152	375 – 502	0.6 – 3.9	0.10 – 0.90

Table 6.4 (continued)

Binary mixture	Number of data points		Covered ranges		
	total[a]	used[b]	Temperature T/K	Pressure p/MPa	Composition[c,d] x
n-C_4H_{10}–n-C_6H_{14} (continued)					
VLE data	365	–	358 – 502	0.6 – 3.9	0.10 – 0.90
Total	**522**	**152**	**358 – 502**	**0.6 – 3.9**	**0.10 – 0.90**
n-C_4H_{10}–n-C_7H_{16}					
$p\rho T$ data	255	250	329 – 530	0.3 – 4.1	0.06 – 0.84
VLE data	477	–	329 – 540	0.3 – 4.1	0.02 – 0.99
Total	**732**	**250**	**329 – 540**	**0.3 – 4.1**	**0.02 – 0.99**
n-C_4H_{10}–n-C_8H_{18}					
$p\rho T$ data	97	72	339 – 555	0.7 – 4.3	0.05 – 0.82
Total	**97**	**72**	**339 – 555**	**0.7 – 4.3**	**0.05 – 0.82**
n-C_4H_{10}–H_2					
VLE data	64	62	328 – 394	2.8 – 16.9	0.02 – 0.27
Total	**64**	**62**	**328 – 394**	**2.8 – 16.9**	**0.02 – 0.27**
n-C_4H_{10}–H_2O					
$p\rho T$ data	219	149	311 – 707	0.7 – 310	0.10 – 0.98
VLE data[y]	51	–	600 – 700	19.3 – 276	0.65 – 0.98
Total	**270**	**149**	**311 – 707**	**0.7 – 310**	**0.10 – 0.98**
n-C_4H_{10}–Ar					
$p\rho T$ data	70	66	340 – 380	1.4 – 18.5	0.02 – 0.82
VLE data	35	21	340 – 380	1.4 – 18.5	0.02 – 0.56
Total	**105**	**87**	**340 – 380**	**1.4 – 18.5**	**0.02 – 0.82**
i-C_4H_{10}–H_2					
VLE data	21	–	311 – 394	3.4 – 20.7	0.02 – 0.25
Total	**21**	**–**	**311 – 394**	**3.4 – 20.7**	**0.02 – 0.25**
i-C_4H_{10}–H_2O					
$p\rho T$ data	66	–	547 – 695	13.5 – 306	0.50 – 0.98
VLE data[y]	77	–	547 – 695	13.5 – 306	0.50 – 0.98
Total	**143**	**–**	**547 – 695**	**13.5 – 306**	**0.50 – 0.98**
n-C_5H_{12}–i-C_5H_{12}					
VLE data	13	–	328 – 385	0.2 – 0.8	0.02 – 0.94
Total	**13**	**–**	**328 – 385**	**0.2 – 0.8**	**0.02 – 0.94**
n-C_5H_{12}–n-C_6H_{14}					
$p\rho T$ data	319	–	273 – 348	0.1 – 40.0	0.10 – 0.90

Table 6.4 (continued)

Binary mixture	Number of data points total[a]	used[b]	Covered ranges Temperature T/K	Pressure p/MPa	Composition[c,d] x
n-C_5H_{12}–n-C_6H_{14} (continued)					
VLE data	8	–	298 – 298	0.03 – 0.1	0.10 – 0.89
Total	**327**	**–**	**273 – 348**	**0.03 – 40.0**	**0.10 – 0.90**
n-C_5H_{12}–n-C_7H_{16}					
$p\rho T$ data	326	–	273 – 348	0.1 – 40.0	0.10 – 0.90
VLE data	26	–	404 – 526	1.0 – 3.1	0.10 – 0.90
Total	**352**	**–**	**273 – 526**	**0.1 – 40.0**	**0.10 – 0.90**
n-C_5H_{12}–n-C_8H_{18}					
$p\rho T$ data	9	–	298	0.1	0.10 – 0.89
VLE data	61	–	292 – 434	0.1 – 1.5	0.05 – 0.95
Total	**70**	**–**	**292 – 434**	**0.1 – 1.5**	**0.05 – 0.95**
n-C_5H_{12}–H_2O					
$p\rho T$ data	55	55	647	4.3 – 40.9	0.31 – 0.97
Total	**55**	**55**	**647**	**4.3 – 40.9**	**0.31 – 0.97**
n-C_6H_{14}–n-C_7H_{16}					
$p\rho T$ data	452	35	273 – 363	0.1 – 71.7	0.09 – 0.91
Speed of sound	28	–	298	0.1	0.01 – 0.96
VLE data	29	14	303 – 367	0.01 – 0.1	0.03 – 0.97
Total	**509**	**49**	**273 – 367**	**0.01 – 71.7**	**0.01 – 0.97**
n-C_6H_{14}–n-C_8H_{18}					
$p\rho T$ data	61	–	283 – 313	0.1	0.07 – 0.94
Total	**61**	**–**	**283 – 313**	**0.1**	**0.07 – 0.94**
n-C_6H_{14}–H_2					
$p\rho T$ data	423	193	278 – 511	1.4 – 68.9	0.19 – 0.79
VLE data	134	98	278 – 478	0.03 – 68.9	0.01 – 0.69
Total	**557**	**291**	**278 – 511**	**0.03 – 68.9**	**0.01 – 0.79**
n-C_6H_{14}–H_2O					
$p\rho T$ data	940	88	327 – 699	0.1 – 247	0.01 – 0.96
Total	**940**	**88**	**327 – 699**	**0.1 – 247**	**0.01 – 0.96**
n-C_7H_{16}–n-C_8H_{18}					
$p\rho T$ data	27	–	293 – 298	0.1	0.10 – 0.90
VLE data	43	20	313 – 394	0.00 – 0.1	0.04 – 0.97
Total	**70**	**20**	**293 – 394**	**0.00 – 0.1**	**0.04 – 0.97**

Table 6.4 (continued)

Binary mixture	Number of data points total[a]	Number of data points used[b]	Covered ranges Temperature T/K	Covered ranges Pressure p/MPa	Covered ranges Composition[c,d] x
n-C_7H_{16}–H_2					
VLE data	29	27	424 – 499	2.5 – 78.5	0.02 – 0.81
Total	**29**	**27**	**424 – 499**	**2.5 – 78.5**	**0.02 – 0.81**
n-C_8H_{18}–H_2O					
$p\rho T$ data	28	28	623	3.1 – 15.3	0.15 – 0.77
Total	**28**	**28**	**623**	**3.1 – 15.3**	**0.15 – 0.77**
H_2–CO					
$p\rho T$ data	54	54	298	0.1 – 17.2	0.34 – 0.67
VLE data	81	80	68.2 – 122	1.7 – 24.1	0.35 – 0.97
Total	**135**	**134**	**68.2 – 298**	**0.1 – 24.1**	**0.34 – 0.97**
H_2–He					
VLE data	264	–	15.5 – 32.5	0.2 – 10.4	0.00 – 0.36
Total	**264**	**–**	**15.5 – 32.5**	**0.2 – 10.4**	**0.00 – 0.36**
O_2–H_2O					
$p\rho T$ data	154	154	472 – 673	19.5 – 324	0.06 – 0.94
Total	**154**	**154**	**472 – 673**	**19.5 – 324**	**0.06 – 0.94**
O_2–He					
VLE data	37	–	77.4 – 143	1.7 – 13.8	0.00 – 0.09
Total	**37**	**–**	**77.4 – 143**	**1.7 – 13.8**	**0.00 – 0.09**
O_2–Ar					
$p\rho T$ data	36	–	70.4 – 88.8	0.1	0.10 – 0.87
VLE data	616	51	83.8 – 139	0.1 – 2.6	0.00 – 1.00
Total	**652**	**51**	**70.4 – 139**	**0.1 – 2.6**	**0.00 – 1.00**
CO–He					
VLE data	98	–	77.4 – 128	0.7 – 13.8	0.00 – 0.17
Total	**98**	**–**	**77.4 – 128**	**0.7 – 13.8**	**0.00 – 0.17**
CO–Ar					
VLE data	16	15	123 – 137	1.5 – 3.8	0.06 – 0.92
Total	**16**	**15**	**123 – 137**	**1.5 – 3.8**	**0.06 – 0.92**
H_2O–Ar					
$p\rho T$ data	152	152	477 – 663	10.4 – 337	0.05 – 0.80
Total	**152**	**152**	**477 – 663**	**10.4 – 337**	**0.05 – 0.80**

Table 6.4 (continued)

Binary mixture	Number of data points total[a]	used[b]	Covered ranges Temperature T/K	Pressure p/MPa	Composition[c,d] x
He–Ar					
$p\rho T$ data	500	–	143 – 323	0.2 – 72.3	0.20 – 0.78
Speed of sound	50	–	298	198 – 1971	0.10 – 0.50
VLE data	288	–	91.4 – 160	1.4 – 422	0.40 – 1.00
Total	**838**	**–**	**91.4 – 323**	**0.2 – 1971**	**0.10 – 1.00**

[a] Number of all available data points.
[b] Number of data points used for the development of the new wide-range equation of state.
[c] Mole fractions of the second component of the binary mixture, i.e. component B of mixture A–B. Values of 0.00 and 1.00 result from a mixture composition close to a pure component.
[d] The composition range for VLE data corresponds to bubble point compositions, unless otherwise stated.
[e] Listed separately due to a different data format. Saturated liquid (and vapour) densities may also be tabulated as ordinary $p\rho T$ or VLE data.
[y] VLE data set contains pTy data only. The composition range corresponds to dew point compositions.
[ρ] Density in $\mathrm{kg \cdot m^{-3}}$ instead of pressure.

6.2 Data for Natural Gases and Other Multi-Component Mixtures

The present database comprises data for natural gases and other multi-component mixtures of more than 300 different compositions[43] including, aside from many ordinary natural gases, for example, the following types of multi-component mixtures:

- Natural gases containing high fractions of methane, nitrogen, carbon dioxide, or ethane
- Natural gases containing substantial amounts of ethane, propane, and heavier alkanes
- Natural gases containing high fractions of hydrogen (natural gas–hydrogen mixtures)
- Natural gases containing large amounts of coke-oven constituents
- Rich natural gases[44]
- LNG mixtures
- Ternary mixtures of light or heavier hydrocarbons[45], such as propane–n-butane–isobutane and n-pentane–n-hexane–n-heptane

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[43] VLE data are not considered in this number.

[44] Rich natural gases contain large amounts of ethane and heavier alkanes (e.g. 18 mole-% ethane, 8 mole-% propane, 3 mole-% n-butane, 0.5 mole-% n-pentane, 0.2 mole-% n-hexane) and fractions of methane down to 50 mole-%.

[45] The thermodynamic properties of hydrocarbon mixtures are of particular interest in connection with the production and refining of petroleum. Moreover, binary and ternary mixtures of propane,

- Other ternary and multi-component mixtures

Some of the covered data contain high fractions of hydrogen sulphide or small amounts of the further secondary alkanes n-nonane and n-decane beside the 18 components considered in this work (see Table 4.2). The three further natural gas components n-nonane, n-decane, and hydrogen sulphide will be included in an extended version of the developed wide-range equation of state in the near future (see also Chap. 9).

A summary of the thermal and caloric properties available for natural gases and other multi-component mixtures of natural gas components is shown in Table 6.5. The table provides information on the covered temperature and pressure ranges as well as the number of data points. Detailed listings of all data sets and the compositions of the mixture data are tabulated in the appendix (see Tables A2.2 – A2.5).

Table 6.5 Summary of the available data for thermal and caloric properties of natural gases and other multi-component mixtures

Data type	Number of data points	Covered ranges Temperature T/K	Covered ranges Pressure p/MPa	Maximum number of components
$p\rho T$ data	21769	91.0 – 573	0.03 – 99.9	18
Speed of sound	1337	213 – 414	0.00 – 70.0	13
Isobaric heat capacity	325	105 – 350	0.5 – 30.0	8
Enthalpy differences	1166	105 – 422	0.2 – 16.5	10
Saturated liquid density	124	105 – 251	0.04 – 3.2	8
VLE data[a]	2284	77.8 – 450	0.1 – 27.6	4
Total	**27005**	**77.8 – 573**	**0.00 – 99.9**	**18**

[a] The total number of VLE data comprises 2,234 $pTxy$ data, 17 pTx data, and 33 pTy data.

The data are dominated by a huge amount of $p\rho T$ data in the gas phase covering temperatures from 270 K to 350 K at pressures up to 30 MPa. Nevertheless, the comparatively few $p\rho T$ data measured at temperatures below 270 K enable, along with the accurate and wide ranging data of important and related binary mixtures[46] (e.g. methane–nitrogen and methane–ethane), a well-founded estimation of the uncertainty in gas phase densities at temperatures below 270 K. The most accurate caloric properties are those for speeds of sound and enthalpy differences. Most of these data cover the temperature range from 250 K to 350 K at pressures up to 12 MPa and 20 MPa, respectively.

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n-butane, and isobutane are considered as promising alternative refrigerants in modern refrigeration and heat-pump systems due to their negligible global warming potential.

[46] For instance, accurate and wide ranging density and speed of sound data for the binary mixtures methane–nitrogen and methane–ethane cover large reduced temperature ranges which include those relevant to natural gases (see also Chap. 8).

As mentioned in the previous sections, the data situation for properties of natural gases and other multi-component mixtures in the liquid phase is poor. The evaluation of the new equation of state is mainly based on experimental data for the saturated liquid densities of LNG-like multi-component mixtures measured by Hiza and Haynes (1980) and Haynes (1982) covering the temperature range from 100 K to 140 K.

Almost all collected VLE data correspond to data measured for ternary mixtures of the considered natural gas components. Further data used for comparisons, which are not included in the tables of this chapter, are, for example, the recent dew point measurements for a number of different natural gas and other multi-component mixtures of Avila *et al.* [Avila *et al.* (2002a-c), Avila *et al.* (2003), Jarne *et al.* (2004a)] and Blanco *et al.* [Blanco *et al.* (2000), Jarne *et al.* (2004b)], and Mørch *et al.* (2006).

In an extended version of the developed mixture model, the very accurate description of the properties of dry air (and possibly also humid air) will be additionally considered in the near future (see also Chap. 9). Therefore, an additional data set was established for the properties of dry air, treated as a three-component mixture of nitrogen, oxygen, and argon, which is not included in the database presented here[47]. The data set comprises more than 3,000 data of thermal and caloric properties and is almost identical to the data set used by Lemmon *et al.* (2000) for the development of a fundamental equation for the properties of dry air. This data set will be updated by the new measurements being performed within the framework of the current research project “Advanced Adiabatic Compressed Air Energy Storage (AA-CAES)” of the European Union, which aims, among other things, to establish a database for the thermophysical properties of humid air over wide ranges of temperature, pressure, and composition.

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[47] VLE data for ternary mixtures of nitrogen, oxygen, and argon are already included in Table 6.5.

7 The New Equation of State (GERG-2004)

To fulfil the requirements for a new equation of state for natural gases as defined in Chap. 3, based on the pure substance equations of state for 18 natural gas components (see Chap. 4), the theoretical background and investigations regarding the development of multi-fluid mixture models (see Chap. 5), and the collected and assessed data for binary and multi-component mixtures of natural gas components (see Chap. 6), a new equation of state for the thermodynamic properties of natural gases, similar gases, and other mixtures was developed in this work. The new equation of state is valid for wide ranges of temperature, pressure, and composition and covers the gas phase, the liquid phase, the supercritical region, and vapour-liquid equilibrium states. The development of this equation 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 new formulation was adopted by GERG in 2004 and called GERG-2004 equation of state or GERG-2004 for short, and is also referred to in the following as GERG-2004 formulation.

Detailed descriptions of the mathematical structure of the new wide-range equation of state and the basic and advanced relations required for property calculations are provided in the first four sections of this chapter. The increased complexity of the mixture model demands a systematic approach in order to avoid inefficient and incorrect computer code. To generate fast and thermodynamically consistent computer codes for the calculation of thermodynamic properties for arbitrary types of mixtures, a modular approach was used. This approach enables modifications of single features of the model, e.g. the composition-dependent reducing functions, without rewriting the entire code. Furthermore, all of the presented relations between the Helmholtz free energy of the mixture and the thermodynamic properties and their derivatives can be applied to other multi-fluid mixture models based on a similar structure with composition-dependent reducing functions. Section 7.1 provides a comprehensive numerical description of the new equation of state. In Sec. 7.2, the basic derivatives and relations required for the calculation of several thermodynamic properties are presented. Further derivatives and advanced relations required for phase equilibrium and other property calculations are summarised in Sec. 7.3. Relations between activity coefficient models, excess Gibbs free energy models, and multi-fluid mixture models explicit in the reduced Helmholtz free energy α are given in Sec. 7.4.

For the development of property calculation routines that allow for “blind” calculations of the thermodynamic properties of mixtures at arbitrary conditions, special algorithms are required for the verification of phase stability and the solution of the isothermal flash problem. Moreover, the calculation of saturation points and the construction of phase envelopes are of practical importance. The basic principles of the respective algorithms used in this work are described in Secs. 7.5 – 7.7. The required properties and their derivatives that need to be calculated from the new equation of state were set up in the course of this work and are given in Sec. 7.3.

The algorithms used for stability analysis and *pT* flash calculations are based on the minimisation of the Gibbs free energy (see also Sec. 5.4.4). For the successful implementation of such advanced property calculation algorithms, a proper density solver is required that takes into account the special characteristics of the new mixture model (see Sec. 7.8).

Aside from the solution of flash situations based on the minimisation of the Gibbs free energy of the overall equilibrium system, there is also the possibility of minimising the overall Helmholtz free energy of a mixture. This is of particular interest for the new equation of state and other mixture models developed as a multi-fluid approximation explicit in the Helmholtz free energy with the independent variables density, temperature, and composition. The basics of Helmholtz free energy based flash formulations and the advantage of such an approach are presented in Sec. 7.9.

Aside from the accurate fundamental pure substance equations for each of the 18 natural gas components (see Table 4.2), the developed mixture model is based on correlation equations developed for binary mixtures. Important details of the development of the numerous binary equations and the new functional form (see Sec. 5.3.4) are given in Secs. 7.10 and 7.11.

To investigate the problem of invariance (see Sec. 5.2.1) and the predictive capabilities of a mixture model with invariant reducing functions for the description of the thermodynamic properties of multi-component mixtures, an alternative (invariant) equation of state was developed. The results of the investigations are summarised in Sec. 7.12.

Detailed information on the range of validity of the new equation of state and estimated uncertainties in selected thermal and caloric properties of binary and multi-component mixtures are given in Sec. 7.13.

Based on the stability analysis and the *pT* flash and phase envelope algorithms described in Secs. 7.5 – 7.7, a comprehensive software package, which is briefly described in Sec. 7.14, was developed enabling the calculation of a number of thermodynamic properties from the new equation of state.

Since the mixture model and the property calculation algorithms are not limited to the current number of considered components ($N = 18$), the variable N is continuously used in this work to denote the maximum number of components.

To simplify the notation of certain relations, the Kronecker delta δ_{ij} (or δ_{sj}) is used [see Table 7.11 and Eqs. (7.107), (7.109), (7.125), (7.128), and (7.142)] and should not be confused with the reduced mixture density δ.

7.1 Numerical Description of the New Equation of State for Natural Gases and Other Mixtures

The new mixture model developed for natural gases, similar gases, and other mixtures is based on a multi-fluid approximation explicit in the reduced Helmholtz free energy

$$\alpha(\delta,\tau,\bar{x}) = \alpha^{\mathrm{o}}(\rho,T,\bar{x}) + \alpha^{\mathrm{r}}(\delta,\tau,\bar{x}), \tag{7.1}$$

where the α^{o} part represents the properties of the ideal-gas mixture at a given mixture density ρ, temperature T, and molar composition $\bar{x}$ according to

$$\alpha^{\mathrm{o}}(\rho,T,\bar{x}) = \sum_{i=1}^{N} x_i \left[\alpha^{\mathrm{o}}_{\mathrm{o}i}(\rho,T) + \ln x_i\right] \tag{7.2}$$

and the residual part α^{r} of the reduced Helmholtz free energy of the mixture is given by

$$\alpha^{\mathrm{r}}(\delta,\tau,\bar{x}) = \sum_{i=1}^{N} x_i\, \alpha^{\mathrm{r}}_{\mathrm{o}i}(\delta,\tau) + \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} x_i x_j F_{ij}\, \alpha^{\mathrm{r}}_{ij}(\delta,\tau), \tag{7.3}$$

where δ is the reduced mixture density and τ is the inverse reduced mixture temperature according to

$$\delta = \frac{\rho}{\rho_{\mathrm{r}}(\bar{x})} \quad \text{and} \quad \tau = \frac{T_{\mathrm{r}}(\bar{x})}{T}. \tag{7.4}$$

Equation (7.3) takes into account the residual behaviour of the mixture at the reduced mixture variables. The first part of Eq. (7.3) is the contribution of the reduced residual Helmholtz free energy of the pure substance equations of state linearly combined using the mole fractions x_i. The double summation in Eq. (7.3) is the departure function $\Delta\alpha^{\mathrm{r}}(\delta,\tau,\bar{x})$ [see Eqs. (5.7) and (5.22)], which is the summation over all binary specific and generalised departure functions $\Delta\alpha^{\mathrm{r}}_{ij}(\delta,\tau,\bar{x})$ developed for the respective binary mixtures [see Eq. (5.23)].

In Eq. (7.2) the dimensionless form of the Helmholtz free energy in the ideal-gas state of component i is given by

$$\begin{aligned}\alpha^{\mathrm{o}}_{\mathrm{o}i}(\rho,T) = \frac{R^*}{R}\Bigg[&\ln\left(\frac{\rho}{\rho_{\mathrm{c},i}}\right) + n^{\mathrm{o}}_{\mathrm{o}i,1} + n^{\mathrm{o}}_{\mathrm{o}i,2}\frac{T_{\mathrm{c},i}}{T} + n^{\mathrm{o}}_{\mathrm{o}i,3}\ln\left(\frac{T_{\mathrm{c},i}}{T}\right) + \sum_{k=4,6} n^{\mathrm{o}}_{\mathrm{o}i,k}\ln\left|\sinh\left(\vartheta^{\mathrm{o}}_{\mathrm{o}i,k}\frac{T_{\mathrm{c},i}}{T}\right)\right| \\ &- \sum_{k=5,7} n^{\mathrm{o}}_{\mathrm{o}i,k}\ln\left|\cosh\left(\vartheta^{\mathrm{o}}_{\mathrm{o}i,k}\frac{T_{\mathrm{c},i}}{T}\right)\right|\Bigg],\end{aligned} \tag{7.5}$$

where $\rho_{\mathrm{c},i}$ and $T_{\mathrm{c},i}$ are the critical parameters of the pure components (see Table A3.5) and

$$R = 8.314\,472\ \mathrm{J \cdot mol^{-1} \cdot K^{-1}} \tag{7.6}$$

is the current, internationally accepted standard for the molar gas constant [Mohr and Taylor (2005)]. As described in Sec. 4.3, the equations for $\alpha^{\mathrm{o}}_{\mathrm{o}i}$ result from the integration of the c^{o}_{p} equations of Jaeschke and Schley (1995) [see Eqs. (4.13) – (4.15)], who used a different molar gas constant than the one used in the developed mixture model. The ratio R^*/R with $R^* = 8.314\,510\ \mathrm{J\cdot mol^{-1}\cdot K^{-1}}$ takes into account this difference and therefore leads to the exact solution of the original c_p^{o} equations. The values of the coefficients $n_{\mathrm{o}i,k}^{\mathrm{o}}$ and the parameters $\vartheta_{\mathrm{o}i,k}^{\mathrm{o}}$ of Eq. (7.5) for all considered 18 components are listed in Table A3.1 of the appendix.

The residual part of the reduced Helmholtz free energy of component i [see Eq. (7.3)] of the pure substance equations of state listed in Table 4.2 is given by

$$\alpha_{\mathrm{o}i}^{\mathrm{r}}(\delta,\tau) = \sum_{k=1}^{K_{\mathrm{Pol},i}} n_{\mathrm{o}i,k}\,\delta^{d_{\mathrm{o}i,k}}\,\tau^{t_{\mathrm{o}i,k}} + \sum_{k=K_{\mathrm{Pol},i}+1}^{K_{\mathrm{Pol},i}+K_{\mathrm{Exp},i}} n_{\mathrm{o}i,k}\,\delta^{d_{\mathrm{o}i,k}}\,\tau^{t_{\mathrm{o}i,k}}\,e^{-\delta^{c_{\mathrm{o}i,k}}} . \tag{7.7}$$

Thus, the equations for $\alpha_{\mathrm{o}i}^{\mathrm{r}}$ use the same basic structure as already mentioned in Sec. 4.7. The respective values for the coefficients $n_{\mathrm{o}i,k}$ and the exponents $d_{\mathrm{o}i,k}$, $t_{\mathrm{o}i,k}$, and $c_{\mathrm{o}i,k}$ for all considered components are given in Tables A3.2 – A3.4[48].

The function $\alpha_{ij}^{\mathrm{r}}(\delta,\tau)$ of Eq. (7.3), which is the part of the departure function $\Delta\alpha_{ij}^{\mathrm{r}}(\delta,\tau,\bar{x})$ that depends only on the reduced mixture variables δ and τ [see Eq. (5.23)], is given by

$$\alpha_{ij}^{\mathrm{r}}(\delta,\tau) = \sum_{k=1}^{K_{\mathrm{Pol},ij}} n_{ij,k}\,\delta^{d_{ij,k}}\,\tau^{t_{ij,k}} + \sum_{k=K_{\mathrm{Pol},ij}+1}^{K_{\mathrm{Pol},ij}+K_{\mathrm{Exp},ij}} n_{ij,k}\,\delta^{d_{ij,k}}\,\tau^{t_{ij,k}}\,e^{-\eta_{ij,k}(\delta-\varepsilon_{ij,k})^2-\beta_{ij,k}(\delta-\gamma_{ij,k})} , \tag{7.8}$$

where $\alpha_{ij}^{\mathrm{r}}(\delta,\tau)$ was developed for either a specific binary mixture (a binary specific departure function with binary specific coefficients and parameters) or a group of binary mixtures (generalised departure function with a uniform structure for the group of binary mixtures). For a binary specific departure function the adjustable factor F_{ij} in Eq. (7.3) is set to unity. The parameter is fitted to binary specific data for each mixture in the group of generalised binary mixtures (see Sec. 5.3.3). F_{ij} equals zero for those binary mixtures where no departure functions were developed. The non-zero F_{ij} parameters are listed in Table A3.6. The values for the coefficients $n_{ij,k}$ and the exponents $d_{ij,k}$, $t_{ij,k}$, $\eta_{ij,k}$, $\varepsilon_{ij,k}$, $\beta_{ij,k}$, and $\gamma_{ij,k}$ for all binary specific and generalised departure functions considered in the new mixture model are given in Table A3.7.

The reduced mixture variables δ and τ are calculated from Eq. (7.4) by means of the composition-dependent reducing functions for the mixture density

$$\frac{1}{\rho_{\mathrm{r}}(\bar{x})} = \sum_{i=1}^{N} x_i^2\,\frac{1}{\rho_{\mathrm{c},i}} + \sum_{i=1}^{N-1}\sum_{j=i+1}^{N} 2x_i x_j\,\beta_{v,ij}\,\gamma_{v,ij}\,\frac{x_i+x_j}{\beta_{v,ij}^2\,x_i+x_j}\,\frac{1}{8}\left(\frac{1}{\rho_{\mathrm{c},i}^{1/3}}+\frac{1}{\rho_{\mathrm{c},j}^{1/3}}\right)^3 \tag{7.9}$$

and the mixture temperature

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[48] For the simultaneously optimised equations of state of Span and Wagner (2003b) and Span (2000a) the old molar gas constant was substituted with the recent one without conversion. This has nearly no effect on the quality of the equations of state.

$$T_\mathrm{r}(\bar{x}) = \sum_{i=1}^{N} x_i^2\, T_{\mathrm{c},i} + \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} 2 x_i x_j\, \beta_{T,ij}\, \gamma_{T,ij}\, \frac{x_i + x_j}{\beta_{T,ij}^2\, x_i + x_j} \left(T_{\mathrm{c},i} \cdot T_{\mathrm{c},j}\right)^{0.5} . \tag{7.10}$$

Equations (7.9) and (7.10) are the simplified formulations of Eqs (5.10) and (5.11) enabling computing-time saving algorithms by using the relations regarding the numbering of mole fractions [Eq. (5.13)]. The binary parameters $\beta_{v,ij}$ and $\gamma_{v,ij}$ in Eq. (7.9) and $\beta_{T,ij}$ and $\gamma_{T,ij}$ in Eq. (7.10) are fitted to data for binary mixtures. The values of the binary parameters for all binary mixtures are listed in Table A3.8 of the appendix. The critical parameters $\rho_{\mathrm{c},i}$ and $T_{\mathrm{c},i}$ of the pure components are given in Table A3.5.

7.2 Derivatives of α, ρ_r, and T_r, and their Relations for the Calculation of Thermodynamic Properties

As mentioned in Sec. 5.4, all thermodynamic properties of a mixture can be derived from Eq. (7.1) by using the appropriate combinations of the ideal-gas mixture part $\alpha^\mathrm{o}(\rho, T, \bar{x})$ [Eq. (7.2)] and the residual part $\alpha^\mathrm{r}(\delta, \tau, \bar{x})$ [Eq. (7.3)] of the dimensionless Helmholtz free energy and their respective derivatives. The thermodynamic properties in the homogeneous gas, liquid, and supercritical regions and for the vapour-liquid equilibrium of a mixture are related to derivatives of α with respect to the reduced mixture variables δ and τ, and the mole fractions x_i. Relations between thermodynamic properties and α^o, α^r, and their derivatives for common thermodynamic properties are summarized in Table 7.1. A comprehensive list of pressure, density, total volume, and temperature derivatives also required for phase equilibrium calculations (see Sec. 7.3) and their relations to α^r is given in Table 7.2. The relations between α and the chemical potential μ_i, the fugacity coefficient φ_i, and the fugacity f_i of component i are presented in Table 7.3. The calculation of these properties requires the determination of composition derivatives of α^o and α^r as described in Sec. 5.4.1. Table 7.4 lists the first partial derivatives of α^o, α^r, and α_δ^r with respect to the mole numbers n_i. The second derivatives with respect to n_i and further relations required for the phase equilibrium algorithms developed in this work are derived in Sec. 7.3.

Since the multi-fluid mixture model is composed of several different correlation equations to take into account the real behaviour of mixtures (see Sec. 7.1), the evaluation of the derivatives of Eq. (7.1) with respect to the reduced mixture variables δ and τ is much more complex than the one of the derivatives of the reduced Helmholtz free energy of a pure substance [see Eq. (4.2)]. For instance, the derivative of α^o [Eq. (7.2)] as a function of ρ, T, and $\bar{x}$ with respect to τ is given by

$$\alpha_\tau^\mathrm{o} = \left(\frac{\partial \alpha^\mathrm{o}}{\partial \tau}\right)_{\delta, \bar{x}} = \sum_{i=1}^{N} x_i \frac{T_{\mathrm{c},i}}{T_\mathrm{r}} \left(\frac{\partial \alpha_{\mathrm{o}i}^\mathrm{o}(\rho, T)}{\partial \left(T_{\mathrm{c},i}/T\right)}\right)_\rho . \tag{7.11}$$

Thus, the derivative of α^{o} with respect to τ requires the evaluation of the derivatives of the equations for $\alpha_{\mathrm{o}i}^{\mathrm{o}}$ with respect to $T_{\mathrm{c},i}/T$, which is the ratio of the critical temperature of component i and the mixture temperature[49]. For the derivative of α^{r} [Eq. (7.3)] as a function of δ, τ, and $\bar{x}$ with respect to, for example, δ, the derivatives of the equations for $\alpha_{\mathrm{o}i}^{\mathrm{r}}$ and α_{ij}^{r} have to be determined:

$$\alpha_{\delta}^{\mathrm{r}} = \left(\frac{\partial \alpha^{\mathrm{r}}}{\partial \delta}\right)_{\tau,\bar{x}} = \sum_{i=1}^{N} x_i \left(\frac{\partial \alpha_{\mathrm{o}i}^{\mathrm{r}}(\delta,\tau)}{\partial \delta}\right)_{\tau} + \sum_{i=1}^{N-1}\sum_{j=i+1}^{N} x_i x_j F_{ij} \left(\frac{\partial \alpha_{ij}^{\mathrm{r}}(\delta,\tau)}{\partial \delta}\right)_{\tau} . \tag{7.12}$$

The calculation of, for example, chemical potentials, fugacity coefficients, fugacities, and derivatives of pressure with respect to n_i or x_i for phase equilibrium calculations requires the determination of composition derivatives of the residual part of the Helmholtz free energy as described in Sec. 5.4.1 (see also Sec. 7.3 for further details regarding first and second derivatives of α^{r} with respect to n_i). For example, the derivative of Eq. (7.3) with respect to the mole fraction x_i of component i is given by

$$\alpha_{x_i}^{\mathrm{r}} = \left(\frac{\partial \alpha^{\mathrm{r}}}{\partial x_i}\right)_{\delta,\tau,x_j} = \alpha_{\mathrm{o}i}^{\mathrm{r}}(\delta,\tau) + \sum_{\substack{k=1 \\ k\neq i}}^{N} x_k F_{ik}\, \alpha_{ik}^{\mathrm{r}}(\delta,\tau). \tag{7.13}$$

A complete list of all fundamental derivatives of Eqs. (7.2) and (7.3) with respect to δ, τ , and x_i required for standard and advanced property calculations (see Tables 7.1 – 7.4) is presented in Table 7.5. The respective derivatives of $\alpha_{\mathrm{o}i}^{\mathrm{o}}$, $\alpha_{\mathrm{o}i}^{\mathrm{r}}$, and α_{ij}^{r} [see Eqs. (7.5), (7.7), and (7.8)] are explicitly listed in Tables 7.6 – 7.9.

Aside from the basic derivatives of α^{o} with respect to δ and τ, and α^{r} with respect to δ, τ, and x_i (see Table 7.5), derivatives of the composition-dependent reducing functions for the mixture density and temperature [Eqs. (7.9) and (7.10)] have to be taken into account for the determination of the first and second derivatives of α^{r} with respect to the mole numbers n_i. Such derivatives are required, for example, either for the calculation of the chemical potential μ_i of component i, the fugacity coefficient φ_i of component i, or the derivatives of pressure with respect to n_i. The derived first and second derivatives of $1/\rho_{\mathrm{r}}(\bar{x})$ and $T_{\mathrm{r}}(\bar{x})$ [see Eqs. (7.9) and (7.10)] are explicitly listed in Table 7.10.

The formalism where the properties and its derivatives are calculated by combining partial derivatives of the Helmholtz free energy of the mixture ensures a consistent set of relations as shown in Tables 7.1 – 7.10 and leads to an efficient computer code. In Sec. 7.3.1 tests for the verification of the calculated fugacity coefficients and their partial derivatives are shown to be straightforward.

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[49] Basically, the evaluation of the derivatives of α^{o} with respect to the reduced mixture variables δ and τ can be reduced to derivatives with respect to mixture density and temperature as shown for the temperature derivative in Eq. (5.31). The derivatives of α^{o} with respect to $\rho/\rho_{\mathrm{c},i}$ and $T_{\mathrm{c},i}/T$ leads to the same results but is more convenient to perform due to the structure of the $\alpha_{\mathrm{o}i}^{\mathrm{o}}$ equations [see Eq. (7.5)].

Table 7.1 Definitions of common thermodynamic properties and their relation to the reduced Helmholtz free energy α, Eq. (7.1)

Property and definition	Relation to α and its derivatives[a,b]
Pressure $p(T,\rho,\bar{x}) = -(\partial a/\partial v)_{T,\bar{x}}$	$\dfrac{p(\delta,\tau,\bar{x})}{\rho RT} = 1+\delta\alpha^\mathrm{r}_\delta$
Compression factor $Z(T,\rho,\bar{x}) = p/(\rho RT)$	$Z(\delta,\tau,\bar{x}) = 1+\delta\alpha^\mathrm{r}_\delta$
Entropy $s(T,\rho,\bar{x}) = -(\partial a/\partial T)_{v,\bar{x}}$	$\dfrac{s(\delta,\tau,\bar{x})}{R} = \tau\left(\alpha^\mathrm{o}_\tau+\alpha^\mathrm{r}_\tau\right)-\alpha^\mathrm{o}-\alpha^\mathrm{r}$
Internal energy $u(T,\rho,\bar{x}) = a+Ts$	$\dfrac{u(\delta,\tau,\bar{x})}{RT} = \tau\left(\alpha^\mathrm{o}_\tau+\alpha^\mathrm{r}_\tau\right)$
Isochoric heat capacity $c_v(T,\rho,\bar{x}) = (\partial u/\partial T)_{v,\bar{x}}$	$\dfrac{c_v(\delta,\tau,\bar{x})}{R} = -\tau^2\left(\alpha^\mathrm{o}_{\tau\tau}+\alpha^\mathrm{r}_{\tau\tau}\right)$
Enthalpy $h(T,p,\bar{x}) = u+pv$	$\dfrac{h(\delta,\tau,\bar{x})}{RT} = 1+\tau\left(\alpha^\mathrm{o}_\tau+\alpha^\mathrm{r}_\tau\right)+\delta\alpha^\mathrm{r}_\delta$
Isobaric heat capacity $c_p(T,p,\bar{x}) = (\partial h/\partial T)_{p,\bar{x}}$	$\dfrac{c_p(\delta,\tau,\bar{x})}{R} = -\tau^2\left(\alpha^\mathrm{o}_{\tau\tau}+\alpha^\mathrm{r}_{\tau\tau}\right)+\dfrac{\left(1+\delta\alpha^\mathrm{r}_\delta-\delta\tau\alpha^\mathrm{r}_{\delta\tau}\right)^2}{1+2\delta\alpha^\mathrm{r}_\delta+\delta^2\alpha^\mathrm{r}_{\delta\delta}}$
Gibbs free energy $g(T,p,\bar{x}) = h-Ts$	$\dfrac{g(\delta,\tau,\bar{x})}{RT} = 1+\alpha^\mathrm{o}+\alpha^\mathrm{r}+\delta\alpha^\mathrm{r}_\delta$
Speed of sound $w(T,p,\bar{x}) = \sqrt{(1/M)(\partial p/\partial\rho)_{s,\bar{x}}}$	$\dfrac{w^2(\delta,\tau,\bar{x})\,M}{RT} = 1+2\delta\alpha^\mathrm{r}_\delta+\delta^2\alpha^\mathrm{r}_{\delta\delta}-\dfrac{\left(1+\delta\alpha^\mathrm{r}_\delta-\delta\tau\alpha^\mathrm{r}_{\delta\tau}\right)^2}{\tau^2\left(\alpha^\mathrm{o}_{\tau\tau}+\alpha^\mathrm{r}_{\tau\tau}\right)}$
Joule - Thomson coefficient $\mu_\mathrm{JT}(T,p,\bar{x}) = (\partial T/\partial p)_{h,\bar{x}}$	$\mu_\mathrm{JT}\,R\rho = \dfrac{-\left(\delta\alpha^\mathrm{r}_\delta+\delta^2\alpha^\mathrm{r}_{\delta\delta}+\delta\tau\alpha^\mathrm{r}_{\delta\tau}\right)}{\left(1+\delta\alpha^\mathrm{r}_\delta-\delta\tau\alpha^\mathrm{r}_{\delta\tau}\right)^2-\tau^2\left(\alpha^\mathrm{o}_{\tau\tau}+\alpha^\mathrm{r}_{\tau\tau}\right)\left(1+2\delta\alpha^\mathrm{r}_\delta+\delta^2\alpha^\mathrm{r}_{\delta\delta}\right)}$
Isothermal throttling coefficient $\delta_T(T,p,\bar{x}) = (\partial h/\partial p)_{T,\bar{x}}$	$\delta_T\,\rho = 1-\dfrac{1+\delta\alpha^\mathrm{r}_\delta-\delta\tau\alpha^\mathrm{r}_{\delta\tau}}{1+2\delta\alpha^\mathrm{r}_\delta+\delta^2\alpha^\mathrm{r}_{\delta\delta}}$
Isentropic exponent $\kappa(T,p,\bar{x}) = -(v/p)(\partial p/\partial v)_{s,\bar{x}}$	$\kappa = \dfrac{1+2\delta\alpha^\mathrm{r}_\delta+\delta^2\alpha^\mathrm{r}_{\delta\delta}}{1+\delta\alpha^\mathrm{r}_\delta}\left[1-\dfrac{\left(1+\delta\alpha^\mathrm{r}_\delta-\delta\tau\alpha^\mathrm{r}_{\delta\tau}\right)^2}{\tau^2\left(\alpha^\mathrm{o}_{\tau\tau}+\alpha^\mathrm{r}_{\tau\tau}\right)\left(1+2\delta\alpha^\mathrm{r}_\delta+\delta^2\alpha^\mathrm{r}_{\delta\delta}\right)}\right]$
Second thermal virial coefficient $B(T,\bar{x}) = \lim\limits_{\rho\to 0}(\partial Z/\partial\rho)_{T,\bar{x}}$	$B(\tau)\,\rho_\mathrm{r} = \lim\limits_{\delta\to 0}\alpha^\mathrm{r}_\delta$
Third thermal virial coefficient $C(T,\bar{x}) = \dfrac{1}{2}\lim\limits_{\rho\to 0}\left(\partial^2 Z/\partial\rho^2\right)_{T,\bar{x}}$	$C(\tau)\,\rho_\mathrm{r}^2 = \lim\limits_{\delta\to 0}\alpha^\mathrm{r}_{\delta\delta}$
Second acoustic virial coefficient[c] $\beta_\mathrm{a}(T,\bar{x}) = \lim\limits_{\rho\to 0}\left(\partial\left(w^2/\left(\kappa^\mathrm{o}RT\right)\right)/\partial\rho\right)_{T,\bar{x}}$	$\beta_\mathrm{a}(\tau)\,\rho_\mathrm{r} = \lim\limits_{\delta\to 0}\left[2\alpha^\mathrm{r}_\delta-2\dfrac{\kappa^\mathrm{o}-1}{\kappa^\mathrm{o}}\tau\alpha^\mathrm{r}_{\delta\tau}+\dfrac{\left(\kappa^\mathrm{o}-1\right)^2}{\kappa^\mathrm{o}}\tau^2\alpha^\mathrm{r}_{\delta\tau\tau}\right]$

[a] See Eq. (7.4) for the definition of δ and τ, and Eq. (7.9) for ρ_r.

[b] See Table 7.5 for the derivatives of α^o and α^r with respect to δ and τ.

[c] $\kappa^\mathrm{o} = c_p^\mathrm{o}/c_v^\mathrm{o}$ is the isentropic exponent of the ideal-gas mixture.

Table 7.2 Derivatives of pressure, density, total volume, and temperature, and their relation to the reduced Helmholtz free energy α, Eq. (7.1)

Pressure derivative	Relation to α and its derivatives[a,b]
Derivatives of pressure p with respect to temperature T, density ρ, and total volume V	
$\left(\frac{\partial p}{\partial T}\right)_{V,\bar{n}}, \left(\frac{\partial p}{\partial T}\right)_{\rho,\bar{x}}$	$\left(\frac{\partial p}{\partial T}\right)_{V,\bar{n}} = \left(\frac{\partial p}{\partial T}\right)_{\rho,\bar{x}} = \rho R\left(1+\delta\alpha_{\delta}^{\mathrm{r}}-\delta\tau\alpha_{\delta\tau}^{\mathrm{r}}\right)$
$\left(\frac{\partial^2 p}{\partial T^2}\right)_{V,\bar{n}}, \left(\frac{\partial^2 p}{\partial T^2}\right)_{\rho,\bar{x}}$	$\left(\frac{\partial^2 p}{\partial T^2}\right)_{V,\bar{n}} = \left(\frac{\partial^2 p}{\partial T^2}\right)_{\rho,\bar{x}} = \frac{\rho R}{T}\delta\tau^2\alpha_{\delta\tau\tau}^{\mathrm{r}}$
$\left(\frac{\partial p}{\partial \rho}\right)_{T,\bar{n}}, \left(\frac{\partial p}{\partial \rho}\right)_{T,\bar{x}}$	$\left(\frac{\partial p}{\partial \rho}\right)_{T,\bar{n}} = \left(\frac{\partial p}{\partial \rho}\right)_{T,\bar{x}} = RT\left(1+2\delta\alpha_{\delta}^{\mathrm{r}}+\delta^2\alpha_{\delta\delta}^{\mathrm{r}}\right)$
$\left(\frac{\partial^2 p}{\partial \rho^2}\right)_{T,\bar{n}}, \left(\frac{\partial^2 p}{\partial \rho^2}\right)_{T,\bar{x}}$	$\left(\frac{\partial^2 p}{\partial \rho^2}\right)_{T,\bar{n}} = \left(\frac{\partial^2 p}{\partial \rho^2}\right)_{T,\bar{x}} = \frac{RT}{\rho}\delta\left(2\alpha_{\delta}^{\mathrm{r}}+4\delta\alpha_{\delta\delta}^{\mathrm{r}}+\delta^2\alpha_{\delta\delta\delta}^{\mathrm{r}}\right)$
$n\left(\frac{\partial p}{\partial V}\right)_{T,\bar{n}}$	$n\left(\frac{\partial p}{\partial V}\right)_{T,\bar{n}} = -\rho^2 RT\left(1+2\delta\alpha_{\delta}^{\mathrm{r}}+\delta^2\alpha_{\delta\delta}^{\mathrm{r}}\right)$
Derivative of pressure p with respect to the mole number n_i of component i[c]	
$n\left(\frac{\partial p}{\partial n_i}\right)_{T,V,n_j}$	$n\left(\frac{\partial p}{\partial n_i}\right)_{T,V,n_j} = \rho RT\left[1+\delta\alpha_{\delta}^{\mathrm{r}}\left[2-\frac{1}{\rho_{\mathrm{r}}}\cdot n\left(\frac{\partial \rho_{\mathrm{r}}}{\partial n_i}\right)_{n_j}\right]+\delta\cdot n\left(\frac{\partial \alpha_{\delta}^{\mathrm{r}}}{\partial n_i}\right)_{T,V,n_j}\right]$
Relations resulting from pressure derivatives	
Derivative of V with respect to T and vice versa	Derivative of ρ with respect to T and vice versa
$\frac{1}{n}\left(\frac{\partial V}{\partial T}\right)_{p,\bar{n}} = \frac{-\left(\frac{\partial p}{\partial T}\right)_{V,\bar{n}}}{n\left(\frac{\partial p}{\partial V}\right)_{T,\bar{n}}} = \frac{1}{n\left(\frac{\partial T}{\partial V}\right)_{p,\bar{n}}}$	$\left(\frac{\partial \rho}{\partial T}\right)_{p,\bar{x}} = \frac{-\left(\frac{\partial p}{\partial T}\right)_{\rho,\bar{x}}}{\left(\frac{\partial p}{\partial \rho}\right)_{T,\bar{x}}} = \frac{1}{\left(\frac{\partial T}{\partial \rho}\right)_{p,\bar{x}}}$
Derivative of V with respect to n_i	Derivative of T with respect to n_i
$\left(\frac{\partial V}{\partial n_i}\right)_{T,p,n_j} = \hat{v}_i = \frac{-\left(\frac{\partial p}{\partial n_i}\right)_{T,V,n_j}}{\left(\frac{\partial p}{\partial V}\right)_{T,\bar{n}}}$	$n\left(\frac{\partial T}{\partial n_i}\right)_{p,V,n_j} = \frac{-n\left(\frac{\partial p}{\partial n_i}\right)_{T,V,n_j}}{\left(\frac{\partial p}{\partial T}\right)_{V,\bar{n}}}$

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[a] See Eq. (7.4) for the definition of δ and τ, and Eq. (7.9) for ρ_{r}.

[b] See Table 7.5 for the derivatives of α^{o} and α^{r} with respect to δ and τ.

[c] See Table 7.4 and Sec. 7.3 for the derivatives of ρ_{r} and $\alpha_{\delta}^{\mathrm{r}}$ with respect to n_i.

Table 7.3 Definitions of the chemical potential, the fugacity coefficient, and the fugacity of component i, and their relation to the reduced Helmholtz free energy α, Eq. (7.1)

Property and definition	Relation to α and its derivatives[a]
Chemical potential of component i $\mu_i(T,V,\bar{n})=\left(\frac{\partial A}{\partial n_i}\right)_{T,V,n_j}$	$\frac{\mu_i}{RT}=\left(\frac{\partial n\alpha^\mathrm{o}}{\partial n_i}\right)_{T,V,n_j}+\left(\frac{\partial n\alpha^\mathrm{r}}{\partial n_i}\right)_{T,V,n_j}$
Fugacity coefficient of component i $\ln\varphi_i(T,p,\bar{n})=\int_0^p\left(\frac{\hat{v}_i}{RT}-\frac{1}{p}\right)\mathrm{d}p_{T,\bar{n}}$	$\ln\varphi_i=\left(\frac{\partial n\alpha^\mathrm{r}}{\partial n_i}\right)_{T,V,n_j}-\ln\left(1+\delta\alpha_\delta^\mathrm{r}\right)$
Fugacity of component i $f_i(T,p,\bar{n})=x_i p\,\varphi_i(T,p,\bar{n})$	$f_i=x_i\rho RT\exp\left(\frac{\partial n\alpha^\mathrm{r}}{\partial n_i}\right)_{T,V,n_j}$

[a] See Table 7.4 for the derivatives of $n\alpha^\mathrm{o}$ and $n\alpha^\mathrm{r}$ with respect to n_i and Table 7.5 for the derivative of α^r with respect to δ, i.e. α_δ^r; see Eq. (7.4) for the definition of δ.

Table 7.4 First derivatives of the Helmholtz free energy α and the reducing functions for mixture density ρ_r and temperature T_r with respect to the mole numbers n_i[a]

Derivatives of $n\alpha^\mathrm{o}$ and $n\alpha^\mathrm{r}$ with respect to the mole number n_i of component i[b]

$$\left(\frac{\partial n\alpha^\mathrm{o}}{\partial n_i}\right)_{T,V,n_j}=\alpha_{\mathrm{o}i}^\mathrm{o}(\rho,T)+1+\ln x_i \tag{7.14}$$

$$\left(\frac{\partial n\alpha^\mathrm{r}}{\partial n_i}\right)_{T,V,n_j}=\alpha^\mathrm{r}+n\left(\frac{\partial\alpha^\mathrm{r}}{\partial n_i}\right)_{T,V,n_j} \tag{7.15}$$

Derivatives of α^r and α_δ^r with respect to the mole number n_i of component i[c]

$$n\left(\frac{\partial\alpha^\mathrm{r}}{\partial n_i}\right)_{T,V,n_j}=\delta\alpha_\delta^\mathrm{r}\left[1-\frac{1}{\rho_\mathrm{r}}\cdot n\left(\frac{\partial\rho_\mathrm{r}}{\partial n_i}\right)_{n_j}\right]+\tau\alpha_\tau^\mathrm{r}\frac{1}{T_\mathrm{r}}\cdot n\left(\frac{\partial T_\mathrm{r}}{\partial n_i}\right)_{n_j}+\alpha_{x_i}^\mathrm{r}-\sum_{k=1}^{N}x_k\alpha_{x_k}^\mathrm{r} \tag{7.16}$$

$$n\left(\frac{\partial\alpha_\delta^\mathrm{r}}{\partial n_i}\right)_{T,V,n_j}=\delta\alpha_{\delta\delta}^\mathrm{r}\left[1-\frac{1}{\rho_\mathrm{r}}\cdot n\left(\frac{\partial\rho_\mathrm{r}}{\partial n_i}\right)_{n_j}\right]+\tau\alpha_{\delta\tau}^\mathrm{r}\frac{1}{T_\mathrm{r}}\cdot n\left(\frac{\partial T_\mathrm{r}}{\partial n_i}\right)_{n_j}+\alpha_{\delta x_i}^\mathrm{r}-\sum_{k=1}^{N}x_k\alpha_{\delta x_k}^\mathrm{r} \tag{7.17}$$

Derivatives of $\rho_\mathrm{r}=\rho_\mathrm{r}(\bar{x})$ and $T_\mathrm{r}=T_\mathrm{r}(\bar{x})$ with respect to the mole number n_i of component i[d]

$$n\left(\frac{\partial\rho_\mathrm{r}}{\partial n_i}\right)_{n_j}=\left(\frac{\partial\rho_\mathrm{r}}{\partial x_i}\right)_{x_j}-\sum_{k=1}^{N}x_k\left(\frac{\partial\rho_\mathrm{r}}{\partial x_k}\right)_{x_j},\ \text{with}\ \left(\frac{\partial\rho_\mathrm{r}}{\partial x_i}\right)_{x_j}=-\rho_\mathrm{r}^2\left(\frac{\partial(1/\rho_\mathrm{r})}{\partial x_i}\right)_{x_j} \tag{7.18}$$

$$n\left(\frac{\partial T_\mathrm{r}}{\partial n_i}\right)_{n_j}=\left(\frac{\partial T_\mathrm{r}}{\partial x_i}\right)_{x_j}-\sum_{k=1}^{N}x_k\left(\frac{\partial T_\mathrm{r}}{\partial x_k}\right)_{x_j} \tag{7.19}$$

[a] See Sec. 7.3 for further and second derivatives of α, ρ_r, and T_r with respect to n_i.

[b] See Eq. (7.5) for $\alpha_{\mathrm{o}i}^\mathrm{o}$ and Eq. (7.3) for α^r.

[c] See Table 7.5 for the derivatives of α^r with respect to δ and τ, Eq. (7.4).

[d] See Table 7.10 for the derivatives of $1/\rho_\mathrm{r}(\bar{x})$ and $T_\mathrm{r}(\bar{x})$, Eqs. (7.9) and (7.10), with respect to x_i.

Table 7.5 The parts $\alpha^{\mathrm{o}}(\rho,T,\bar{x})$ and $\alpha^{\mathrm{r}}(\delta,\tau,\bar{x})$ of the dimensionless Helmholtz free energy α and their derivatives with respect to the reduced mixture variables δ and τ, and the mole fractions x_i[a]

First and second derivatives of α^{o} with respect to δ and τ[b,c]		
$\alpha^{\mathrm{o}}(\rho,T,\bar{x})$	$\alpha^{\mathrm{o}} = \sum_{i=1}^{N} x_i \left[\alpha^{\mathrm{o}}_{\mathrm{o}i}(\rho,T) + \ln x_i\right]$	(7.20a)
$\left(\frac{\partial \alpha^{\mathrm{o}}}{\partial \delta}\right)_{\tau,\bar{x}}$	$\alpha^{\mathrm{o}}_{\delta} = \sum_{i=1}^{N} x_i \frac{\rho_{\mathrm{r}}}{\rho_{\mathrm{c},i}} \left(\frac{\partial \alpha^{\mathrm{o}}_{\mathrm{o}i}}{\partial\left(\rho/\rho_{\mathrm{c},i}\right)}\right)_T$	(7.20b)
$\left(\frac{\partial^2 \alpha^{\mathrm{o}}}{\partial \delta^2}\right)_{\tau,\bar{x}}$	$\alpha^{\mathrm{o}}_{\delta\delta} = \sum_{i=1}^{N} x_i \left(\frac{\rho_{\mathrm{r}}}{\rho_{\mathrm{c},i}}\right)^2 \left(\frac{\partial^2 \alpha^{\mathrm{o}}_{\mathrm{o}i}}{\partial\left(\rho/\rho_{\mathrm{c},i}\right)^2}\right)_T$	(7.20c)
$\left(\frac{\partial^2 \alpha^{\mathrm{o}}}{\partial \delta\, \partial \tau}\right)_{\bar{x}}$	$\alpha^{\mathrm{o}}_{\delta\tau} = \sum_{i=1}^{N} x_i \frac{\rho_{\mathrm{r}}}{\rho_{\mathrm{c},i}} \frac{T_{\mathrm{c},i}}{T_{\mathrm{r}}} \left(\frac{\partial^2 \alpha^{\mathrm{o}}_{\mathrm{o}i}}{\partial\left(\rho/\rho_{\mathrm{c},i}\right)\partial\left(T_{\mathrm{c},i}/T\right)}\right)$	(7.20d)
$\left(\frac{\partial \alpha^{\mathrm{o}}}{\partial \tau}\right)_{\delta,\bar{x}}$	$\alpha^{\mathrm{o}}_{\tau} = \sum_{i=1}^{N} x_i \frac{T_{\mathrm{c},i}}{T_{\mathrm{r}}} \left(\frac{\partial \alpha^{\mathrm{o}}_{\mathrm{o}i}}{\partial\left(T_{\mathrm{c},i}/T\right)}\right)_{\rho}$	(7.20e)
$\left(\frac{\partial^2 \alpha^{\mathrm{o}}}{\partial \tau^2}\right)_{\delta,\bar{x}}$	$\alpha^{\mathrm{o}}_{\tau\tau} = \sum_{i=1}^{N} x_i \left(\frac{T_{\mathrm{c},i}}{T_{\mathrm{r}}}\right)^2 \left(\frac{\partial^2 \alpha^{\mathrm{o}}_{\mathrm{o}i}}{\partial\left(T_{\mathrm{c},i}/T\right)^2}\right)_{\rho}$	(7.20f)
First and second derivatives of α^{r} with respect to δ, τ, and x_i[d]		
$\alpha^{\mathrm{r}}(\delta,\tau,\bar{x})$	$\alpha^{\mathrm{r}} = \sum_{i=1}^{N} x_i\, \alpha^{\mathrm{r}}_{\mathrm{o}i}(\delta,\tau) + \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} x_i x_j F_{ij}\, \alpha^{\mathrm{r}}_{ij}(\delta,\tau)$	(7.21a)
$\left(\frac{\partial \alpha^{\mathrm{r}}}{\partial \delta}\right)_{\tau,\bar{x}}$	$\alpha^{\mathrm{r}}_{\delta} = \sum_{i=1}^{N} x_i \left(\frac{\partial \alpha^{\mathrm{r}}_{\mathrm{o}i}}{\partial \delta}\right)_{\tau} + \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} x_i x_j F_{ij} \left(\frac{\partial \alpha^{\mathrm{r}}_{ij}}{\partial \delta}\right)_{\tau}$	(7.21b)
$\left(\frac{\partial^2 \alpha^{\mathrm{r}}}{\partial \delta^2}\right)_{\tau,\bar{x}}$	$\alpha^{\mathrm{r}}_{\delta\delta} = \sum_{i=1}^{N} x_i \left(\frac{\partial^2 \alpha^{\mathrm{r}}_{\mathrm{o}i}}{\partial \delta^2}\right)_{\tau} + \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} x_i x_j F_{ij} \left(\frac{\partial^2 \alpha^{\mathrm{r}}_{ij}}{\partial \delta^2}\right)_{\tau}$	(7.21c)
$\left(\frac{\partial^2 \alpha^{\mathrm{r}}}{\partial \delta\, \partial \tau}\right)_{\bar{x}}$	$\alpha^{\mathrm{r}}_{\delta\tau} = \sum_{i=1}^{N} x_i \left(\frac{\partial^2 \alpha^{\mathrm{r}}_{\mathrm{o}i}}{\partial \delta\, \partial \tau}\right) + \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} x_i x_j F_{ij} \left(\frac{\partial^2 \alpha^{\mathrm{r}}_{ij}}{\partial \delta\, \partial \tau}\right)$	(7.21d)
$\left(\frac{\partial \alpha^{\mathrm{r}}}{\partial \tau}\right)_{\delta,\bar{x}}$	$\alpha^{\mathrm{r}}_{\tau} = \sum_{i=1}^{N} x_i \left(\frac{\partial \alpha^{\mathrm{r}}_{\mathrm{o}i}}{\partial \tau}\right)_{\delta} + \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} x_i x_j F_{ij} \left(\frac{\partial \alpha^{\mathrm{r}}_{ij}}{\partial \tau}\right)_{\delta}$	(7.21e)
$\left(\frac{\partial^2 \alpha^{\mathrm{r}}}{\partial \tau^2}\right)_{\delta,\bar{x}}$	$\alpha^{\mathrm{r}}_{\tau\tau} = \sum_{i=1}^{N} x_i \left(\frac{\partial^2 \alpha^{\mathrm{r}}_{\mathrm{o}i}}{\partial \tau^2}\right)_{\delta} + \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} x_i x_j F_{ij} \left(\frac{\partial^2 \alpha^{\mathrm{r}}_{ij}}{\partial \tau^2}\right)_{\delta}$	(7.21f)

Table 7.5 (continued)

First and second derivatives of α^r with respect to δ, τ, and x_i [d] (continued)		
$\left(\frac{\partial\alpha^\mathrm{r}}{\partial x_i}\right)_{\delta,\tau,x_j}$	$\alpha^\mathrm{r}_{x_i} = \alpha^\mathrm{r}_{\mathrm{o}i} + \sum\limits_{\substack{k=1\\k\neq i}}^{N} x_k F_{ik}\,\alpha^\mathrm{r}_{ik}$	(7.21g)
$\left(\frac{\partial^2\alpha^\mathrm{r}}{\partial x_i^2}\right)_{\delta,\tau,x_j}$	$\alpha^\mathrm{r}_{x_i x_i} = 0$	(7.21h)
$\left(\frac{\partial^2\alpha^\mathrm{r}}{\partial x_i\,\partial x_j}\right)_{\delta,\tau}$	$\alpha^\mathrm{r}_{x_i x_j} = F_{ij}\,\alpha^\mathrm{r}_{ij}(\delta,\tau), \quad i\neq j$	(7.21i)
$\left(\frac{\partial^2\alpha^\mathrm{r}}{\partial\delta\,\partial x_i}\right)_{\tau,x_j}$	$\alpha^\mathrm{r}_{\delta x_i} = \left(\frac{\partial\alpha^\mathrm{r}_{\mathrm{o}i}}{\partial\delta}\right)_\tau + \sum\limits_{\substack{k=1\\k\neq i}}^{N} x_k F_{ik}\left(\frac{\partial\alpha^\mathrm{r}_{ik}}{\partial\delta}\right)_\tau$	(7.21j)
$\left(\frac{\partial^2\alpha^\mathrm{r}}{\partial\tau\,\partial x_i}\right)_{\delta,x_j}$	$\alpha^\mathrm{r}_{\tau x_i} = \left(\frac{\partial\alpha^\mathrm{r}_{\mathrm{o}i}}{\partial\tau}\right)_\delta + \sum\limits_{\substack{k=1\\k\neq i}}^{N} x_k F_{ik}\left(\frac{\partial\alpha^\mathrm{r}_{ik}}{\partial\tau}\right)_\delta$	(7.21k)
Third derivatives of α^r with respect to δ and τ [e]		
$\left(\frac{\partial^3\alpha^\mathrm{r}}{\partial\delta^3}\right)_{\tau,\bar{x}}$	$\alpha^\mathrm{r}_{\delta\delta\delta} = \sum\limits_{i=1}^{N} x_i\left(\frac{\partial^3\alpha^\mathrm{r}_{\mathrm{o}i}}{\partial\delta^3}\right)_\tau + \sum\limits_{i=1}^{N-1}\sum\limits_{j=i+1}^{N} x_i x_j F_{ij}\left(\frac{\partial^3\alpha^\mathrm{r}_{ij}}{\partial\delta^3}\right)_\tau$	(7.21l)
$\left(\frac{\partial^3\alpha^\mathrm{r}}{\partial\delta\,\partial\tau^2}\right)_{\bar{x}}$	$\alpha^\mathrm{r}_{\delta\tau\tau} = \sum\limits_{i=1}^{N} x_i\left(\frac{\partial^3\alpha^\mathrm{r}_{\mathrm{o}i}}{\partial\delta\,\partial\tau^2}\right) + \sum\limits_{i=1}^{N-1}\sum\limits_{j=i+1}^{N} x_i x_j F_{ij}\left(\frac{\partial^3\alpha^\mathrm{r}_{ij}}{\partial\delta\,\partial\tau^2}\right)$	(7.21m)

[a] See Eq. (7.4) for the definition of δ and τ.

[b] See Table 7.6 for the equation of $\alpha^\mathrm{o}_{\mathrm{o}i}$ and its derivatives with respect to $\rho/\rho_{\mathrm{c},i}$ and $T_{\mathrm{c},i}/T$.

[c] See Eqs. (7.9) and (7.10) for the reducing functions $\rho_\mathrm{r} = \rho_\mathrm{r}(\bar{x})$ and $T_\mathrm{r} = T_\mathrm{r}(\bar{x})$; $\rho_{\mathrm{c},i}$ and $T_{\mathrm{c},i}$ are the critical parameters of component *i*.

[d] See Tables 7.7 and 7.8 for the equations of $\alpha^\mathrm{r}_{\mathrm{o}i}$ and α^r_{ij} and their derivatives with respect to δ and τ.

[e] See Table 7.9 for the third derivatives of $\alpha^\mathrm{r}_{\mathrm{o}i}$ and α^r_{ij} with respect to δ and τ.

Table 7.6 The dimensionless Helmholtz free energy in the ideal-gas state of component i, $\alpha_{\mathrm{o}i}^{\mathrm{o}}(\rho,T)$, and its derivatives with respect to $\rho/\rho_{\mathrm{c},i}$ and $T_{\mathrm{c},i}/T$

$$\alpha_{\mathrm{o}i}^{\mathrm{o}}(\rho,T)=\frac{R^*}{R}\left[\ln\left(\frac{\rho}{\rho_{\mathrm{c},i}}\right)+n_{\mathrm{o}i,1}^{\mathrm{o}}+n_{\mathrm{o}i,2}^{\mathrm{o}}\frac{T_{\mathrm{c},i}}{T}+n_{\mathrm{o}i,3}^{\mathrm{o}}\ln\left(\frac{T_{\mathrm{c},i}}{T}\right)+\sum_{k=4,6}n_{\mathrm{o}i,k}^{\mathrm{o}}\ln\left|\sinh\left(\vartheta_{\mathrm{o}i,k}^{\mathrm{o}}\frac{T_{\mathrm{c},i}}{T}\right)\right|-\sum_{k=5,7}n_{\mathrm{o}i,k}^{\mathrm{o}}\ln\left|\cosh\left(\vartheta_{\mathrm{o}i,k}^{\mathrm{o}}\frac{T_{\mathrm{c},i}}{T}\right)\right|\right]$$

$$\left(\frac{\partial\alpha_{\mathrm{o}i}^{\mathrm{o}}}{\partial\left(\rho/\rho_{\mathrm{c},i}\right)}\right)_T=\frac{R^*}{R}\frac{\rho_{\mathrm{c},i}}{\rho}$$

$$\left(\frac{\partial^2\alpha_{\mathrm{o}i}^{\mathrm{o}}}{\partial\left(\rho/\rho_{\mathrm{c},i}\right)^2}\right)_T=-\frac{R^*}{R}\left(\frac{\rho_{\mathrm{c},i}}{\rho}\right)^2$$

$$\left(\frac{\partial^2\alpha_{\mathrm{o}i}^{\mathrm{o}}}{\partial\left(\rho/\rho_{\mathrm{c},i}\right)\partial\left(T_{\mathrm{c},i}/T\right)}\right)=0$$

$$\left(\frac{\partial\alpha_{\mathrm{o}i}^{\mathrm{o}}}{\partial\left(T_{\mathrm{c},i}/T\right)}\right)_\rho=\frac{R^*}{R}\left[n_{\mathrm{o}i,2}^{\mathrm{o}}+n_{\mathrm{o}i,3}^{\mathrm{o}}\frac{T}{T_{\mathrm{c},i}}+\sum_{k=4,6}n_{\mathrm{o}i,k}^{\mathrm{o}}\frac{\vartheta_{\mathrm{o}i,k}^{\mathrm{o}}}{\tanh\left(\vartheta_{\mathrm{o}i,k}^{\mathrm{o}}\frac{T_{\mathrm{c},i}}{T}\right)}-\sum_{k=5,7}n_{\mathrm{o}i,k}^{\mathrm{o}}\vartheta_{\mathrm{o}i,k}^{\mathrm{o}}\tanh\left(\vartheta_{\mathrm{o}i,k}^{\mathrm{o}}\frac{T_{\mathrm{c},i}}{T}\right)\right]$$

$$\left(\frac{\partial^2\alpha_{\mathrm{o}i}^{\mathrm{o}}}{\partial\left(T_{\mathrm{c},i}/T\right)^2}\right)_\rho=\frac{R^*}{R}\left[-n_{\mathrm{o}i,3}^{\mathrm{o}}\left(\frac{T}{T_{\mathrm{c},i}}\right)^2-\sum_{k=4,6}n_{\mathrm{o}i,k}^{\mathrm{o}}\frac{\left(\vartheta_{\mathrm{o}i,k}^{\mathrm{o}}\right)^2}{\left(\sinh\left(\vartheta_{\mathrm{o}i,k}^{\mathrm{o}}\frac{T_{\mathrm{c},i}}{T}\right)\right)^2}-\sum_{k=5,7}n_{\mathrm{o}i,k}^{\mathrm{o}}\frac{\left(\vartheta_{\mathrm{o}i,k}^{\mathrm{o}}\right)^2}{\left(\cosh\left(\vartheta_{\mathrm{o}i,k}^{\mathrm{o}}\frac{T_{\mathrm{c},i}}{T}\right)\right)^2}\right]$$

Table 7.7 The residual part of the dimensionless Helmholtz free energy of component i, $\alpha^{\mathrm{r}}_{\mathrm{o}i}(\delta,\tau)$, and its derivatives with respect to the reduced mixture variables δ and τ, Eq. (7.4)

$$\alpha^{\mathrm{r}}_{\mathrm{o}i}(\delta,\tau) = \sum_{k=1}^{K_{\mathrm{Pol},i}} n_{\mathrm{o}i,k}\,\delta^{d_{\mathrm{o}i,k}}\,\tau^{t_{\mathrm{o}i,k}} + \sum_{k=K_{\mathrm{Pol},i}+1}^{K_{\mathrm{Pol},i}+K_{\mathrm{Exp},i}} n_{\mathrm{o}i,k}\,\delta^{d_{\mathrm{o}i,k}}\,\tau^{t_{\mathrm{o}i,k}}\exp\left(-\delta^{c_{\mathrm{o}i,k}}\right)$$

$$\left(\frac{\partial\alpha^{\mathrm{r}}_{\mathrm{o}i}}{\partial\delta}\right)_{\tau} = \sum_{k=1}^{K_{\mathrm{Pol},i}} n_{\mathrm{o}i,k}\,d_{\mathrm{o}i,k}\,\delta^{d_{\mathrm{o}i,k}-1}\,\tau^{t_{\mathrm{o}i,k}} + \sum_{k=K_{\mathrm{Pol},i}+1}^{K_{\mathrm{Pol},i}+K_{\mathrm{Exp},i}} n_{\mathrm{o}i,k}\,\delta^{d_{\mathrm{o}i,k}-1}\left(d_{\mathrm{o}i,k}-c_{\mathrm{o}i,k}\,\delta^{c_{\mathrm{o}i,k}}\right)\tau^{t_{\mathrm{o}i,k}}\exp\left(-\delta^{c_{\mathrm{o}i,k}}\right)$$

$$\left(\frac{\partial^2\alpha^{\mathrm{r}}_{\mathrm{o}i}}{\partial\delta^2}\right)_{\tau} = \sum_{k=1}^{K_{\mathrm{Pol},i}} n_{\mathrm{o}i,k}\,d_{\mathrm{o}i,k}\left(d_{\mathrm{o}i,k}-1\right)\delta^{d_{\mathrm{o}i,k}-2}\,\tau^{t_{\mathrm{o}i,k}} + \sum_{k=K_{\mathrm{Pol},i}+1}^{K_{\mathrm{Pol},i}+K_{\mathrm{Exp},i}} n_{\mathrm{o}i,k}\,\delta^{d_{\mathrm{o}i,k}-2}\left(\left(d_{\mathrm{o}i,k}-c_{\mathrm{o}i,k}\,\delta^{c_{\mathrm{o}i,k}}\right)\left(d_{\mathrm{o}i,k}-1-c_{\mathrm{o}i,k}\,\delta^{c_{\mathrm{o}i,k}}\right)-c^2_{\mathrm{o}i,k}\,\delta^{c_{\mathrm{o}i,k}}\right)\tau^{t_{\mathrm{o}i,k}}\exp\left(-\delta^{c_{\mathrm{o}i,k}}\right)$$

$$\left(\frac{\partial^2\alpha^{\mathrm{r}}_{\mathrm{o}i}}{\partial\delta\,\partial\tau}\right) = \sum_{k=1}^{K_{\mathrm{Pol},i}} n_{\mathrm{o}i,k}\,d_{\mathrm{o}i,k}\,t_{\mathrm{o}i,k}\,\delta^{d_{\mathrm{o}i,k}-1}\,\tau^{t_{\mathrm{o}i,k}-1} + \sum_{k=K_{\mathrm{Pol},i}+1}^{K_{\mathrm{Pol},i}+K_{\mathrm{Exp},i}} n_{\mathrm{o}i,k}\,t_{\mathrm{o}i,k}\,\delta^{d_{\mathrm{o}i,k}-1}\left(d_{\mathrm{o}i,k}-c_{\mathrm{o}i,k}\,\delta^{c_{\mathrm{o}i,k}}\right)\tau^{t_{\mathrm{o}i,k}-1}\exp\left(-\delta^{c_{\mathrm{o}i,k}}\right)$$

$$\left(\frac{\partial\alpha^{\mathrm{r}}_{\mathrm{o}i}}{\partial\tau}\right)_{\delta} = \sum_{k=1}^{K_{\mathrm{Pol},i}} n_{\mathrm{o}i,k}\,t_{\mathrm{o}i,k}\,\delta^{d_{\mathrm{o}i,k}}\,\tau^{t_{\mathrm{o}i,k}-1} + \sum_{k=K_{\mathrm{Pol},i}+1}^{K_{\mathrm{Pol},i}+K_{\mathrm{Exp},i}} n_{\mathrm{o}i,k}\,t_{\mathrm{o}i,k}\,\delta^{d_{\mathrm{o}i,k}}\,\tau^{t_{\mathrm{o}i,k}-1}\exp\left(-\delta^{c_{\mathrm{o}i,k}}\right)$$

$$\left(\frac{\partial^2\alpha^{\mathrm{r}}_{\mathrm{o}i}}{\partial\tau^2}\right)_{\delta} = \sum_{k=1}^{K_{\mathrm{Pol},i}} n_{\mathrm{o}i,k}\,t_{\mathrm{o}i,k}\left(t_{\mathrm{o}i,k}-1\right)\delta^{d_{\mathrm{o}i,k}}\,\tau^{t_{\mathrm{o}i,k}-2} + \sum_{k=K_{\mathrm{Pol},i}+1}^{K_{\mathrm{Pol},i}+K_{\mathrm{Exp},i}} n_{\mathrm{o}i,k}\,t_{\mathrm{o}i,k}\left(t_{\mathrm{o}i,k}-1\right)\delta^{d_{\mathrm{o}i,k}}\,\tau^{t_{\mathrm{o}i,k}-2}\exp\left(-\delta^{c_{\mathrm{o}i,k}}\right)$$

Table 7.8 The function $\alpha_{ij}^{\mathrm{r}}(\delta,\tau)$ and its derivatives with respect to the reduced mixture variables δ and τ, Eq. (7.4)

$$\alpha_{ij}^{\mathrm{r}}(\delta,\tau)=\sum_{k=1}^{K_{\mathrm{Pol},ij}} n_{ij,k}\,\delta^{d_{ij,k}}\,\tau^{t_{ij,k}}+\sum_{k=K_{\mathrm{Pol},ij}+1}^{K_{\mathrm{Pol},ij}+K_{\mathrm{Exp},ij}} n_{ij,k}\,\delta^{d_{ij,k}}\,\tau^{t_{ij,k}}\exp\!\Big(-\eta_{ij,k}\left(\delta-\varepsilon_{ij,k}\right)^2-\beta_{ij,k}\left(\delta-\gamma_{ij,k}\right)\Big)$$

$$\left(\frac{\partial\alpha_{ij}^{\mathrm{r}}}{\partial\delta}\right)_{\tau}=\sum_{k=1}^{K_{\mathrm{Pol},ij}} n_{ij,k}\,d_{ij,k}\,\delta^{d_{ij,k}-1}\,\tau^{t_{ij,k}}+\sum_{k=K_{\mathrm{Pol},ij}+1}^{K_{\mathrm{Pol},ij}+K_{\mathrm{Exp},ij}} n_{ij,k}\,\delta^{d_{ij,k}}\,\tau^{t_{ij,k}}\exp\!\Big(-\eta_{ij,k}\left(\delta-\varepsilon_{ij,k}\right)^2-\beta_{ij,k}\left(\delta-\gamma_{ij,k}\right)\Big)\left[\frac{d_{ij,k}}{\delta}-2\eta_{ij,k}\left(\delta-\varepsilon_{ij,k}\right)-\beta_{ij,k}\right]$$

$$\left(\frac{\partial^2\alpha_{ij}^{\mathrm{r}}}{\partial\delta^2}\right)_{\tau}=\sum_{k=1}^{K_{\mathrm{Pol},ij}} n_{ij,k}\,d_{ij,k}\left(d_{ij,k}-1\right)\delta^{d_{ij,k}-2}\,\tau^{t_{ij,k}}$$
$$+\sum_{k=K_{\mathrm{Pol},ij}+1}^{K_{\mathrm{Pol},ij}+K_{\mathrm{Exp},ij}} n_{ij,k}\,\delta^{d_{ij,k}}\,\tau^{t_{ij,k}}\exp\!\Big(-\eta_{ij,k}\left(\delta-\varepsilon_{ij,k}\right)^2-\beta_{ij,k}\left(\delta-\gamma_{ij,k}\right)\Big)\left[\left(\frac{d_{ij,k}}{\delta}-2\eta_{ij,k}\left(\delta-\varepsilon_{ij,k}\right)-\beta_{ij,k}\right)^2-\frac{d_{ij,k}}{\delta^2}-2\eta_{ij,k}\right]$$

$$\left(\frac{\partial^2\alpha_{ij}^{\mathrm{r}}}{\partial\delta\,\partial\tau}\right)=\sum_{k=1}^{K_{\mathrm{Pol},ij}} n_{ij,k}\,d_{ij,k}\,t_{ij,k}\,\delta^{d_{ij,k}-1}\,\tau^{t_{ij,k}-1}+\sum_{k=K_{\mathrm{Pol},ij}+1}^{K_{\mathrm{Pol},ij}+K_{\mathrm{Exp},ij}} n_{ij,k}\,t_{ij,k}\,\delta^{d_{ij,k}}\,\tau^{t_{ij,k}-1}\exp\!\Big(-\eta_{ij,k}\left(\delta-\varepsilon_{ij,k}\right)^2-\beta_{ij,k}\left(\delta-\gamma_{ij,k}\right)\Big)\left[\frac{d_{ij,k}}{\delta}-2\eta_{ij,k}\left(\delta-\varepsilon_{ij,k}\right)-\beta_{ij,k}\right]$$

$$\left(\frac{\partial\alpha_{ij}^{\mathrm{r}}}{\partial\tau}\right)_{\delta}=\sum_{k=1}^{K_{\mathrm{Pol},ij}} n_{ij,k}\,t_{ij,k}\,\delta^{d_{ij,k}}\,\tau^{t_{ij,k}-1}+\sum_{k=K_{\mathrm{Pol},ij}+1}^{K_{\mathrm{Pol},ij}+K_{\mathrm{Exp},ij}} n_{ij,k}\,t_{ij,k}\,\delta^{d_{ij,k}}\,\tau^{t_{ij,k}-1}\exp\!\Big(-\eta_{ij,k}\left(\delta-\varepsilon_{ij,k}\right)^2-\beta_{ij,k}\left(\delta-\gamma_{ij,k}\right)\Big)$$

$$\left(\frac{\partial^2\alpha_{ij}^{\mathrm{r}}}{\partial\tau^2}\right)_{\delta}=\sum_{k=1}^{K_{\mathrm{Pol},ij}} n_{ij,k}\,t_{ij,k}\left(t_{ij,k}-1\right)\delta^{d_{ij,k}}\,\tau^{t_{ij,k}-2}+\sum_{k=K_{\mathrm{Pol},ij}+1}^{K_{\mathrm{Pol},ij}+K_{\mathrm{Exp},ij}} n_{ij,k}\,t_{ij,k}\left(t_{ij,k}-1\right)\delta^{d_{ij,k}}\,\tau^{t_{ij,k}-2}\exp\!\Big(-\eta_{ij,k}\left(\delta-\varepsilon_{ij,k}\right)^2-\beta_{ij,k}\left(\delta-\gamma_{ij,k}\right)\Big)$$

Table 7.9 Third derivatives of $\alpha^{\mathrm{r}}_{\mathrm{o}i}(\delta,\tau)$ and $\alpha^{\mathrm{r}}_{ij}(\delta,\tau)$ with respect to the reduced mixture variables δ and τ, Eq. (7.4)

Third derivatives of $\alpha^{\mathrm{r}}_{\mathrm{o}i}$ with respect to δ and τ

$$\left(\frac{\partial^3\alpha^{\mathrm{r}}_{\mathrm{o}i}}{\partial\delta^3}\right)_{\tau} = \sum_{k=1}^{K_{\mathrm{Pol},i}} n_{\mathrm{o}i,k}\, d_{\mathrm{o}i,k}\left(d_{\mathrm{o}i,k}-1\right)\left(d_{\mathrm{o}i,k}-2\right)\delta^{d_{\mathrm{o}i,k}-3}\,\tau^{t_{\mathrm{o}i,k}}$$

$$+\sum_{k=K_{\mathrm{Pol},i}+1}^{K_{\mathrm{Pol},i}+K_{\mathrm{Exp},i}} n_{\mathrm{o}i,k}\,\delta^{d_{\mathrm{o}i,k}-3}\Big(\Big(\Big(d_{\mathrm{o}i,k}-c_{\mathrm{o}i,k}\,\delta^{c_{\mathrm{o}i,k}}\Big)\Big(d_{\mathrm{o}i,k}-2-c_{\mathrm{o}i,k}\,\delta^{c_{\mathrm{o}i,k}}\Big)-3c^2_{\mathrm{o}i,k}\,\delta^{c_{\mathrm{o}i,k}}\Big)\Big(d_{\mathrm{o}i,k}-1-c_{\mathrm{o}i,k}\,\delta^{c_{\mathrm{o}i,k}}\Big)-c^3_{\mathrm{o}i,k}\,\delta^{c_{\mathrm{o}i,k}}\Big)\tau^{t_{\mathrm{o}i,k}}\exp\Big(-\delta^{c_{\mathrm{o}i,k}}\Big)$$

$$\left(\frac{\partial^3\alpha^{\mathrm{r}}_{\mathrm{o}i}}{\partial\delta\,\partial\tau^2}\right) = \sum_{k=1}^{K_{\mathrm{Pol},i}} n_{\mathrm{o}i,k}\, d_{\mathrm{o}i,k}\, t_{\mathrm{o}i,k}\left(t_{\mathrm{o}i,k}-1\right)\delta^{d_{\mathrm{o}i,k}-1}\,\tau^{t_{\mathrm{o}i,k}-2} + \sum_{k=K_{\mathrm{Pol},i}+1}^{K_{\mathrm{Pol},i}+K_{\mathrm{Exp},i}} n_{\mathrm{o}i,k}\, t_{\mathrm{o}i,k}\left(t_{\mathrm{o}i,k}-1\right)\delta^{d_{\mathrm{o}i,k}-1}\left(d_{\mathrm{o}i,k}-c_{\mathrm{o}i,k}\,\delta^{c_{\mathrm{o}i,k}}\right)\tau^{t_{\mathrm{o}i,k}-2}\exp\left(-\delta^{c_{\mathrm{o}i,k}}\right)$$

Third derivatives of α^{r}_{ij} with respect to δ and τ

$$\left(\frac{\partial^3\alpha^{\mathrm{r}}_{ij}}{\partial\delta^3}\right)_{\tau} = \sum_{k=1}^{K_{\mathrm{Pol},ij}} n_{ij,k}\, d_{ij,k}\left(d_{ij,k}-1\right)\left(d_{ij,k}-2\right)\delta^{d_{ij,k}-3}\,\tau^{t_{ij,k}}$$

$$+\sum_{k=K_{\mathrm{Pol},ij}+1}^{K_{\mathrm{Pol},ij}+K_{\mathrm{Exp},ij}} n_{ij,k}\,\delta^{d_{ij,k}}\,\tau^{t_{ij,k}}\exp\left(-\eta_{ij,k}\left(\delta-\varepsilon_{ij,k}\right)^2-\beta_{ij,k}\left(\delta-\gamma_{ij,k}\right)\right)\left[\left(\frac{d_{ij,k}}{\delta}-2\eta_{ij,k}\left(\delta-\varepsilon_{ij,k}\right)-\beta_{ij,k}\right)^3\right.$$

$$\left.-3\left(\frac{d_{ij,k}}{\delta}-2\eta_{ij,k}\left(\delta-\varepsilon_{ij,k}\right)-\beta_{ij,k}\right)\left(\frac{d_{ij,k}}{\delta^2}+2\eta_{ij,k}\right)+2\frac{d_{ij,k}}{\delta^3}\right]$$

$$\left(\frac{\partial^3\alpha^{\mathrm{r}}_{ij}}{\partial\delta\,\partial\tau^2}\right) = \sum_{k=1}^{K_{\mathrm{Pol},ij}} n_{ij,k}\, d_{ij,k}\, t_{ij,k}\left(t_{ij,k}-1\right)\delta^{d_{ij,k}-1}\,\tau^{t_{ij,k}-2}$$

$$+\sum_{k=K_{\mathrm{Pol},ij}+1}^{K_{\mathrm{Pol},ij}+K_{\mathrm{Exp},ij}} n_{ij,k}\, t_{ij,k}\left(t_{ij,k}-1\right)\delta^{d_{ij,k}}\,\tau^{t_{ij,k}-2}\exp\left(-\eta_{ij,k}\left(\delta-\varepsilon_{ij,k}\right)^2-\beta_{ij,k}\left(\delta-\gamma_{ij,k}\right)\right)\left[\frac{d_{ij,k}}{\delta}-2\eta_{ij,k}\left(\delta-\varepsilon_{ij,k}\right)-\beta_{ij,k}\right]$$

Table 7.10 The reducing functions for mixture density $1/\rho_\mathrm{r}(\bar{x})$ and temperature $T_\mathrm{r}(\bar{x})$ and their derivatives with respect to the mole fractions x_i

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Reducing function for density $1/\rho_\mathrm{r}$ $(Y = v)$ and temperature T_r $(Y = T)$[a]

$$Y_\mathrm{r} = Y_\mathrm{r}(\bar{x}) = \sum_{i=1}^{N}\sum_{j=1}^{N} x_i x_j\, \beta_{Y,ij}\, \gamma_{Y,ij}\, \frac{x_i + x_j}{\beta_{Y,ij}^2\, x_i + x_j}\, Y_{\mathrm{c},ij} = \sum_{i=1}^{N} x_i^2\, Y_{\mathrm{c},i} + \sum_{i=1}^{N-1}\sum_{j=i+1}^{N} c_{Y,ij}\, f_{Y,ij}(x_i, x_j), \qquad (7.22a)$$

where $c_{Y,ij} = 2\,\beta_{Y,ij}\,\gamma_{Y,ij}\, Y_{\mathrm{c},ij}$ and $f_{Y,ij}(x_i, x_j) = x_i x_j \dfrac{x_i + x_j}{\beta_{Y,ij}^2\, x_i + x_j}$

Combining rules for $Y_{\mathrm{c},ij}$

$$\frac{1}{\rho_{\mathrm{c},ij}} = \frac{1}{8}\left(\frac{1}{\rho_{\mathrm{c},i}^{1/3}} + \frac{1}{\rho_{\mathrm{c},j}^{1/3}}\right)^3 \text{ for } Y = v \text{ and } T_{\mathrm{c},ij} = \left(T_{\mathrm{c},i} \cdot T_{\mathrm{c},j}\right)^{0.5} \text{ for } Y = T$$

Derivatives of $Y_\mathrm{r} = Y_\mathrm{r}(\bar{x})$ with respect to x_i

$$\left(\frac{\partial Y_\mathrm{r}}{\partial x_i}\right)_{x_j} = 2x_i\, Y_{\mathrm{c},i} + \sum_{k=1}^{i-1} c_{Y,ki} \frac{\partial f_{Y,ki}(x_k, x_i)}{\partial x_i} + \sum_{k=i+1}^{N} c_{Y,ik} \frac{\partial f_{Y,ik}(x_i, x_k)}{\partial x_i} \qquad (7.22b)$$

$$\left(\frac{\partial^2 Y_\mathrm{r}}{\partial x_i^2}\right)_{x_j} = 2\, Y_{\mathrm{c},i} + \sum_{k=1}^{i-1} c_{Y,ki} \frac{\partial^2 f_{Y,ki}(x_k, x_i)}{\partial x_i^2} + \sum_{k=i+1}^{N} c_{Y,ik} \frac{\partial^2 f_{Y,ik}(x_i, x_k)}{\partial x_i^2} \qquad (7.22c)$$

$$\left(\frac{\partial^2 Y_\mathrm{r}}{\partial x_i\, \partial x_j}\right) = c_{Y,ij} \frac{\partial^2 f_{Y,ij}(x_i, x_j)}{\partial x_i\, \partial x_j}, \quad i \neq j \qquad (7.22d)$$

Derivatives of $f_{Y,ki}(x_k, x_i)$, $f_{Y,ik}(x_i, x_k)$, and $f_{Y,ij}(x_i, x_j)$ with respect to x_i

$$\left(\frac{\partial f_{Y,ki}(x_k, x_i)}{\partial x_i}\right)_{x_k} = x_k \frac{x_k + x_i}{\beta_{Y,ki}^2\, x_k + x_i} + x_k x_i \frac{1}{\beta_{Y,ki}^2\, x_k + x_i}\left(1 - \frac{x_k + x_i}{\beta_{Y,ki}^2\, x_k + x_i}\right)$$

$$\left(\frac{\partial f_{Y,ik}(x_i, x_k)}{\partial x_i}\right)_{x_k} = x_k \frac{x_i + x_k}{\beta_{Y,ik}^2\, x_i + x_k} + x_i x_k \frac{1}{\beta_{Y,ik}^2\, x_i + x_k}\left(1 - \beta_{Y,ik}^2 \frac{x_i + x_k}{\beta_{Y,ik}^2\, x_i + x_k}\right)$$

$$\left(\frac{\partial^2 f_{Y,ki}(x_k, x_i)}{\partial x_i^2}\right)_{x_k} = \frac{1}{\beta_{Y,ki}^2\, x_k + x_i}\left(1 - \frac{x_k + x_i}{\beta_{Y,ki}^2\, x_k + x_i}\right)\left(2x_k - x_k x_i \frac{2}{\beta_{Y,ki}^2\, x_k + x_i}\right)$$

$$\left(\frac{\partial^2 f_{Y,ik}(x_i, x_k)}{\partial x_i^2}\right)_{x_k} = \frac{1}{\beta_{Y,ik}^2\, x_i + x_k}\left(1 - \beta_{Y,ik}^2 \frac{x_i + x_k}{\beta_{Y,ik}^2\, x_i + x_k}\right)\left(2x_k - x_i x_k \frac{2\beta_{Y,ik}^2}{\beta_{Y,ik}^2\, x_i + x_k}\right)$$

$$\begin{aligned}\left(\frac{\partial^2 f_{Y,ij}(x_i, x_j)}{\partial x_i\, \partial x_j}\right) = {} & \frac{x_i + x_j}{\beta_{Y,ij}^2\, x_i + x_j} + x_j \frac{1}{\beta_{Y,ij}^2\, x_i + x_j}\left(1 - \frac{x_i + x_j}{\beta_{Y,ij}^2\, x_i + x_j}\right) \\ & + x_i \frac{1}{\beta_{Y,ij}^2\, x_i + x_j}\left(1 - \beta_{Y,ij}^2 \frac{x_i + x_j}{\beta_{Y,ij}^2\, x_i + x_j}\right) \\ & - x_i x_j \frac{1}{\left(\beta_{Y,ij}^2\, x_i + x_j\right)^2}\left(1 + \beta_{Y,ij}^2 - 2\beta_{Y,ij}^2 \frac{x_i + x_j}{\beta_{Y,ij}^2\, x_i + x_j}\right)\end{aligned}$$

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[a] $\gamma_{Y,ji} = \gamma_{Y,ij}$ and $\beta_{Y,ji} = 1/\beta_{Y,ij}$ for the symmetric numbering of mole fractions.

7.3 Determination of Derivatives from Multi-Fluid Mixture Models Required for Phase Equilibrium and Other Property Calculations

The algorithms for carrying out phase equilibrium calculations used in this work are based on procedures using several kinds of partial derivatives to solve the set of equations for the equilibrium and secondary conditions for the unknown variables (see Secs. 5.4.1 and 7.6), to perform Gibbs free energy minimisation using a second order method (see Sec. 7.6.1), and to also verify the stability of the solution by means of minimising the tangent plane distance using a second order minimisation approach (see Secs. 7.5.1 and 7.6.2). All the required derivatives were determined analytically in order to develop robust and efficient property calculation routines. The results are described in the following paragraphs. Even the very sophisticated composition derivatives are formulated in a general manner which enables the use of the derived formulations for any multi-fluid approximation based on a similar structure as the new mixture model presented here.

The basis for the stability analysis as well as for flash and phase envelope calculations using temperature and pressure as the independent variables (see Secs. 7.5.1, 7.6, and 7.7.1) is the fugacity coefficient φ_i of component i which is defined as follows:

$$RT\ln\varphi_i(T,p,\bar{n}) = \int_0^p \left(\hat{v}_i - \frac{RT}{p}\right)\mathrm{d}p_{T,\bar{n}} = -\int_\infty^V \left(\left(\frac{\partial p}{\partial n_i}\right)_{T,V,n_j} - \frac{RT}{V}\right)\mathrm{d}V_{T,\bar{n}} - RT\ln Z. \tag{7.23}$$

Equation (7.23) can be used to determine the fugacity coefficients from equations of state for mixtures explicit in volume $V(T,p,\bar{n})$ or pressure $p(T,V,\bar{n})$. Changing the order of integration and of differentiation in Eq. (7.23) leads to the equivalent, but much more convenient expression

$$RT\ln\varphi_i(T,p,\bar{n}) = \left(\frac{\partial G^{\mathrm{r}}(T,p,\bar{n})}{\partial n_i}\right)_{T,p,n_j} = \left(\frac{\partial A^{\mathrm{r}}(T,V,\bar{n})}{\partial n_i}\right)_{T,V,n_j} - RT\ln Z, \tag{7.24}$$

which can be used for the calculation of fugacity coefficients from equations of state explicit in the Gibbs free energy $G(T,p,\bar{n})$ or the Helmholtz free energy $A(T,V,\bar{n})$. By inserting the relation

$$\frac{A^{\mathrm{r}}(T,V,\bar{n})}{RT} = n\alpha^{\mathrm{r}} \tag{7.25}$$

in Eq. (7.24), where $\alpha^{\mathrm{r}} = \alpha^{\mathrm{r}}(\delta,\tau,\bar{x})$ is the residual part of the reduced Helmholtz free energy [see Eqs. (5.7) and (7.3)] and n is the total mole number according to

$$n = \sum_{i=1}^{N} n_i, \tag{7.26}$$

the connection between the logarithm of the fugacity coefficient of component i in the mixture and the multi-fluid approximation is obtained as follows:

$$\ln \varphi_i = \left(\frac{\partial n\alpha^{\mathrm{r}}}{\partial n_i} \right)_{T,V,n_j} - \ln Z, \tag{7.27}$$

where the compression factor is

$$Z = \frac{pV}{nRT} = 1 + \delta\alpha_\delta^{\mathrm{r}}. \tag{7.28}$$

By applying basic mathematical relations among partial derivatives, the required derivatives of $\ln \varphi_i$ [see Eq. (7.27)] with respect to temperature T (at constant pressure and composition), pressure p (at constant temperature and composition), and mole numbers n_j (at constant temperature and pressure, and constant moles of other components n_k with $k \neq j$, which is implicitly assumed throughout this chapter to take advantage of a simpler notation for such composition derivatives) can be written according to the following equations [see Michelsen and Mollerup (1986) and Mollerup and Michelsen (1992) for the corresponding relations when using other models]:

$$\left(\frac{\partial \ln \varphi_i}{\partial T} \right)_{p,\bar{n}} = \left(\frac{\partial^2 n\alpha^{\mathrm{r}}}{\partial T \partial n_i} \right)_{V,n_j} + \frac{1}{T} - \frac{\hat{v}_i}{RT} \left(\frac{\partial p}{\partial T} \right)_{V,\bar{n}}, \tag{7.29}$$

$$\left(\frac{\partial \ln \varphi_i}{\partial p} \right)_{T,\bar{n}} = \frac{\hat{v}_i}{RT} - \frac{1}{p}, \tag{7.30}$$

$$n \left(\frac{\partial \ln \varphi_i}{\partial n_j} \right)_{T,p} = n \left(\frac{\partial^2 n\alpha^{\mathrm{r}}}{\partial n_j \partial n_i} \right)_{T,V} + 1 + \frac{n}{RT} \frac{\left(\frac{\partial p}{\partial n_j} \right)_{T,V,n_i} \left(\frac{\partial p}{\partial n_i} \right)_{T,V,n_j}}{\left(\frac{\partial p}{\partial V} \right)_{T,\bar{n}}}, \tag{7.31}$$

where the partial molar volume $\hat{v}_i$ is given by

$$\hat{v}_i = \left(\frac{\partial V}{\partial n_i} \right)_{T,p,n_j} = \frac{-\left(\frac{\partial p}{\partial n_i} \right)_{T,V,n_j}}{\left(\frac{\partial p}{\partial V} \right)_{T,\bar{n}}}. \tag{7.32}$$

Aside from the traditional approach using temperature and pressure as the independent variables, an alternative phase envelope algorithm which uses temperature and total volume as the independent variables was used (see Sec. 7.7.2). For this volume-based phase envelope algorithm, the ratio of the fugacity of component i and its mole number is used. Dividing the fugacity of component i according to

$$f_i = x_i \rho RT \exp \left(\frac{\partial n\alpha^{\mathrm{r}}}{\partial n_i} \right)_{T,V,n_j} \tag{7.33}$$

by the mole number n_i of component i, and performing several further conversions leads to:

$$\ln\left(\frac{f_i}{n_i}\right)=\ln\left(\frac{RT}{V}\right)+\left(\frac{\partial n\alpha^{\mathrm{r}}}{\partial n_i}\right)_{T,V,n_j}, \tag{7.34}$$

where the total volume

$$V=nv=\frac{n}{\rho}. \tag{7.35}$$

From Eq. (7.34) the required derivatives with respect to temperature T (at constant total volume and composition), total volume V (at constant temperature and composition), and mole numbers n_j (at constant temperature, total volume, and moles of other components) are obtained as follows:

$$\left(\frac{\partial\ln(f_i/n_i)}{\partial T}\right)_{V,\bar{n}}=\frac{1}{T}+\left(\frac{\partial^2 n\alpha^{\mathrm{r}}}{\partial T\,\partial n_i}\right)_{V,n_j}, \tag{7.36}$$

$$\left(\frac{\partial\ln(f_i/n_i)}{\partial V}\right)_{T,\bar{n}}=-\frac{1}{V}+\left(\frac{\partial^2 n\alpha^{\mathrm{r}}}{\partial V\,\partial n_i}\right)_{T,n_j}, \tag{7.37}$$

$$\left(\frac{\partial\ln(f_i/n_i)}{\partial n_j}\right)_{T,V}=\left(\frac{\partial^2 n\alpha^{\mathrm{r}}}{\partial n_j\,\partial n_i}\right)_{T,V}. \tag{7.38}$$

In the resulting expressions for the scaled composition derivatives of $\ln\varphi_i$ in terms of the reduced Helmholtz free energy as a function of the mixture variables δ and τ and the mole fractions x_i, the total number of moles n cancels out of the equations. Thus, the scaled derivatives only depend on the mixture composition, not on the total number of moles. Note that Eq. (7.38) is not scaled and therefore the mole number n is required for the calculation of these derivatives as well as for the equations where the total volume [Eq. (7.35)] is involved [see Eqs. (7.34) and (7.37)]. Since this is internally controlled in the algorithm, only the scaled derivatives will be derived in the following paragraphs.

Aside from the first derivative of $n\alpha^{\mathrm{r}}$ with respect to n_i required to calculate $\ln\varphi_i$ and $\ln(f_i/n_i)$ [see Eqs. (7.27) and (7.34)], the determination of pressure derivatives with respect to temperature, total volume, and mole numbers, and of the following second derivatives of $n\alpha^{\mathrm{r}}$ are required to determine the derivatives of $\ln\varphi_i$ and $\ln(f_i/n_i)$ listed above:

$$\left(\frac{\partial^2 n\alpha^{\mathrm{r}}}{\partial T\,\partial n_i}\right)_{V,n_j}=\left(\frac{\partial}{\partial T}\left(\frac{\partial n\alpha^{\mathrm{r}}}{\partial n_i}\right)_{T,V,n_j}\right)_{V,\bar{n}}, \tag{7.39}$$

$$n\left(\frac{\partial^2 n\alpha^{\mathrm{r}}}{\partial V\,\partial n_i}\right)_{T,n_j}=n\left(\frac{\partial}{\partial V}\left(\frac{\partial n\alpha^{\mathrm{r}}}{\partial n_i}\right)_{T,V,n_j}\right)_{T,\bar{n}}, \tag{7.40}$$

$$n\left(\frac{\partial^2 n\alpha^{\mathrm{r}}}{\partial n_j\,\partial n_i}\right)_{T,V} = n\left(\frac{\partial}{\partial n_j}\left(\frac{\partial n\alpha^{\mathrm{r}}}{\partial n_i}\right)_{T,V,n_j}\right)_{T,V,n_i} . \tag{7.41}$$

With the derivative of $n\alpha^{\mathrm{r}}$ with respect to n_i at constant temperature T, total volume V, and other mole numbers n_j with $j \neq i$ [see Eq. (5.44)] according to

$$\left(\frac{\partial n\alpha^{\mathrm{r}}}{\partial n_i}\right)_{T,V,n_j} = \alpha^{\mathrm{r}} + n\left(\frac{\partial \alpha^{\mathrm{r}}}{\partial n_i}\right)_{T,V,n_j} , \tag{7.42}$$

where the derivative of α^{r} with respect to n_i at constant T, V, and other mole numbers n_j [see Eqs. (5.45) and (5.50)] can be expressed as

$$n\left(\frac{\partial \alpha^{r}}{\partial n_i}\right)_{T,V,n_j} = \delta\alpha^{\mathrm{r}}_{\delta}\left[1-\frac{1}{\rho_{\mathrm{r}}}\cdot n\left(\frac{\partial \rho_{\mathrm{r}}}{\partial n_i}\right)_{n_j}\right] + \tau\alpha^{\mathrm{r}}_{\tau}\frac{1}{T_{\mathrm{r}}}\cdot n\left(\frac{\partial T_{\mathrm{r}}}{\partial n_i}\right)_{n_j} + \alpha^{\mathrm{r}}_{x_i} - \sum_{k=1}^{N} x_k\,\alpha^{\mathrm{r}}_{x_k} , \tag{7.43}$$

for the second derivatives according to Eqs. (7.39) – (7.41) the following results are obtained:

$$\left(\frac{\partial}{\partial T}\left(\frac{\partial n\alpha^{\mathrm{r}}}{\partial n_i}\right)_{T,V,n_j}\right)_{V,\bar{n}} = -\frac{\tau}{T}\left[\alpha^{\mathrm{r}}_{\tau} + \left(\frac{\partial}{\partial \tau}\left(n\left(\frac{\partial \alpha^{\mathrm{r}}}{\partial n_i}\right)_{T,V,n_j}\right)\right)_{\delta,\bar{x}}\right], \tag{7.44}$$

$$n\left(\frac{\partial}{\partial V}\left(\frac{\partial n\alpha^{\mathrm{r}}}{\partial n_i}\right)_{T,V,n_j}\right)_{T,\bar{n}} = -\rho\delta\left[\alpha^{\mathrm{r}}_{\delta} + \left(\frac{\partial}{\partial \delta}\left(n\left(\frac{\partial \alpha^{\mathrm{r}}}{\partial n_i}\right)_{T,V,n_j}\right)\right)_{\tau,\bar{x}}\right], \tag{7.45}$$

$$n\left(\frac{\partial}{\partial n_j}\left(\frac{\partial n\alpha^{\mathrm{r}}}{\partial n_i}\right)_{T,V,n_j}\right)_{T,V,n_i} = n\left(\frac{\partial \alpha^{\mathrm{r}}}{\partial n_j}\right)_{T,V,n_i} + n\left(\frac{\partial}{\partial n_j}\left(n\left(\frac{\partial \alpha^{\mathrm{r}}}{\partial n_i}\right)_{T,V,n_j}\right)\right)_{T,V,n_i} . \tag{7.46}$$

The second part of the sum in Eq. (7.46) results in

$$\begin{aligned}
n\left(\frac{\partial}{\partial n_j}\left(n\left(\frac{\partial \alpha^{\mathrm{r}}}{\partial n_i}\right)_{T,V,n_j}\right)\right)_{T,V,n_i} &= \left(\frac{\partial}{\partial \delta}\left(n\left(\frac{\partial \alpha^{\mathrm{r}}}{\partial n_i}\right)_{T,V,n_j}\right)\right)_{\tau,\bar{x}}\cdot n\left(\frac{\partial \delta}{\partial n_j}\right)_{T,V,n_i} \\
&+ \left(\frac{\partial}{\partial \tau}\left(n\left(\frac{\partial \alpha^{\mathrm{r}}}{\partial n_i}\right)_{T,V,n_j}\right)\right)_{\delta,\bar{x}}\cdot n\left(\frac{\partial \tau}{\partial n_j}\right)_{T,V,n_i} \\
&+ \left(\frac{\partial}{\partial x_j}\left(n\left(\frac{\partial \alpha^{\mathrm{r}}}{\partial n_i}\right)_{T,V,n_j}\right)\right)_{\delta,\tau,x_i} - \sum_{k=1}^{N} x_k\left(\frac{\partial}{\partial x_k}\left(n\left(\frac{\partial \alpha^{\mathrm{r}}}{\partial n_i}\right)_{T,V,n_j}\right)\right)_{\delta,\tau,x_i} ,
\end{aligned} \tag{7.47}$$

and the derivatives of the mixture variables δ and τ with respect to the mole numbers n_j at constant T, V, and other mole numbers n_i [see Eqs. (5.47) and (5.48)] are obtained according to

$$n\left(\frac{\partial\delta}{\partial n_j}\right)_{T,V,n_i} = \delta - \frac{\delta}{\rho_{\mathrm{r}}}\cdot n\left(\frac{\partial\rho_{\mathrm{r}}}{\partial n_j}\right)_{n_i}, \tag{7.48}$$

$$n\left(\frac{\partial\tau}{\partial n_j}\right)_{T,V,n_i} = \frac{\tau}{T_{\mathrm{r}}}\cdot n\left(\frac{\partial T_{\mathrm{r}}}{\partial n_j}\right)_{n_i}. \tag{7.49}$$

Equation (7.47) is valid for all i and j; the distinction between $i = j$ and $i \neq j$ is necessary only for the second derivatives with respect to mole fractions of the fundamental elements of the mixture model, namely α^{r} and the reducing functions ρ_{r} and T_{r} [see Eqs. (7.21h) and (7.21i) in Table 7.5, and Eqs. (7.22c) and (7.22d) in Table 7.10].

Equations (7.44), (7.45), and (7.47) require the partial derivatives of Eq. (7.43) with respect to δ, τ, and x_j. Setting up the derivatives of Eq. (7.43) with respect to δ and τ is comparatively simple as these are taken at constant composition $\bar{x}$:

$$\left(\frac{\partial}{\partial\delta}\left(n\left(\frac{\partial\alpha^{\mathrm{r}}}{\partial n_i}\right)_{T,V,n_j}\right)\right)_{\tau,\bar{x}} = \left(\alpha_\delta^{\mathrm{r}} + \delta\alpha_{\delta\delta}^{\mathrm{r}}\right)\left[1 - \frac{1}{\rho_{\mathrm{r}}}\cdot n\left(\frac{\partial\rho_{\mathrm{r}}}{\partial n_i}\right)_{n_j}\right] + \tau\alpha_{\delta\tau}^{\mathrm{r}}\frac{1}{T_{\mathrm{r}}}\cdot n\left(\frac{\partial T_{\mathrm{r}}}{\partial n_i}\right)_{n_j}$$
$$+\ \alpha_{\delta x_i}^{\mathrm{r}} - \sum_{k=1}^{N} x_k\,\alpha_{\delta x_k}^{\mathrm{r}}, \tag{7.50}$$

$$\left(\frac{\partial}{\partial\tau}\left(n\left(\frac{\partial\alpha^{\mathrm{r}}}{\partial n_i}\right)_{T,V,n_j}\right)\right)_{\delta,\bar{x}} = \delta\alpha_{\delta\tau}^{\mathrm{r}}\left[1 - \frac{1}{\rho_{\mathrm{r}}}\cdot n\left(\frac{\partial\rho_{\mathrm{r}}}{\partial n_i}\right)_{n_j}\right] + \left(\alpha_\tau^{\mathrm{r}} + \tau\alpha_{\tau\tau}^{\mathrm{r}}\right)\frac{1}{T_{\mathrm{r}}}\cdot n\left(\frac{\partial T_{\mathrm{r}}}{\partial n_i}\right)_{n_j}$$
$$+\ \alpha_{\tau x_i}^{\mathrm{r}} - \sum_{k=1}^{N} x_k\,\alpha_{\tau x_k}^{\mathrm{r}}. \tag{7.51}$$

The derivative of Eq. (7.43) with respect to x_j at constant δ, τ, and other mole fractions x_i can be determined in the following manner:

$$\left(\frac{\partial}{\partial x_j}\left(n\left(\frac{\partial\alpha^{\mathrm{r}}}{\partial n_i}\right)_{T,V,n_j}\right)\right)_{\delta,\tau,x_i} = \delta\alpha_{\delta x_j}^{\mathrm{r}}\left[1 - \frac{1}{\rho_{\mathrm{r}}}\cdot n\left(\frac{\partial\rho_{\mathrm{r}}}{\partial n_i}\right)_{n_j}\right]$$
$$-\ \delta\alpha_\delta^{\mathrm{r}}\frac{1}{\rho_{\mathrm{r}}}\left[\left(\frac{\partial}{\partial x_j}\left(n\left(\frac{\partial\rho_{\mathrm{r}}}{\partial n_i}\right)_{n_j}\right)\right)_{x_i} - \frac{1}{\rho_{\mathrm{r}}}\left(\frac{\partial\rho_{\mathrm{r}}}{\partial x_j}\right)_{x_i}\cdot n\left(\frac{\partial\rho_{\mathrm{r}}}{\partial n_i}\right)_{n_j}\right]$$
$$+\ \tau\alpha_{\tau x_j}^{\mathrm{r}}\frac{1}{T_{\mathrm{r}}}\cdot n\left(\frac{\partial T_{\mathrm{r}}}{\partial n_i}\right)_{n_j}$$

$$+\ \tau\alpha_{\tau}^{\mathrm{r}}\frac{1}{T_{\mathrm{r}}}\left[\left(\frac{\partial}{\partial x_j}\left(n\left(\frac{\partial T_{\mathrm{r}}}{\partial n_i}\right)_{n_j}\right)\right)_{x_i}-\frac{1}{T_{\mathrm{r}}}\left(\frac{\partial T_{\mathrm{r}}}{\partial x_j}\right)_{x_i}\cdot n\left(\frac{\partial T_{\mathrm{r}}}{\partial n_i}\right)_{n_j}\right]$$

$$+\ \alpha_{x_i x_j}^{\mathrm{r}}-\alpha_{x_j}^{\mathrm{r}}-\sum_{m=1}^{N}x_m\,\alpha_{x_j x_m}^{\mathrm{r}}\,. \tag{7.52}$$

Note that Eq. (7.47) requires the summation over all composition derivatives of Eq. (7.43), and according to Eq. (7.52) each of the elements of this summation again require the summation over all second composition derivatives of α^{r}.

The first derivatives of the reducing functions for the mixture density $\rho_{\mathrm{r}}=\rho_{\mathrm{r}}(\bar{x})$ and mixture temperature $T_{\mathrm{r}}=T_{\mathrm{r}}(\bar{x})$ with respect to n_i with the other mole numbers n_j kept constant, which are required for Eqs. (7.43) and (7.48) – (7.52), result in:

$$n\left(\frac{\partial\rho_{\mathrm{r}}}{\partial n_i}\right)_{n_j}=\left(\frac{\partial\rho_{\mathrm{r}}}{\partial x_i}\right)_{x_j}-\sum_{k=1}^{N}x_k\left(\frac{\partial\rho_{\mathrm{r}}}{\partial x_k}\right)_{x_j}, \tag{7.53}$$

$$n\left(\frac{\partial T_{\mathrm{r}}}{\partial n_i}\right)_{n_j}=\left(\frac{\partial T_{\mathrm{r}}}{\partial x_i}\right)_{x_j}-\sum_{k=1}^{N}x_k\left(\frac{\partial T_{\mathrm{r}}}{\partial x_k}\right)_{x_j}. \tag{7.54}$$

The second derivatives of the reducing functions with respect to composition, which are also needed for Eq. (7.52), are given by the expressions below:

$$\left(\frac{\partial}{\partial x_j}\left(n\left(\frac{\partial\rho_{\mathrm{r}}}{\partial n_i}\right)_{n_j}\right)\right)_{x_i}=\left(\frac{\partial^2\rho_{\mathrm{r}}}{\partial x_j\,\partial x_i}\right)-\left(\frac{\partial\rho_{\mathrm{r}}}{\partial x_j}\right)_{x_i}-\sum_{k=1}^{N}x_k\left(\frac{\partial^2\rho_{\mathrm{r}}}{\partial x_j\,\partial x_k}\right), \tag{7.55}$$

$$\left(\frac{\partial}{\partial x_j}\left(n\left(\frac{\partial T_{\mathrm{r}}}{\partial n_i}\right)_{n_j}\right)\right)_{x_i}=\left(\frac{\partial^2 T_{\mathrm{r}}}{\partial x_j\,\partial x_i}\right)-\left(\frac{\partial T_{\mathrm{r}}}{\partial x_j}\right)_{x_i}-\sum_{k=1}^{N}x_k\left(\frac{\partial^2 T_{\mathrm{r}}}{\partial x_j\,\partial x_k}\right). \tag{7.56}$$

As the reduced density is explicit in $1/\rho_{\mathrm{r}}$, the following relations have to be applied for the derivatives of ρ_{r} [see also Eq. (7.9) and Table 7.10]:

$$\left(\frac{\partial\rho_{\mathrm{r}}}{\partial x_i}\right)_{x_j}=-\rho_{\mathrm{r}}^2\left(\frac{\partial(1/\rho_{\mathrm{r}})}{\partial x_i}\right)_{x_j}, \tag{7.57}$$

$$\left(\frac{\partial^2\rho_{\mathrm{r}}}{\partial x_i^2}\right)_{x_j}=2\rho_{\mathrm{r}}^3\left(\frac{\partial(1/\rho_{\mathrm{r}})}{\partial x_i}\right)_{x_j}\left(\frac{\partial(1/\rho_{\mathrm{r}})}{\partial x_i}\right)_{x_j}-\rho_{\mathrm{r}}^2\left(\frac{\partial^2(1/\rho_{\mathrm{r}})}{\partial x_i^2}\right)_{x_j}, \tag{7.58}$$

$$\left(\frac{\partial^2\rho_{\mathrm{r}}}{\partial x_i\,\partial x_j}\right)=2\rho_{\mathrm{r}}^3\left(\frac{\partial(1/\rho_{\mathrm{r}})}{\partial x_i}\right)_{x_j}\left(\frac{\partial(1/\rho_{\mathrm{r}})}{\partial x_j}\right)_{x_i}-\rho_{\mathrm{r}}^2\left(\frac{\partial^2(1/\rho_{\mathrm{r}})}{\partial x_i\,\partial x_j}\right),\quad i\neq j\,. \tag{7.59}$$

The determination of the pressure derivatives required in Eqs. (7.29), (7.31), and (7.32) follows from the relation between pressure and the reduced residual Helmholtz free energy [Eq. (7.3)] according to

$$p(\delta,\tau,\bar{x}) = \rho RT\left(1+\delta\alpha_{\delta}^{\mathrm{r}}\right). \tag{7.60}$$

Forming the partial derivatives of Eq. (7.60) with respect to T, V, and n_i with the respective properties kept constant, the required pressure derivatives can be written as follows:

$$\left(\frac{\partial p}{\partial T}\right)_{V,\bar{n}} = \rho R\left(1+\delta\alpha_{\delta}^{\mathrm{r}}-\delta\tau\alpha_{\delta\tau}^{\mathrm{r}}\right), \tag{7.61}$$

$$n\left(\frac{\partial p}{\partial V}\right)_{T,\bar{n}} = -\rho^2 RT\left(1+2\delta\alpha_{\delta}^{\mathrm{r}}+\delta^2\alpha_{\delta\delta}^{\mathrm{r}}\right), \tag{7.62}$$

$$n\left(\frac{\partial p}{\partial n_i}\right)_{T,V,n_j} = \rho RT\left[1+\delta\alpha_{\delta}^{\mathrm{r}}\left[2-\frac{1}{\rho_{\mathrm{r}}}\cdot n\left(\frac{\partial \rho_{\mathrm{r}}}{\partial n_i}\right)_{n_j}\right]+\delta\cdot n\left(\frac{\partial \alpha_{\delta}^{\mathrm{r}}}{\partial n_i}\right)_{T,V,n_j}\right]. \tag{7.63}$$

In Eq. (7.63) the derivative of $\alpha_{\delta}^{\mathrm{r}}$ with respect to n_i is required as a further derivative. Similar to the derivation of Eq. (5.50), the derivative of $\alpha_{\delta}^{\mathrm{r}}$ with respect to n_i at constant T, V, and other mole numbers n_j results in:

$$n\left(\frac{\partial \alpha_{\delta}^{\mathrm{r}}}{\partial n_i}\right)_{T,V,n_j} = \delta\alpha_{\delta\delta}^{\mathrm{r}}\left[1-\frac{1}{\rho_{\mathrm{r}}}\cdot n\left(\frac{\partial \rho_{\mathrm{r}}}{\partial n_i}\right)_{n_j}\right]+\tau\alpha_{\delta\tau}^{\mathrm{r}}\frac{1}{T_{\mathrm{r}}}\cdot n\left(\frac{\partial T_{\mathrm{r}}}{\partial n_i}\right)_{n_j}+\alpha_{\delta x_i}^{\mathrm{r}}-\sum_{k=1}^{N}x_k\,\alpha_{\delta x_k}^{\mathrm{r}}. \tag{7.64}$$

Similar to Eq. (7.64), the derivative of $\alpha_{\tau}^{\mathrm{r}}$ with respect to n_i at constant T, V, and other mole numbers n_j results in

$$n\left(\frac{\partial \alpha_{\tau}^{\mathrm{r}}}{\partial n_i}\right)_{T,V,n_j} = \delta\alpha_{\delta\tau}^{\mathrm{r}}\left[1-\frac{1}{\rho_{\mathrm{r}}}\cdot n\left(\frac{\partial \rho_{\mathrm{r}}}{\partial n_i}\right)_{n_j}\right]+\tau\alpha_{\tau\tau}^{\mathrm{r}}\frac{1}{T_{\mathrm{r}}}\cdot n\left(\frac{\partial T_{\mathrm{r}}}{\partial n_i}\right)_{n_j}+\alpha_{\tau x_i}^{\mathrm{r}}-\sum_{k=1}^{N}x_k\,\alpha_{\tau x_k}^{\mathrm{r}}. \tag{7.65}$$

It is important to note that Eqs. (7.64) and (7.65) do not equal Eqs. (7.50) and (7.51) since the order of differentiation is not immaterial due to the different variables kept constant for their determination.

Additionally, derivatives of $\ln\varphi_i$ with respect to or at constant total volume can easily be derived and are directly related to Eqs. (7.29) – (7.31) and the pressure and temperature derivatives listed in Table 7.2. By applying the relations of the fugacity and chemical potential derivatives listed in Table 7.11, the derivatives of the fugacity f_i of component i [see Eqs. (7.33) and (5.42)] and the chemical potential μ_i of component i [see Eq. (5.35)] with respect to temperature, pressure, and mole numbers can be calculated from the previously derived relations (see Table 7.3 and Sec. 5.4.1 for the definition of μ_i). For example, for the derivative of μ_i with respect to T at constant pressure and composition, the following equation is obtained:

$$\left(\frac{\partial \mu_i}{\partial T}\right)_{p,\bar{n}} = \left(\frac{\partial \mu_i}{\partial T}\right)_{V,\bar{n}} + \left(\frac{\partial \mu_i}{\partial V}\right)_{T,\bar{n}} \left(\frac{\partial V}{\partial T}\right)_{p,\bar{n}}, \tag{7.66}$$

where

$$\left(\frac{\partial \mu_i}{\partial T}\right)_{V,\bar{n}} = \left(\frac{\partial \mu_i^{\mathrm{o}}}{\partial T}\right)_{V,\bar{n}} + \left(\frac{\partial \mu_i^{\mathrm{r}}}{\partial T}\right)_{V,\bar{n}} \tag{7.67}$$

and

$$\left(\frac{\partial \mu_i}{\partial V}\right)_{T,\bar{n}} = \left(\frac{\partial \mu_i^{\mathrm{o}}}{\partial V}\right)_{T,\bar{n}} + \left(\frac{\partial \mu_i^{\mathrm{r}}}{\partial V}\right)_{T,\bar{n}} = -\left(\frac{\partial p}{\partial n_i}\right)_{T,V,n_j}; \tag{7.68}$$

see Table 7.2 for the derivative of the total volume V with respect to T which is additionally required in Eq. (7.66). By substituting the relations for μ_i^{o} and μ_i^{r} [see Eq. (5.36)] in Eqs. (7.67) and (7.68) given by

$$\mu_i^{\mathrm{o}} = RT\left(\frac{\partial n\alpha^{\mathrm{o}}}{\partial n_i}\right)_{T,V,n_j} \quad \text{and} \quad \mu_i^{\mathrm{r}} = RT\left(\frac{\partial n\alpha^{\mathrm{r}}}{\partial n_i}\right)_{T,V,n_j}, \tag{7.69}$$

the derivatives according to Eqs. (7.44) and (7.45) are required, whereas the derivatives of μ_i^{o} follow from Eq. (5.37) by differentiating $\alpha_{\mathrm{o}i}^{\mathrm{o}}$ with respect to T and V. Note that instead of the derivative of μ_i with respect to V at constant T and $\bar{n}$, the negative of the derivative of pressure with respect to n_i at constant temperature, total volume, and other mole numbers n_j according to Eq. (7.63) can be used. This relation also enables the verification of the second derivative of $n\alpha^{\mathrm{r}}$ according to Eq. (7.45) in addition to the relations for the respective straightforward verification of the different derivatives of $\ln\varphi_i$ (and also of μ_i) with respect to temperature, pressure, and composition, as described in the following section.

Thus, virtually all derivatives required for phase equilibrium and other property calculations have been determined. The derived equations are valid for any multi-fluid mixture model explicit in the reduced Helmholtz free energy α based on the structure presented in Chap. 5, and using composition-dependent reducing functions for the mixture density and temperature. The derivatives were successfully tested with other models, e.g. those of Lemmon *et al.* [Lemmon and Jacobsen (1999), Lemmon *et al.* (2000)].

The use of composition derivatives of the logarithm of fugacity coefficients as derivatives with respect to total moles (scaled or not scaled by the total number of moles) according to Eq. (7.31) instead of mole fraction derivatives is recommended for multi-component property calculations. For instance, it is very unlikely that differentiation of a fugacity coefficient expression with respect to mole fractions will yield a symmetric matrix as it does for the derivatives with respect to total moles. This is advantageous since the computational effort is reduced by a factor of about two. Although scaled derivatives with respect to total moles only depend on the mixture composition (not on the total number of moles), the scaled composition derivatives should not be confused with mole fraction derivatives, but can be used instead of mole fraction derivatives in iterative procedures.

Table 7.11 Derivatives of the fugacity and the chemical potential of component *i* with respect to temperature, pressure, and mole numbers, and their relation to other properties

Derivatives of the fugacity[a]	Derivatives of the chemical potential[b]
$\left(\frac{\partial \ln f_i}{\partial T}\right)_{p,\bar{n}} = -\frac{\hat{h}_i^{\mathrm{r}}(T,p,\bar{n})}{RT^2}$	$\left(\frac{\partial \mu_i}{\partial T}\right)_{p,\bar{n}} = -\hat{s}_i$
$\left(\frac{\partial \ln f_i}{\partial p}\right)_{T,\bar{n}} = \frac{\hat{v}_i}{RT}$	$\left(\frac{\partial \mu_i}{\partial p}\right)_{T,\bar{n}} = \hat{v}_i$
$\left(\frac{\partial \ln f_i}{\partial n_j}\right)_{T,p} = \left(\frac{\partial \ln \varphi_i}{\partial n_j}\right)_{T,p} + \left(\frac{\delta_{ij}}{n_i} - \frac{1}{n}\right)$	$\left(\frac{\partial \mu_i}{\partial n_j}\right)_{T,p} = \left(\frac{\partial \mu_j}{\partial n_i}\right)_{T,p} = RT\left(\frac{\partial \ln f_i}{\partial n_j}\right)_{T,p}$

[a] See also Eqs. (7.31), (7.32), and (7.78).

[b] See also Eqs. (7.32) and (7.66).

7.3.1 Test of Calculated Fugacity Coefficients, Chemical Potentials, and their Partial Derivatives

For the successful development of property calculation algorithms, the correctness of the derivatives determined in the preceeding section is extremely important. Unfortunately, even a systematic approach does not prevent coding errors, and it is necessary that computer codes are tested for internal consistency. To verify the correctness of the various derivatives, the identities listed below are very useful.

The analytical derivatives can always be tested by numerical evaluation of the respective derivatives, preferably carried out by means of central differences, i.e.

$$\frac{\partial f}{\partial n_i} = \frac{f(n_1, n_2, \ldots, n_i + \varepsilon, \ldots, n_N) - f(n_1, n_2, \ldots, n_i - \varepsilon, \ldots, n_N)}{2\varepsilon}. \tag{7.70}$$

For composition derivatives, ε should be chosen as about 10^{-5} times the sum of moles, which should yield results accurate to 8 – 10 digits [see Mollerup and Michelsen (1992)].

Aside from comparisons with numerical derivatives, a straightforward procedure for checking the fugacity coefficients and their derivatives was used in this work. For that reason, the following identities, which are obtained from standard thermodynamic relations, have to be satisfied:

$$\sum_{i=1}^{N} n_i \ln \varphi_i = \frac{G^{\mathrm{r}}(T,p,\bar{n})}{RT} = n\left[\alpha^{\mathrm{r}} + \delta\alpha_\delta^{\mathrm{r}} - \ln\left(1 + \delta\alpha_\delta^{\mathrm{r}}\right)\right], \tag{7.71}$$

$$\sum_{i=1}^{N} n_i \left(\frac{\partial \ln \varphi_i}{\partial T} \right)_{p,\bar{n}} = -\frac{H^{\mathrm{r}}(T,p,\bar{n})}{RT^2} = -\frac{n}{T}\left[\delta\alpha_\delta^{\mathrm{r}} + \tau\alpha_\tau^{\mathrm{r}}\right], \tag{7.72}$$

$$\sum_{i=1}^{N} n_i \left(\frac{\partial \ln \varphi_i}{\partial p} \right)_{T,\bar{n}} = \frac{n(Z-1)}{p} = \frac{n}{p}\delta\alpha_\delta^{\mathrm{r}}, \tag{7.73}$$

$$\sum_{i=1}^{N} n_i \left(\frac{\partial \ln \varphi_i}{\partial n_j} \right)_{T,p} = 0, \quad \text{for all } j, \tag{7.74}$$

$$\left(\frac{\partial \ln \varphi_i}{\partial n_j} \right)_{T,p} = \left(\frac{\partial \ln \varphi_j}{\partial n_i} \right)_{T,p}, \quad \text{for all } i \text{ and } j. \tag{7.75}$$

For constant temperature and pressure, Eq. (7.74) follows from the Gibbs-Duhem equation:

$$S\,\mathrm{d}T - V\,\mathrm{d}p + \sum_{i=1}^{N} n_i\,\mathrm{d}\mu_i = 0. \tag{7.76}$$

Equation (7.71) results from the relation between the partial molar residual Gibbs free energy $\hat{g}_i^{\mathrm{r}}(T,p,\bar{n})$ and the logarithm of the fugacity coefficient of component i [see Eq. (7.27)] which equals

$$\frac{\hat{g}_i^{\mathrm{r}}(T,p,\bar{n})}{RT} = \ln \varphi_i, \tag{7.77}$$

and Eq. (7.72) from the relation between the partial molar residual enthalpy $\hat{h}_i^{\mathrm{r}}(T,p,\bar{n})$ and the derivative of $\ln \varphi_i$ with respect to T [see Eq. (7.29)] according to

$$\frac{\hat{h}_i^{\mathrm{r}}(T,p,\bar{n})}{RT} = -T\left(\frac{\partial \ln \varphi_i}{\partial T} \right)_{p,\bar{n}}. \tag{7.78}$$

To verify the fugacity coefficients and their temperature derivatives, access to the residual Gibbs free energy $G^{\mathrm{r}}(T,p,\bar{n})$ and to the residual enthalpy $H^{\mathrm{r}}(T,p,\bar{n})$ is needed as evident from Eqs. (7.71) and (7.72). Further residual properties and their relation to the reduced residual Helmholtz free energy α^{r} of a multi-fluid mixture model are given in Table 7.12.

In a similar manner, the chemical potentials μ_i and their derivatives with respect to temperature, pressure, and composition can be tested for correctness by applying standard thermodynamic relations among partial molar properties, and the Gibbs-Duhem equation [Eq. (7.76)]. In terms of the reduced Helmholtz free energy α [Eq. (7.1)], the following identities are obtained (see also Table 7.1):

$$\sum_{i=1}^{N} n_i\,\mu_i = G(T,p,\bar{n}) = nRT\left[1 + \alpha^{\mathrm{o}} + \alpha^{\mathrm{r}} + \delta\alpha_\delta^{\mathrm{r}}\right], \tag{7.79}$$

$$\sum_{i=1}^{N} n_i \left(\frac{\partial \mu_i}{\partial T} \right)_{p,\bar{n}} = -S(T,p,\bar{n}) = -nR\left[\tau\left(\alpha_\tau^{\mathrm{o}} + \alpha_\tau^{\mathrm{r}}\right) - \alpha^{\mathrm{o}} - \alpha^{\mathrm{r}}\right], \tag{7.80}$$

$$\sum_{i=1}^{N} n_i \left(\frac{\partial \mu_i}{\partial p}\right)_{T,\bar{n}} = V(T,p,\bar{n}) = \frac{nRT}{p}\left[1+\delta\alpha_\delta^\mathrm{r}\right], \tag{7.81}$$

$$\sum_{i=1}^{N} n_i \left(\frac{\partial \mu_i}{\partial n_j}\right)_{T,p} = 0, \quad \text{for all } j, \tag{7.82}$$

$$\left(\frac{\partial \mu_i}{\partial n_j}\right)_{T,p} = \left(\frac{\partial \mu_j}{\partial n_i}\right)_{T,p}, \quad \text{for all } i \text{ and } j. \tag{7.83}$$

The composition derivatives of μ_i are directly related to the respective composition derivatives of $\ln f_i$ and $\ln \varphi_i$ as shown in Table 7.11.

Table 7.12 Definitions of residual thermodynamic properties and their relation to the reduced residual Helmholtz free energy α^r, Eq. (7.3)

Residual property and definition	Relation to α^r and its derivatives[a,b]
Residual Helmholtz free energy $A^\mathrm{r}(T,p,\bar{n}) = A^\mathrm{r}(T,V,\bar{n}) - nRT\ln Z$	$\frac{a^\mathrm{r}(\delta,\tau,\bar{x})}{RT} = \alpha^\mathrm{r} - \ln\left(1+\delta\alpha_\delta^\mathrm{r}\right)$
Residual entropy $S^\mathrm{r}(T,p,\bar{n}) = S^\mathrm{r}(T,V,\bar{n}) + nR\ln Z$	$\frac{s^\mathrm{r}(\delta,\tau,\bar{x})}{R} = \tau\alpha_\tau^\mathrm{r} - \alpha^\mathrm{r} + \ln\left(1+\delta\alpha_\delta^\mathrm{r}\right)$
Residual internal energy $U^\mathrm{r}(T,p,\bar{n}) = U^\mathrm{r}(T,V,\bar{n})$	$\frac{u^\mathrm{r}(\delta,\tau,\bar{x})}{RT} = \tau\alpha_\tau^\mathrm{r}$
Residual enthalpy $H^\mathrm{r}(T,p,\bar{n}) = H^\mathrm{r}(T,V,\bar{n})$	$\frac{h^\mathrm{r}(\delta,\tau,\bar{x})}{RT} = \tau\alpha_\tau^\mathrm{r} + \delta\alpha_\delta^\mathrm{r}$
Residual Gibbs free energy $G^\mathrm{r}(T,p,\bar{n}) = G^\mathrm{r}(T,V,\bar{n}) - nRT\ln Z$	$\frac{g^\mathrm{r}(\delta,\tau,\bar{x})}{RT} = \alpha^\mathrm{r} + \delta\alpha_\delta^\mathrm{r} - \ln\left(1+\delta\alpha_\delta^\mathrm{r}\right)$

Relations between A^r, S^r, U^r, H^r, and G^r

$$U^\mathrm{r}(T,V,\bar{n}) = A^\mathrm{r}(T,V,\bar{n}) + TS^\mathrm{r}(T,V,\bar{n})$$

$$H^\mathrm{r}(T,V,\bar{n}) = U^\mathrm{r}(T,V,\bar{n}) + pV - nRT$$

$$G^\mathrm{r}(T,V,\bar{n}) = A^\mathrm{r}(T,V,\bar{n}) + pV - nRT$$

[a] See Eq. (7.4) for the definition of δ and τ.

[b] See Table 7.5 for the derivatives of α^r with respect to δ and τ.

7.4 Relations Between Activity Coefficients, Excess Properties, and α

Since multi-fluid mixture models are able to accurately describe the properties of mixtures in the liquid phase, activity coefficient and excess Gibbs free energy models are no longer needed for those mixtures where such an approach is available (see Table 5.1). Several drawbacks are associated with the use of activity coefficient and excess Gibbs free energy models. For example, in equilibrium calculations the liquid phase is often described by an activity coefficient or excess Gibbs free energy model and the vapour phase by an equation of state, e.g. a cubic equation of state, which is in general not able to accurately describe the liquid phase (see Sec. 2.1.2). This will never lead to a closed phase boundary or a vapour-liquid critical point as the combination of these models is inconsistent. Since a multi-fluid mixture model is able to accurately describe both phases with a single approach, such models are far superior as they yield accurate and consistent results for the extended fluid surface including the vapour-liquid equilibrium. Nevertheless, the activity a_i and the activity coefficient γ_i of component i can be calculated from a mixture model based on a multi-fluid approximation explicit in the reduced Helmholtz free energy α by the following expressions:

$$a_i(T,p,\bar{n}) = \frac{f_i(T,p,\bar{n})}{f_{\mathrm{o}i}(T,p)} = \frac{\rho RT}{f_{\mathrm{o}i}} x_i \exp\left(\frac{\partial n\alpha^{\mathrm{r}}}{\partial n_i}\right)_{T,V,n_j} \tag{7.84}$$

and

$$\ln\gamma_i(T,p,\bar{n}) = \ln\frac{a_i(T,p,\bar{n})}{x_i} = \ln\frac{\varphi_i(T,p,\bar{n})}{\varphi_{\mathrm{o}i}(T,p)} = \left(\frac{\partial n\alpha^{\mathrm{r}}}{\partial n_i}\right)_{T,V,n_j} - \ln\left[\left(1+\delta\alpha_\delta^{\mathrm{r}}\right)\varphi_{\mathrm{o}i}\right], \tag{7.85}$$

where $f_{\mathrm{o}i} = f_{\mathrm{o}i}(T,p)$ and $\varphi_{\mathrm{o}i} = \varphi_{\mathrm{o}i}(T,p)$ are the fugacity and the fugacity coefficient of the respective pure component; see Eq. (7.42) for the derivative of $n\alpha^{\mathrm{r}}$ with respect to n_i.

The connection between excess Gibbs free energy models and multi-fluid mixture models explicit in the reduced Helmholtz free energy α is given by

$$\frac{g^{\mathrm{E}}}{RT} = 1 + \alpha^{\mathrm{o}} + \alpha^{\mathrm{r}} + \delta\alpha_\delta^{\mathrm{r}} - \sum_{i=1}^{N} x_i \left[\frac{g_{\mathrm{o}i}(T,p)}{RT} + \ln x_i\right] = \sum_{i=1}^{N} x_i \ln\gamma_i\,, \tag{7.86}$$

where $g_{\mathrm{o}i}(T,p)$ is the molar Gibbs free energy of the respective pure component. Experimental mixture data for the molar excess enthalpy h^{E} and the molar excess volume v^{E}, which are useful for the development of multi-fluid mixture models when no other experimental information is available, can be compared to calculated values from α according to

$$\frac{h^{\mathrm{E}}}{RT} = 1 + \tau\left(\alpha_\tau^{\mathrm{o}} + \alpha_\tau^{\mathrm{r}}\right) + \delta\alpha_\delta^{\mathrm{r}} - \sum_{i=1}^{N} x_i \frac{h_{\mathrm{o}i}(T,p)}{RT} = -T\sum_{i=1}^{N} x_i \left(\frac{\partial\ln\gamma_i}{\partial T}\right)_{p,\bar{n}} \tag{7.87}$$

and

$$v^{\mathrm{E}}\frac{p}{RT} = 1 + \delta\alpha_\delta^{\mathrm{r}} - \sum_{i=1}^{N} x_i\, v_{\mathrm{o}i}(T,p)\frac{p}{RT} = p\sum_{i=1}^{N} x_i \left(\frac{\partial\ln\gamma_i}{\partial p}\right)_{T,\bar{n}}, \tag{7.88}$$

where $h_{\mathrm{o}i}(T,p)$ and $v_{\mathrm{o}i}(T,p)$ are the molar enthalpy and molar volume of the respective pure component.

7.5 Phase Stability

In the following train of thoughts a closed multi-component system is considered which is comprised of a single phase, e.g. a homogeneous vapour, liquid, or supercritical phase, initially having the Gibbs free energy $G(T, p, \overline{n})$. The chemical potentials μ_i equal the partial derivatives of G with respect to the variables $\overline{n}$. A new phase is formed by removing a differential amount of matter $\delta\overline{n}$ and with that changing the initial system[50]. Assuming that the changes in the independent variables of the initial phase are so small that the chemical potentials μ_i of the initial system remain unchanged, the change in the Gibbs free energy of the initial phase equals

$$\delta G = -\sum_{i=1}^{N} \mu_i \, \delta n_i \tag{7.89}$$

and the Gibbs free energy of the new phase becomes

$$\delta G^* = \sum_{i=1}^{N} \mu_i^* \, \delta n_i , \tag{7.90}$$

where the μ_i^* are the chemical potentials of the new phase. The initial phase will be stable (i.e. homogeneous in this example) if the formation of a new phase does not lead to a decrease in the Gibbs free energy of the whole system. This means that

$$\Delta G = \delta G^* + \delta G = \sum_{i=1}^{N} \left(\mu_i^* - \mu_i \right) \delta n_i > 0 \tag{7.91}$$

for any changes of the independent variables $\delta\overline{n}$. Aside from this stability criterion for the independent variables T, p, and $\overline{n}$, similar criteria can be derived for other independent variables which must remain constant for the overall system. For instance, for T, V, and $\overline{n}$ as the natural independent variables of the Helmholtz free energy A of a mixture, the following corresponding stability criteria is obtained:

$$\Delta A = -\left(p^* - p \right) \delta V + \sum_{i=1}^{N} \left(\mu_i^* - \mu_i \right) \delta n_i > 0 . \tag{7.92}$$

The star denotes an intensive or extensive property of the segregated phase and δ denotes the quantity of the extensive property transferred to the new phase.

Since the equality of component chemical potentials or fugacities in the fluid phases of a system comprised of any number of phases is only a necessary condition for equilibrium, the solution has to be verified for stability as well. At a given temperature, pressure, and composition of the overall system, the equilibrium mixture is stable if and only if the overall Gibbs free energy is at its global minimum. The same is true for the overall Helmholtz free

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[50] In this context, δ denotes a differential quantity and should not be confused with the reduced mixture density.

energy of an equilibrium system at a given temperature, overall total volume, and overall mixture composition.

Thus, analysing the phase stability enables the development of property calculation algorithms which allow for “blind” calculations where the number of phases is not known in advance. If a phase turns out to be unstable, adding phases (or perhaps removing, if a two- or multi-phase equilibrium system turns out to be unstable) to obtain the global minimum of G or A of the overall system leads to the correct results of the present property calculation to be solved. Most methods for phase stability determination are based on Gibbs free energy minimisation. The basic principle of the stability analysis algorithm used for the developed property calculation routines in this work is explained in the following section.

7.5.1 Stability Condition and Stability Analysis

Considering the case of two-phase equilibrium, the change in Gibbs free energy resulting from transferring δn_i moles of component i from the liquid phase to the vapour phase is

$$\delta G = (\mu_i'' - \mu_i')\,\delta n_i . \tag{7.93}$$

At the global minimum, δG must be zero for any transfer of material. Equation (7.93) then yields the condition of equality of chemical potentials or of fugacities as a necessary condition for phase equilibrium.

For the following derivation of a necessary condition for phase stability, a phase with composition $\bar{x}$ and with the chemical potentials $\bar{\mu}(\bar{x})$ is considered. Assuming that an infinitesimal amount δe of a new phase with the molar composition $\bar{w}$ is formed from this phase, the change in Gibbs free energy associated with the formation of the new phase is given by

$$\delta G = \delta e \sum_{i=1}^{N} w_i \left[\mu_i(\bar{w}) - \mu_i(\bar{x}) \right] \tag{7.94}$$

with $w_i\,\delta e$ the amount of component i transferred. A necessary condition for the stability of the original phase is that δG is nonnegative for any positive δe. This results in

$$\sum_{i=1}^{N} w_i \left[\mu_i(\bar{w}) - \mu_i(\bar{x}) \right] \geq 0 \tag{7.95}$$

for any composition $\bar{w}$, which is the tangent plane condition of Gibbs.

A solution to the phase equilibrium equations has identical chemical potentials for each component in all phases (see Sec. 5.4.1). This implies that the vapour phase composition and the liquid phase composition have identical tangent planes. A stability analysis by means of the tangent plane distance [see Eqs. (7.96) and (7.99)] will thus yield identical results for both phases, or for all phases in case more than two equilibrium phases are present. It can easily be shown that the tangent plane condition is not only a necessary condition, but even a sufficient condition for stability [see Michelsen and Mollerup (2004)].

According to Eq. (7.95), for a mixture of composition $\bar{x}$ at specified temperature and pressure, the necessary and sufficient condition for stability is that the tangent plane distance function

$$TPD(\bar{w}) = \sum_{i=1}^{N} w_i \left[\mu_i(\bar{w}) - \mu_i(\bar{x}) \right] \tag{7.96}$$

is nonnegative for any trial phase composition $\bar{w}$. Rewriting the condition in terms of fugacity coefficients [see Eq. (7.27)] is done by substituting

$$\mu_i(T,p,\bar{w}) = \mu_{0i}^{\mathrm{o}}(T,p) + RT \ln w_i + RT \ln \varphi_i(T,p,\bar{w}) \tag{7.97}$$

and

$$\mu_i(T,p,\bar{x}) = \mu_{0i}^{\mathrm{o}}(T,p) + RT \ln x_i + RT \ln \varphi_i(T,p,\bar{x}), \tag{7.98}$$

where $\mu_{0i}^{\mathrm{o}}(T,p)$ is the ideal chemical potential of the pure component i at a given temperature and pressure, into the reduced tangent plane distance from Eq. (7.96), resulting in

$$tpd(\bar{w}) = \frac{TPD(\bar{w})}{RT} = \sum_{i=1}^{N} w_i \left[\ln w_i + \ln \varphi_i(\bar{w}) - \ln x_i - \ln \varphi_i(\bar{x}) \right]. \tag{7.99}$$

In order to verify stability, $tpd(\bar{w})$ must be nonnegative for all valid phase compositions.

A graphical (geometric) interpretation of phase equilibrium and the described stability condition in terms of Gibbs free energy plots and tangent plane distances is given for binary mixtures, for example, by Baker *et al.* (1982), Michelsen (1982a), and Michelsen and Mollerup (2004).

Verifying the tangent plane condition is not a trivial task since it requires a search over the entire composition range (of mixtures consisting of any number of components). When such an extensive "search" does not reveal violations, the tangent plane condition for stability is satisfied.

The practical application of the tangent plane condition of Gibbs [Eq. (7.95)] was demonstrated in connection with phase equilibrium by Baker *et al.* (1982). A computational approach based on minimising the tangent plane distance was suggested by Michelsen (1982a,b) and included guidelines for its use in connection with multi-phase equilibrium calculations. This approach is based on the fact that the tangent plane condition is nonnegative everywhere if and only if it is nonnegative at all its minima. Thus, the task is to

- locate all (local) minima of the tangent plane distance and to
- check whether all their values of *tpd* are nonnegative.

If a negative value of *tpd* is encountered during the search for the local minima, the mixture is known to be unstable.

Several other methods for resolving the question of stability are reported in the literature. Developments of considerable interest are based on global optimisation methods [e.g. McDonald and Floudas (1995), (1997), Harding and Floudas (2000), Nichita *et al.* (2002a,b)], interval analysis [e.g. Hua *et al.* (1996), (1998)], and homotopy-continuation methods [e.g. Sun and Seider (1995)]. All of these algorithms are based on the Gibbs free energy minimisation.

For certain specifications of practical importance, e.g. specification of overall composition along with either p and T, p and H, p and S, or T and V (see Sec. 5.4.3), the satisfaction of the tangent plane condition not only implies that a valid solution of the phase equilibrium calculation is located, but also that this solution is unique. For a number of other specifications, the satisfaction of the condition only verifies that the solution is proper, whereas the possible existence of alternative and equally valid solutions is not excluded. The dew point calculation at a specified temperature or pressure (see Table 5.3) in the retrograde region is an example where two solutions are frequently expected.

A further important feature associated with the tangent plane condition is that by locating a trial phase composition that yields a negative tangent plane distance, the stability analysis usually provides a good starting point (concerning proper initial estimates) for the subsequent calculation of the correct phase distribution [see Michelsen and Mollerup (2004)]. Moreover, criteria for critical point calculations of mixtures consisting of an arbitrary number of components are readily derived from the properties of the tangent plane surface. The computational implementations of such criteria are briefly discussed by Michelsen and Mollerup (2004); see also Heidemann and Khalil (1980), Michelsen (1984), Michelsen and Heidemann (1988), and the recent articles of, for example, Henderson *et al.* (2004) and Nichita (2005), for further information and methodologies regarding the calculation of critical points in multi-component mixtures.

Based on the principles described in this section, a well-founded and robust procedure for stability investigation combined with a two-phase pT flash algorithm (see Sec. 7.6.2), which was developed and provided by Michelsen (2001), was used in this work to develop routines which enable extensive and reliable property calculations from the new mixture model for natural gases and other mixtures. The developed user-friendly software (see Sec. 7.14) enables the calculation of a variety of thermodynamic properties in the homogeneous gas, liquid, and supercritical regions as well as the vapour-liquid equilibrium of multi-component mixtures consisting of any number of components considered in the new equation of state (see Table 4.2) with arbitrary composition. Note that no user-provided initial estimates are required, and the number of phases do not need to be known in advance. Furthermore, the algorithms and routines are not limited to the current number of considered components in the new mixture model, but are easily extendable to additional components.

To the knowledge of the author, this is the first time that such algorithms (which have so far been used, for example, for cubic equations of state, excess Gibbs free energy models, and "hybrid" models[51]) were successfully applied to a multi-fluid mixture model explicit in the reduced Helmholtz free energy. Aside from the required fugacity coefficients and its sophisticated partial derivatives (see Sec. 7.3) required, for example, for minimising *tpd* [Eq. (7.99)], the provided algorithms were modified to meet the requirements of the developed multi-fluid mixture model. Moreover, a proper interface between the algorithm and the new equation of state had to be developed. Since the Michelsen algorithms use temperature, pressure, and composition as the independent variables, a very important condition for the successful implementation of these procedures is the development of a suitable and robust density solver. The density solver must supply the stability analysis and other routines with the proper and correct density which has to be iteratively determined for a specified T, p, and composition. Therefore, the characteristics of high accuracy mixture models based on multi-fluid approximations have to be taken into account (see Sec. 7.8).

7.6 The Isothermal Two-Phase Flash

The most important equilibrium calculation is probably the isothermal flash calculation, which is the equilibrium calculation at a specified mixture temperature T, pressure p, and overall composition, given as mole fractions $\bar{x}$ or mole numbers $\bar{n}$. For these flash specifications, the corresponding equilibrium conditions (see also Sec. 5.4.1) can be written using fugacities according to

$$\ln f_i'' - \ln f_i' = 0\,, \quad i = 1, 2, ..., N, \tag{7.100}$$

or fugacity coefficients and K-factors:

$$\ln \varphi_i'' - \ln \varphi_i' + \ln K_i = 0\,, \quad i = 1, 2, ..., N. \tag{7.101}$$

The Rachford-Rice equation relates the feed composition $\bar{x}$ and the phase compositions for the liquid $\bar{x}'$ and the vapour $\bar{x}''$, the vapour fraction β, and the K-factors [see also Eqs. (5.53) and (5.56)]:

$$\sum_{i=1}^{N} (x_i'' - x_i') = \sum_{i=1}^{N} \frac{x_i (K_i - 1)}{1 - \beta + \beta K_i} = 0\,. \tag{7.102}$$

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[51] In a hybrid model different models are used to describe the equilibrium phases, e.g. an activity coefficient or excess Gibbs free energy model for the liquid phase and a virial or cubic equation of state for the vapour phase.

A complicating factor in equilibrium calculations is that the number of phases may not be known in advance. Although in many practical applications at least two phases, namely a liquid and a vapour phase, may be expected, it is required to verify the solution by means of a stability analysis (see Sec. 7.5.1), as mixtures capable of forming multiple liquid phases may exceed the current (assumed) number of equilibrium phases, and thus, new phases have to be introduced.

As mentioned in Sec. 5.4.3, successive substitution and the Newton-Raphson method are frequently applied solution methods, which directly solve the set of nonlinear equations for the unknown variables. In this work, property calculation routines were developed which are based on a flash algorithm developed by Michelsen [Michelsen (2001), Michelsen (1982b)]. This algorithm uses a combined and sophisticated strategy comprised of different classical and advanced numerical methods, such as successive substitution, Newton's method, accelerated successive substitution, and a second order approach. Additionally, a tangent plane stability analysis is performed in questionable situations as described in Sec. 7.5.1. This strategy is briefly described in the following text. Further details are given by Michelsen and Mollerup (2004) and Michelsen (1982b).

7.6.1 Gibbs Free Energy Minimisation

As already mentioned in Sec. 5.4.4, the correct solution of the isothermal equilibrium represents the global minimum of the overall Gibbs free energy. This important feature allows the equilibrium equations to be solved as an unconstrained minimisation problem using molar amounts as the independent variables and eliminating the amounts in one phase by means of the overall material balance [see Eqs. (5.67) and (5.68)].

At a given T and p, the equilibrium equations can be written as

$$g_i(\bar{v}) = \ln f_i'' - \ln f_i' = 0\,, \quad i = 1, 2, \ldots, N, \tag{7.103}$$

where the independent variables $\bar{v}$ are a vector of the vapour amounts v_i. Rather than directly applying a Newton-Raphson procedure to solve Eq. (7.103) for the independent variables, it is advantageous to treat the flash calculation as a minimisation problem, using $G/(nRT)$ as the objective function and the vapour amounts v_i as the independent variables[52]. For the minimisation, the gradient vector of $G/(nRT)$ is needed and obtained as [see also Eq. (7.103)]:

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[52] Note that the total Gibbs free energy of the overall (equilibrium) system G equals the sum of the total Gibbs free energies of the equilibrium phases, i.e., $G' + G''$. In terms of mole numbers, Eqs. (5.54) and (5.67) show that the molar flows of the vapour and liquid phases can be expressed as $v_i = n_i''/n$ and $l_i = n_i'/n$, where the total number of moles in the overall system $n = n' + n''$ is a constant due to the flash specification. Furthermore, it follows that $\partial l_i / \partial v_i = -1$.

$$\frac{\partial}{\partial v_i}\left(\frac{G}{nRT}\right)=g_i=\ln f_i''-\ln f_i',\quad i=1,2,...,N. \tag{7.104}$$

The calculation of the elements H_{ij} of the Hessian matrix $\boldsymbol{H}$ according to

$$H_{ij}=\frac{\partial g_i}{\partial v_j}=\frac{\partial \ln f_i''}{\partial v_i}+\frac{\partial \ln f_i'}{\partial l_i},\quad \text{for all } i \text{ and } j, \tag{7.105}$$

is required and carried out analytically, which involves the composition derivatives from the multi-fluid mixture model as derived in Sec. 7.3. In terms of fugacity coefficients and with Eq. (5.67), for the vapour and liquid phases follows

$$\ln f_i''=\ln\frac{v_i}{\beta}+\ln p+\ln\varphi_i''\quad \text{and}\quad \ln f_i'=\ln\frac{l_i}{1-\beta}+\ln p+\ln\varphi_i', \tag{7.106}$$

and the derivatives are

$$\frac{\partial \ln f_i''}{\partial v_j}=\frac{1}{\beta}\left(\frac{1}{x_i''}\delta_{ij}-1+\phi_{ij}''\right)\quad \text{and}\quad \frac{\partial \ln f_i'}{\partial l_j}=\frac{1}{1-\beta}\left(\frac{1}{x_i'}\delta_{ij}-1+\phi_{ij}'\right), \tag{7.107}$$

where the elements ϕ_{ij} for a phase of composition $\bar{n}$ are given by

$$\phi_{ij}=n\left(\frac{\partial \ln\varphi_i}{\partial n_j}\right)_{T,p}. \tag{7.108}$$

Equation (7.108) equals the scaled composition derivatives of $\ln\varphi_i$ that were determined in Sec. 7.3 [see Eq. (7.31)]. Finally, the complete expression for the Hessian matrix follows from Eqs. (7.105) and (7.107):

$$H_{ij}=\frac{1}{\beta(1-\beta)}\left[\frac{x_i}{x_i' x_i''}\delta_{ij}-1+(1-\beta)\phi_{ij}''+\beta\phi_{ij}'\right]. \tag{7.109}$$

It should be noted that the Hessian matrix for the minimisation problem is identical to the Jacobian matrix which would be required to solve the flash problem by means of a direct solution procedure based on the Newton-Raphson method (see Sec. 5.4.3).

A Newton-Raphson method, which basically calculates the correction vector $\Delta\bar{v}$ to the vapour flows $\bar{v}$ from

$$\boldsymbol{H}\cdot\Delta\bar{v}=-\bar{g}(\bar{v}), \tag{7.110}$$

can be used for solving the minimisation problem. This procedure is thus identical to the Newton-Raphson method for solving the flash as a set of algebraic equations. If the current estimate is sufficiently close to the solution, the Hessian matrix is positive definite and second order convergence is obtained. The iterations may fail if the Hessian matrix is not positive definite, which frequently is the case in early iterations. In order to guarantee convergence, a modified (“restricted step”) method using a diagonal correction term, multiplied by a stepsize control factor and added to the Hessian matrix, is used in the algorithm developed by

Michelsen in case the step calculated with the unmodified Hessian matrix exceeds a prespecified maximum size.

Each iterative step can be tested against the previous for a reduction in the overall Gibbs free energy of the mixture, thus providing a high level of safety by maintaining efficiency resulting from the second order convergence. Moreover, convergence to the trivial solution (see Sec. 5.4.1) can never occur as the algorithm requires a decrease in the Gibbs free energy at each step, which is of particular importance for calculations in the critical region. Unproductive iteration steps can be corrected to prevent divergence.

A drawback in the use of second order methods is the requirement of the composition derivatives of the fugacity coefficients. These derivatives can, however, be coded quite efficiently, even for a complex equation of state such as the developed multi-fluid mixture model. By using a systematic approach where all derivatives are evaluated analytically (see Sec. 7.3), elements necessary for the calculation of the fugacity coefficients can, if required, also be used in a subsequent calculation of their derivatives. The computational effort of evaluating derivatives is easily compensated by the reduction of the number of iterations [see also Michelsen and Mollerup (1986) and Mollerup and Michelsen (1992)].

7.6.2 The Combined Strategy of Michelsen

The traditional approach for two-phase flash calculations is based on the assumption that two phases will be present at equilibrium and an initial estimate of the phase compositions is used to initiate calculations. Vanishing of a phase during the iterative process is taken as indication that the specification corresponds to a single phase. The alternative approach starts with the stability analysis and the result is used to generate initial estimates for the flash calculation in case the feed mixture is concluded to be unstable. Both methods have their advantages and their disadvantages concerning efficiency and reliability.

The strategy for solving the two-phase flash calculation problem pursued by the algorithm of Michelsen (2001) is a combination of the advantages of both approaches resulting in a very efficient and reliable algorithm. The calculations are initiated with the assumption that two phases will be present, but stability analysis is used at a very early stage if instability of the specified overall system (the feed) has not been verified.

The algorithm starts by calculating feed fugacity coefficients and Wilson K-factors [Eq. (5.61)], which are used for calculating an initial estimate of the phase compositions by solving the Rachford-Rice equation, Eq. (7.102), for the vapour fraction β using Newton's method. If the phases do not split with the Wilson K-factors (i.e. no solution of β exists in the range $0 < \beta < 1$), the algorithm proceeds to the stability analysis (see Sec. 7.5.1). Otherwise, three steps of successive substitution are carried out to verify that the Gibbs free energy can be decreased.

The difference between the Gibbs free energy of the split phases and the specified feed is given by

$$\frac{\Delta G}{nRT} = (1-\beta)\sum_{i=1}^{N} x_i'(\ln x_i' + \ln\varphi_i') + \beta\sum_{i=1}^{N} x_i''(\ln x_i'' + \ln\varphi_i'') - \sum_{i=1}^{N} x_i(\ln x_i + \ln\varphi_i), \qquad (7.111)$$

where $\ln\varphi_i' = \ln\varphi_i(T,p,\bar{x}')$, $\ln\varphi_i'' = \ln\varphi_i(T,p,\bar{x}'')$, and $\ln\varphi_i = \ln\varphi_i(T,p,\bar{x})$ [see Eq. (7.27)]. Using the material balance, $x_i = (1-\beta)x_i' + \beta x_i''$ [see Eq. (5.53)], Eq. (7.111) can be written as

$$\frac{\Delta G}{nRT} = (1-\beta)\,tpd' + \beta\,tpd'', \qquad (7.112)$$

where

$$tpd' = tpd(\bar{x}') = \sum_{i=1}^{N} x_i'(\ln x_i' + \ln\varphi_i' - \ln x_i - \ln\varphi_i) \qquad (7.113)$$

and

$$tpd'' = tpd(\bar{x}'') = \sum_{i=1}^{N} x_i''(\ln x_i'' + \ln\varphi_i'' - \ln x_i - \ln\varphi_i) \qquad (7.114)$$

are the reduced tangent plane distances for the feed composition, using the current liquid- and vapour composition as the trial phases [see also Eq. (7.99)].

After the initial three steps of successive substitution, the following conditions may occur:

- If the overall Gibbs free energy of the resulting vapour and liquid phases, i.e. $G(T,p,\bar{n}') + G(T,p,\bar{n}'')$, is lower than G of the specified feed (assumed to be homogeneous), i.e. $G(T,p,\bar{n})$, the presence of (at least) two equilibrium phases is verified. The calculation is then continued with an accelerated successive substitution procedure (three cycles of successive substitution, where each cycle consists of three steps, followed by an extrapolation). Each step of the iterative procedure requires the calculation of new, updated thermodynamic properties (e.g. the fugacity coefficients of the equilibrium phases), where the Rachford-Rice solver is used to calculate new phase compositions from the revised K-factors obtained from Eq. (5.58). If the accelerated successive substitution fails to converge, a Gibbs free energy minimisation using a second order, restricted step approach is performed as described earlier in this section.
- Even if $\Delta G/(nRT)$ is positive it may occur that either tpd' or tpd'' [see Eqs. (7.113) and (7.114)] is negative, and with that the feed is also known to be unstable.
- If none of these events has occurred after three iterations, i.e. the initial three steps of successive substitution are inconclusive, the algorithm continues with the tangent plane stability analysis.

- If β exceeds its bounds, it is very likely that the specification corresponds to a single phase. As this is not a sufficient criterion, the algorithm continues with the stability analysis in this situation.

Similar to the phase split calculation, the stability analysis is performed starting with a successive substitution approach. If required, the algorithm continues with a second order minimisation using the same principles as in the phase split calculation. In case the stability analysis reveals a phase split, an improved K-factor estimate is generated by the tangent plane analysis, and the algorithm proceeds with the phase split calculation. Otherwise the mixture is concluded to be homogeneous.

As described in the previous paragraphs, many of the sophisticated routines used in the flash algorithm and tangent plane stability analysis require distinctive thermodynamic properties and, occasional, their derivatives. As with the stability analysis (see Sec. 7.5.1), it is again extremely important that the correct density is calculated from the multi-fluid mixture model for the specified flash variables (temperature, pressure, feed composition) and the phase compositions during the iterative process (see also Sec. 7.8).

7.7 Calculation of Saturation Points and Phase Envelopes

Aside from flash calculations at a specified mixture temperature, pressure, and overall composition as described in the previous section, phase equilibrium calculations with specified values of the vapour fraction β and either the temperature or the pressure are also of considerable interest in industrial applications. The most important cases are bubble point calculations (i.e. $\beta = 0$) and dew point calculations (i.e. $\beta = 1$), where, for a given composition $\bar{x} = \bar{x}'$ or $\bar{x} = \bar{x}''$, the determination of the saturation point at a specified p or T requires the calculation of either the temperature or pressure, and the composition of the incipient phase (i.e. the arising equilibrium phase).

When the equilibrium pressure is low to moderate, for which the vapour phase behaves nearly ideally, the individual direct calculation of the mixture bubble and dew points is comparatively straightforward by using ideal solution based methods (where the fugacity coefficients are assumed to be composition independent). At elevated pressures, however, these type of calculations are much more difficult than the flash calculation. The essential problem associated with saturation point calculations is the unknown number of solutions. Moreover, a solution corresponding to a specified set of conditions may not even exist, for instance, for a specified pressure above the maximum pressure or a specified temperature above the maximum temperature at which two phases can coexist.

A further difficulty is the trivial solution (see Sec. 5.4.1) as a false solution to the specified conditions (often resulting from inaccurate initial estimates), since the trivial solution can exist for a wide range of values of the missing primary variable (i.e. T when p is specified, or *p* when *T* is specified). Unfortunately, stability analysis cannot be used in the same manner as for *pT* flash calculations (see Sec. 7.6) to verify that the trivial solution is in fact the "true solution", i.e. that a saturation point at the specified conditions does not exist, since either the temperature or the pressure is unknown[53].

As no entirely satisfactory method exists for "blind" calculations (i.e. without initial estimates) of saturation points at arbitrary mixture conditions, the most reliable procedure for locating all solutions to a given set of specifications may be the stepwise construction of the entire phase boundary as recommended by Michelsen. Two different types of such algorithms enabling a rapid and accurate construction of the complete vapour-liquid phase boundaries for mixtures consisting of any number of components were applied and implemented in this work. The individual points on the phase boundary are calculated using a full Newton-Raphson method, and initial estimates for subsequent calculations are obtained from information generated in earlier steps. The basic principles of these sophisticated algorithms, which were provided by Michelsen [Michelsen (2001), (2004)] and originally developed using cubic equations of state [see Michelsen (1980)], are described in the following sections. The new routines enable the calculation of phase boundaries and lines of constant vapour fraction (i.e. for vapour fractions in the range $0 < \beta < 1$) including the compositions of the incipient or equilibrium phases from the new mixture model for any type of mixture consisting of the considered 18 natural gas components (see Table 4.2). In addition, dew and bubble points including the saturated phase densities can be calculated at user-defined values of temperature or pressure without any user-provided initial estimates. The algorithms are also capable of accurately determining the critical points and extrema in temperature and pressure[54].

Further information on the direct calculation of saturation points and the construction of coexistence curves for two-phase and multi-phase multi-component systems are given by Asselineau *et al.* (1979), Michelsen (1980), (1984), (1985), (1986), (1994), and Michelsen and Mollerup (2004).

7.7.1 Pressure-Based Phase Envelope Algorithm

The pressure-based algorithm for the construction of phase boundaries is initiated by specifying the overall mixture composition $\bar{x}$ and the vapour fraction β, which can equal any

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[53] For a given overall composition, the stability analysis is able to verify that a current pair of *T* and *p* is located in the single-phase region, but this does not exclude the possibility that other values of the missing primary variable can represent a point on the phase boundary or in the two-phase region as well.

[54] Aside from the ordinary mixture behaviour showing one critical point and a maximum in temperature and pressure on its phase boundary, different behaviour without any or more than one critical point as well as minima in temperature and pressure, or more than one temperature maximum can occur (see also Sec. 7.7.3).

value between 0 and 1 (note that $\bar{x}' = \bar{x}$ for $\beta = 0$, $\bar{x}'' = \bar{x}$ for $\beta = 1$, and for $0 < \beta < 1$, $\bar{x}$ is the composition of the overall equilibrium system). For the vector of independent variables[55] $\bar{X}$, it is advantageous to choose the logarithm of the K-factor of each component i, and the logarithm of temperature and pressure, i.e. $X_i = \ln K_i$ (for $i = 1, 2, ..., N$), $X_{N+1} = \ln T$, and $X_{N+2} = \ln p$. These $N+2$ variables are related by the following $N+1$ equations:

$$F_i = \ln \varphi_i(T, p, \bar{x}'') - \ln \varphi_i(T, p, \bar{x}') + \ln K_i = 0, \quad i = 1, 2, ..., N, \tag{7.115}$$

$$F_{N+1} = \sum_{i=1}^{N} (x_i'' - x_i') = 0, \tag{7.116}$$

where the mole fractions in the liquid and vapour phases are given by (see Sec. 5.4.1)

$$x_i' = \frac{x_i}{1 - \beta + \beta K_i} \quad \text{and} \quad x_i'' = \frac{K_i x_i}{1 - \beta + \beta K_i}. \tag{7.117}$$

To complete the set of equations to be solved, an additional equation, namely the specification equation [see also the passage "Formulation of a Set of Equations" in Sec. 5.4.1], is introduced which can be written in the general form[56]:

$$F_{N+2} = X_s - S = 0, \tag{7.118}$$

where the subscript "s" denotes the variable to be specified (this can be any of the $N+2$ chosen variables), and S is the desired value of this variable. Thus, the complete set of $N+2$ equations can be written as

$$\bar{F}(\bar{X}) = \mathbf{0}. \tag{7.119}$$

To solve Eq. (7.119) for the unknown variables by means of a Newton-Raphson procedure, the set of nonlinear equations is linearised by a Taylor series keeping terms only to first order. The correction vector $\Delta\bar{X}$ is then calculated from solving the corresponding linearised set of equations:

$$\boldsymbol{J} \cdot \Delta\bar{X} = -\bar{F}(\bar{X}). \tag{7.120}$$

Similar to the elements H_{ij} of the Hessian matrix required for solving the flash problem by means of a Gibbs free energy minimisation approach (see Sec. 7.6), the elements J_{ij} of the Jacobian matrix $\boldsymbol{J}$ required to solve Eq. (7.120) are determined from the partial derivatives of all functions $\bar{F}(\bar{X})$ with respect to all variables $\bar{X}$ according to

$$J_{ij} = \frac{\partial F_i}{\partial X_j}, \quad \text{for all } i \text{ and } j. \tag{7.121}$$

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[55] For a given vapour fraction and overall mixture composition, temperature (at a specified pressure) or pressure (at a specified temperature), and the K-factors are the dependent variables. But they are the independent variables of the set of equations to be solved.

[56] The specification equation is not fixed to a certain variable. In the pressure-based algorithm, the specified variable that is automatically selected can be $\ln T$, $\ln p$, or $\ln K_i$ of any component i; see the passage "Step Selection and Stepsize Control" in this subsection for further details.

The derivatives of Eq. (7.115) with respect to $\ln T$ and $\ln p$ require the derivatives of $\ln \varphi_i$ with respect to T and p [see Eqs. (7.29) and (7.30)] according to

$$\frac{\partial F_i}{\partial \ln T} = T\left(\phi''_{iT} - \phi'_{iT}\right), \tag{7.122}$$

$$\frac{\partial F_i}{\partial \ln p} = p\left(\phi''_{ip} - \phi'_{ip}\right), \tag{7.123}$$

where

$$\phi_{iT} = \left(\frac{\partial \ln \varphi_i}{\partial T}\right)_{p,\bar{n}} \quad \text{and} \quad \phi_{ip} = \left(\frac{\partial \ln \varphi_i}{\partial p}\right)_{T,\bar{n}}. \tag{7.124}$$

For the derivatives of Eq. (7.115) with respect to $\ln K_j$, the scaled composition derivatives of $\ln \varphi_i$ [see Eq. (7.31)] are required[57]:

$$\frac{\partial F_i}{\partial \ln K_j} = \frac{K_j x_j}{\left(1-\beta+\beta K_j\right)^2}\left[(1-\beta)\,\phi''_{ij} + \beta\,\phi'_{ij}\right] + \delta_{ij}, \tag{7.125}$$

where

$$\phi_{ij} = n\left(\frac{\partial \ln \varphi_i}{\partial n_j}\right)_{T,p}. \tag{7.126}$$

Furthermore, the following equation is obtained for derivatives of the summation of mole fractions [Eq. (7.116)] with respect to $\ln K_j$:

$$\frac{\partial F_{N+1}}{\partial \ln K_j} = \frac{K_j x_j}{\left(1-\beta+\beta K_j\right)^2}, \tag{7.127}$$

and for the specification equation [Eq. (7.118)] follows

$$\frac{\partial F_{N+2}}{\partial X_s} = \delta_{sj}. \tag{7.128}$$

To provide the required thermodynamic property information from the mixture model, the iterative calculation of the saturated phase densities in each iteration step is required since pressure is used as the independent variable.

Constructing the Phase Envelope

The sequence of calculations is initiated using a specification for which convergence is easily obtained and for which reasonable initial estimates can be generated. In the following example, a low pressure bubble point of $p = 0.5$ MPa is specified. Thus, $s = N + 2$ and

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[57] Actually, the derivative of F_i [Eq. (7.115)] with respect to $\ln K_j$ would require the mole fraction derivatives of $\ln \varphi'_i$ and $\ln \varphi''_i$. As mentioned in Sec. 7.3, the scaled derivatives with respect to total moles should be used instead.

$S = \ln 0.5$ [see Eq. (7.118)]. An initial estimate of the bubble point temperature can be calculated by iteratively solving the equation[58]

$$\sum_{i=1}^{N} K_i\, x_i - 1 = 0 \tag{7.129}$$

for T, where the K-factors are obtained from the Wilson K-factor approximation (see also Sec. 5.4.1):

$$\ln K_i = \ln\left(\frac{p_{\mathrm{c},i}}{p}\right) + 5.373\,(1+\omega_i)\left(1-\frac{T_{\mathrm{c},i}}{T}\right). \tag{7.130}$$

Equation (7.129) ensures a unique solution since the K-factors calculated from Eq. (7.130) increase monotonically with temperature. If the temperature is specified, Eq. (7.129) can be explicitly solved for p. The initial saturation point then converges by taking a few steps using a successive substitution approach followed by a partial Newton's method (neglecting composition derivatives) for final convergence.

After the initial point has been generated, subsequent phase envelope points are calculated using a full Newton-Raphson method with initial estimates obtained from the previous points. For this purpose, the sensitivities of the independent variables with respect to the value of the specification S are evaluated by differentiating Eq. (7.119) with respect to S and solving the resulting set of linear equations

$$\frac{\partial \overline{F}}{\partial \overline{X}}\frac{\partial \overline{X}}{\partial S} = -\frac{\partial \overline{F}}{\partial S} \tag{7.131}$$

for the sensitivity vector $\partial \overline{X}/\partial S$. The matrix of coefficients $\partial \overline{F}/\partial \overline{X}$ does not require any extra calculations since it equals the Jacobian matrix $\boldsymbol{J}$ used for solving the system of equations [see Eqs. (7.120) and (7.121)] by means of the Newton-Raphson method. The right hand side vector is easily obtained since only Eq. (7.118) depends on the specification:

$$-\frac{\partial \overline{F}}{\partial S} = (0,0,\ldots,0,1)^{\mathrm{T}}. \tag{7.132}$$

The location of a new point on the phase boundary is then estimated from

$$\overline{X}(S+\Delta S) = \overline{X}(S) + \frac{\partial \overline{X}}{\partial S}\Delta S. \tag{7.133}$$

If, for example, the next point is calculated at a pressure of 1.0 MPa, $\Delta S = \ln 1.0 - \ln 0.5 = \ln 2$, and an initial estimate for $\overline{X}(S+\Delta S)$ can be calculated from Eq. (7.133). For the following points on the phase boundary, a refined generation of initial estimates is used. The information of $\overline{X}$ and its derivatives with respect to S determined at

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[58] Equation (7.129) is obtained at the bubble point ($\beta = 0$), for which $x_i' = x_i$ and $x_i'' = K_i\, x_i' = K_i\, x_i$. When assuming composition-independent fugacity coefficients for an ideal solution approximation, the saturation point calculation reduces to solving this single equation for T or p.

two previous points is used to generate a polynomial expansion for each of the independent variables according to

$$X_i = C_{i,0} + C_{i,1}\,S + C_{i,2}\,S^2 + C_{i,3}\,S^3. \tag{7.134}$$

The approximation by a third degree polynomial enables the calculation of very accurate interpolations of the points on the phase boundary as well as accurate extrapolations for initial estimates for the subsequent points to be calculated.

Step Selection and Stepsize Control

The variable to be specified for generating the entire phase boundary is initially selected as the pressure (see the example above). For the construction of subsequent points, other choices are more convenient due to several reasons as, for example:

- In the vicinity of the critical point, the selection of either the temperature or the pressure as the specified variable may easily lead to the trivial solution, with a subsequent breakdown as a result.
- As pressure increases towards the maximum pressure on the two-phase boundary, the sensitivities increase in magnitude and ultimately become infinite. Consequently, the point of maximum pressure cannot be passed in this manner.

To overcome these difficulties during the sequential construction of the phase boundary, the variable to be specified is automatically selected by the algorithm depending on the magnitude of the largest sensitivity for each variable. Convergence is easier obtained by limiting all elements of the sensitivity vector to a magnitude of about 1, and selecting the most rapidly varying variable for the next step to be specified. In most cases, the automatic selection leads to the selection of $\ln K_i$ for the least volatile or the most volatile component in the mixture. Specifying the (non-zero) value of $\ln K_i$ for component i has the advantage that the risk of converging towards the trivial solution is eliminated. The disadvantage that, in principle, incomparable quantities like pressure and K-factor are to be compared, does not create problems in practice.

The magnitude of the step is determined by the number of iterations used to obtain convergence in the equations at the previous point. A very small number of iterations indicates that the initial estimate is very accurate and that it is permissible to increase the stepsize, whereas much iteration indicates an initial estimate of poor quality requiring a more cautious approach. The iteration at the current point is abandoned in case a potential failure is indicated, and a new attempt is made with a smaller stepsize. The “target iteration count” is set to 3 or 4. One to three iterations lead to an increase in the stepsize and four or more iterations lead to a decrease.

The entire phase envelope can be traced in this manner without problems in passing critical points or the pressure and temperature extrema, which are found from the interpolation polynomials according to Eq. (7.134) based on the calculation of circumjacent points. Interpolated points are usually accurate to $\leq(0.01-0.02)$ K and $\leq(0.001-0.002)$ MPa. To be able to generate the bubble point line and the dew point line in the same sequence, the value of the vapour fraction β is kept fixed when passing the critical point, but the liquid phase now becomes the lighter phase and the vapour phase becomes the heavier phase. Using such an efficient and sophisticated procedure, only about 20 to 30 points with an average of 2 to 4 iterations for each point need to be calculated on average for the construction of the entire (and well-shaped) phase boundary or of lines of constant vapour fraction for mixtures of arbitrary composition.

7.7.2 Volume-Based Phase Envelope Algorithm

A similar procedure as described in the previous section can be pursued by an alternative phase envelope algorithm. Although the basic principles concerning the sequential construction of the complete phase boundary along with the step selection and the stepsize control are identical, the temperature and total volumes of the saturated liquid and saturated vapour phases, i.e. V' and V'', (or rather their logarithms) are chosen as the independent variables instead of temperature and pressure as was done for the pressure-based algorithm (see Sec. 7.7.1). For the $N+3$ independent variables, namely $X_i = \ln K_i$ (for $i = 1, 2, ..., N$), $X_{N+1} = \ln T$, $X_{N+2} = \ln V'$, and $X_{N+3} = \ln V''$, the following set of nonlinear equations can be formulated:

$$F_i = \ln \frac{f_i(T, V'', \bar{x}'')}{n_i''} - \ln \frac{f_i(T, V', \bar{x}')}{n_i'} + \ln K_i = 0, \quad i = 1, 2, ..., N, \tag{7.135}$$

$$F_{N+1} = \sum_{i=1}^{N} (x_i'' - x_i') = 0, \tag{7.136}$$

$$F_{N+2} = -p(T, V'', \bar{x}'') + p(T, V', \bar{x}') = 0, \tag{7.137}$$

$$F_{N+3} = X_s - S = 0. \tag{7.138}$$

The mole fractions in the liquid and vapour phases are given by

$$x_i' = \frac{x_i}{1-\beta+\beta K_i} \quad \text{and} \quad x_i'' = \frac{K_i\, x_i}{1-\beta+\beta K_i}. \tag{7.139}$$

Equation (7.138) is the specification equation enabling the automatic selection of the variable to be specified by the algorithm for the subsequent point. Instead of using the fugacity coefficient, the ratio of the fugacity of component i and its mole number according to Eq. (7.34) is used to set up the equilibrium equations[59]. To be able to additionally determine

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[59] The use of fugacity coefficients does not allow for calculations at negative pressures.

saturation points at specified pressures (e.g. at a user-defined value), the pressure (not its logarithm[60]) is used as an additional variable, i.e. $X_{N+4} = p$, and another equation, namely the difference between the specified pressure and the saturated liquid phase pressure, is added to the above set of equations:

$$F_{N+4} = -p + p(T, V', \bar{x}') = 0. \tag{7.140}$$

To solve the resulting set of $N+4$ equations for the $N+4$ independent variables by means of the Newton-Raphson method, the Jacobian matrix is required. Differentiation of all equations $\bar{F}$ with respect to all independent variables $\bar{X}$ yields the elements J_{ij} of the Jacobian matrix. The elements resulting from the partial derivatives of the equilibrium equations [Eq. (7.135)] with respect to $\ln T$, $\ln V'$, $\ln V''$, p, and $\ln K_j$ are obtained as follows [see also Eqs. (7.36) – (7.38)]:

$$\frac{\partial F_i}{\partial \ln T} = T(\psi''_{iT} - \psi'_{iT}), \quad \frac{\partial F_i}{\partial \ln V'} = -V'\psi'_{iV}, \quad \frac{\partial F_i}{\partial \ln V''} = V''\psi''_{iV}, \quad \frac{\partial F_i}{\partial p} = 0, \tag{7.141}$$

and

$$\frac{\partial F_i}{\partial \ln K_j} = \frac{K_j x_j}{\left(1-\beta+\beta K_j\right)^2}\left[(1-\beta)\psi''_{ij} + \beta\psi'_{ij}\right] + \delta_{ij}, \tag{7.142}$$

where

$$\psi_{iT} = \left(\frac{\partial \ln(f_i/n_i)}{\partial T}\right)_{V,\bar{n}}, \quad \psi_{iV} = \left(\frac{\partial \ln(f_i/n_i)}{\partial V}\right)_{T,\bar{n}}, \quad \text{and} \quad \psi_{ij} = \left(\frac{\partial \ln(f_i/n_i)}{\partial n_j}\right)_{T,V}. \tag{7.143}$$

The single prime indicates that the derivative of the abbreviated property has to be taken for the properties of the (saturated) liquid phase, whereas the double prime refers to the properties of the (saturated) vapour phase. Thus, the abbreviation ψ'_{iV} corresponds to the derivative of $\ln(f'_i/n'_i)$ with respect to V', and ψ''_{iV} is the derivative of $\ln(f''_i/n''_i)$ with respect to V''. Instead of using the non-scaled composition derivatives according to Eq. (7.38) for ψ_{ij}, the respective scaled composition derivatives, i.e. $n\psi_{ij}$, can be used since it is iterated on a mixture where total moles will finally sum to unity. Furthermore, the advantage of a symmetric matrix occurs since $\psi_{ij} = \psi_{ji}$.

For the difference in phase pressures [Eq. (7.137)], the partial derivatives can be expressed as:

$$\frac{\partial F_{N+2}}{\partial \ln T} = T(-\pi''_T + \pi'_T), \quad \frac{\partial F_{N+2}}{\partial \ln V'} = V'\pi'_V, \quad \frac{\partial F_{N+2}}{\partial \ln V''} = -V''\pi''_V, \quad \frac{\partial F_{N+2}}{\partial p} = 0, \tag{7.144}$$

and

$$\frac{\partial F_{N+2}}{\partial \ln K_j} = RT\frac{K_j x_j}{\left(1-\beta+\beta K_j\right)^2}\left[(1-\beta)\psi''_{iV} + \beta\psi'_{iV}\right], \tag{7.145}$$

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[60] For making the pressure specification comparable in the automatic step selection, a scaling factor is used.

where

$$\pi_T = \left(\frac{\partial p}{\partial T}\right)_{V,\bar{n}} \quad \text{and} \quad \pi_V = \left(\frac{\partial p}{\partial V}\right)_{T,\bar{n}} . \tag{7.146}$$

For the additional equation which allows the specification of the pressure [Eq. (7.140)], it follows:

$$\frac{\partial F_{N+4}}{\partial \ln T} = T\pi'_T, \quad \frac{\partial F_{N+4}}{\partial \ln V'} = V'\pi'_V, \quad \frac{\partial F_{N+4}}{\partial \ln V''} = 0, \quad \frac{\partial F_{N+4}}{\partial p} = -1, \tag{7.147}$$

and

$$\frac{\partial F_{N+4}}{\partial \ln K_j} = RT\frac{K_j\, x_j}{\left(1-\beta+\beta K_j\right)^2}\beta\,\psi'_{iV} . \tag{7.148}$$

The non-zero derivatives of F_{N+1} with respect to $\ln K_j$ and of F_{N+3} with respect to the specification variable X_s are basically the same as those required for the pressure-based algorithm [see Eqs. (7.127) and (7.128)]. Aside from the derivatives of $\ln(f_i/n_i)$ with respect to the independent variables, the calculation of pressure and its derivatives with respect to temperature and total volume (V' or V'') is required as evident from Eqs. (7.144) and (7.147) (see also Sec. 7.3). These calculations are straightforward. Since the total phase volumes are used as independent variables, no iterative density calculations are required during the sequential construction of the phase boundary. Note that the partial derivatives of F_i, F_{N+2}, and F_{N+4} with respect to $\ln K_j$ would actually require mole fraction derivatives of $\ln(f'_i/n'_i)$, $\ln(f''_i/n''_i)$, p', and p''. As mentioned before, this is not recommended and the derivatives with respect to total moles (here not scaled by n) are used instead[61]. The derivatives according to Eqs. (7.145) and (7.148) utilise the following identity:

$$\left(\frac{\partial p}{\partial n_i}\right)_{T,V,n_j} = -RT\left(\frac{\partial \ln(f_i/n_i)}{\partial V}\right)_{T,\bar{n}} . \tag{7.149}$$

Aside from the advantage that equations of state for which it is difficult to solve for the correct density, such as multi-fluid mixture models based on multi-parameter equations of state for the considered pure components (see also Sec. 7.8), are easy to handle, using the total phase volumes as independent variables instead of pressure has several further advantages [Michelsen (2005)]:

- Phase envelopes can be continued through unstable branches, where the derivative of pressure with respect to total volume, $\partial p/\partial V$, is positive. Pressure-based algorithms are normally only allowed to choose the outer roots for the density, for which $\partial p/\partial V$ is negative.

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[61] For a normalised mixture, which becomes ultimately the case in phase envelope calculations, the mole numbers finally become mole fractions, but in the differentiation they are treated as independent.

- Problems associated with numerical round-off are less severe. This is particularly pronounced when $\partial p/\partial V$ is small.
- Near critical azeotropes can be handled, which is difficult for numerical and other reasons with pressure-based algorithms.
- Phase envelopes can be followed to negative pressures. Quite often, negative branches are continuations of what is actually a liquid-liquid equilibrium and come back up again (see also Sec. 7.7.3). Therefore, only a single run is necessary to construct the complete phase boundary, whereas the pressure-based algorithm would require separate runs (one for $\beta = 1$, and another one for $\beta = 0$).

The volume-based phase boundary calculations are initiated by specifying the overall mixture composition $\bar{x}$ and the vapour fraction β as for the pressure-based algorithm (see Sec. 7.7.1). To determine the initial point for the sequential construction, the same procedure as for the pressure-based algorithm is used, which requires the algorithm to be supplied with the fugacity coefficients and its temperature derivatives. All subsequent points on the phase boundary are calculated using only the volume-based approach.

7.7.3 Usual and Unusual Phase Envelopes

The following selected examples demonstrate the capabilities of the implemented phase envelope algorithms and show usual and unusual phase behaviours of binary and multi-component mixtures calculated using the new wide-range equation of state for natural gases and other mixtures (GERG-2004).

Figure 7.1 shows a pT plot calculated for the 10-component mixture “NIST2”, representing a typical natural gas mixture containing about 91 mole-% of methane, 3 mole-% of nitrogen, and 4.5 mole-% of ethane (see also Table 7.13). In order to simplify the notation throughout this and the following sections, and the following chapters, all of the concentrations given in percent are in mole-%. In addition to the phase boundary indicated by the solid line (where β equals 1 or 0), three lines of constant vapour fraction[62], namely $\beta = 0.99$ (or $\beta = 0.01$), $\beta = 0.90$ (or $\beta = 0.10$), and $\beta = 0.50$, indicated by the dashed, dot-dashed, and dot-dot-dashed lines, are calculated. All of these lines have the same tangent at the mixture critical point, except for $\beta = 0.50$, which appears similar to a vapour pressure curve of a pure component. A large retrograde region extends from the critical point at 205.19 K and 6.058 MPa to the maximum temperature of 241.16 K and the maximum pressure of 6.748 MPa.

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[62] The calculations were performed with $\beta = 1$, $\beta = 0.99$, and $\beta = 0.90$. The algorithm continues the calculation when passing the critical point, and thus, the lines for $1 - \beta$ are obtained from the same run (see the passages “Constructing the Phase Envelope” and “Step Selection and Stepsize Control” in Sec. 7.7.1). For $\beta = 0.50$, only a single curve, which does not span an area in the pT surface, exists.

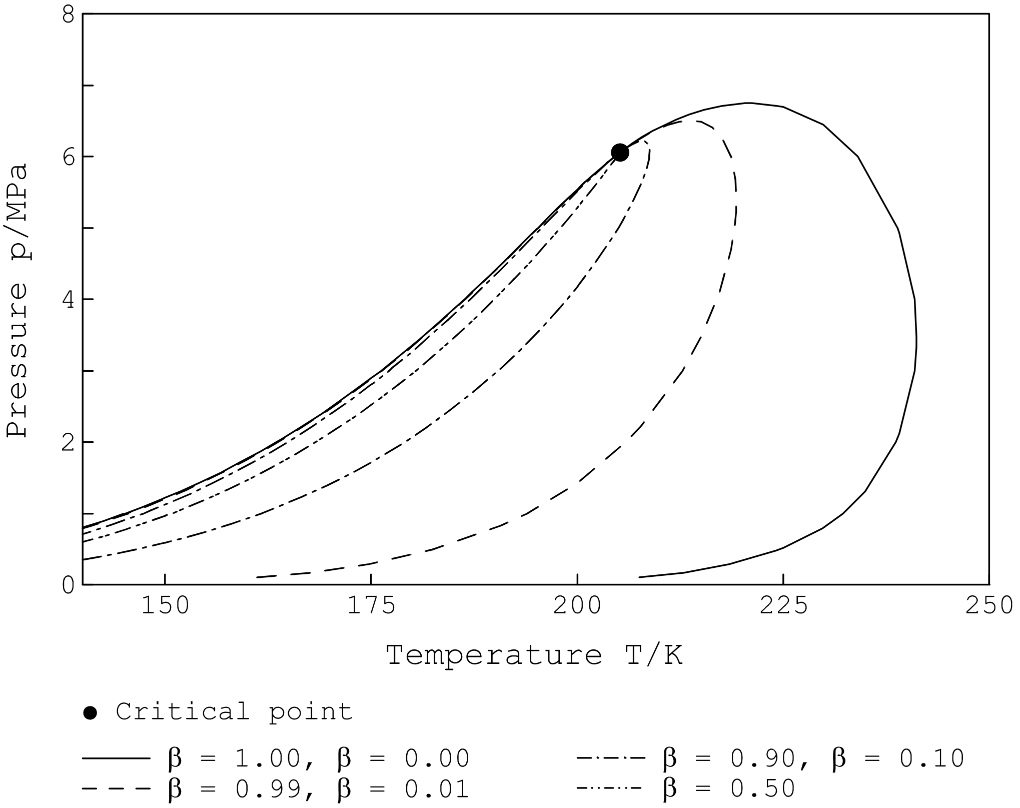

Fig. 7.1 Phase envelope and lines of constant vapour fraction β for the simulated natural gas "NIST2" as calculated from the new equation of state (GERG-2004), Eqs. (7.1) – (7.10); for the mixture composition see Table 7.13. The definition of β is given by Eq. (5.54).

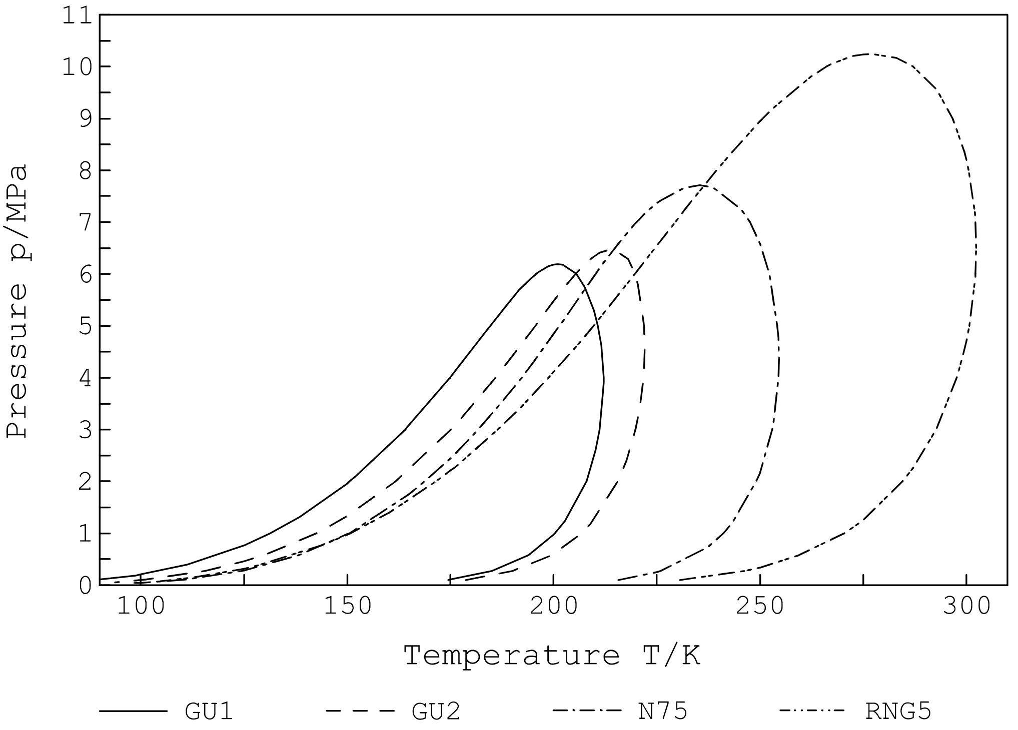

Fig. 7.2 Phase envelopes for the simulated natural gases "GU1" and "GU2", the natural gas "N75", and the simulated rich natural gas mixture "RNG5" as calculated from the new equation of state (GERG-2004), Eqs. (7.1) – (7.10); for the mixture compositions see Table 7.13.

The phase boundaries of different natural gases containing comparatively high fractions of nitrogen ("GU1", solid line), carbon dioxide ("GU2", dashed line), and ethane ("N75", dot-dashed line) are shown in Fig. 7.2. The maxima in temperature and pressure of the respective phase boundaries vary between 212.07 K and 254.55 K, and 6.189 MPa and 7.714 MPa. Natural gases containing comparatively large amounts of ethane, propane, n-butane, and heavier alkanes are characterised by a phase behaviour similar to the one shown for the rich natural gas "RNG5" (dot-dot-dashed line), which has a maximum temperature of 302.38 K and a maximum pressure of 10.246 MPa. The complete molar compositions of all of these selected mixtures are listed in Table 7.13.

Table 7.13 Molar compositions of selected simulated and true natural gases, and a simulated rich natural gas mixture[a]

Component	Mixture composition (mole fractions)					
	NIST2	GU1	GU2	N29	N75	RNG5
Methane	0.906724	0.814410	0.812120	0.757200	0.859284	0.639757
Nitrogen	0.031284	0.134650	0.057020	0.137510	0.009617	0.020246
Carbon dioxide	0.004676	0.009850	0.075850	0.071770	0.015021	0.079923
Ethane	0.045279	0.033000	0.043030	0.025220	0.084563	0.119742
Propane	0.008280	0.006050	0.008950	0.004110	0.023022	0.100102
n-Butane	0.001563	0.001040	0.001520	0.000850	0.004604	0.033144
Isobutane	0.001037	0.001000	0.001510	0.000580	0.002381	–
n-Pentane	0.000443	–	–	0.000470	0.000630	0.005074
Isopentane	0.000321	–	–	0.000260	0.000588	–
n-Hexane	0.000393	–	–	0.000230	0.000228	0.002012
n-Heptane	–	–	–	0.000190	0.000057	–
n-Octane	–	–	–	0.000030	0.000005	–
Helium	–	–	–	0.001580	–	–

[a] See also Table A2.3 of the appendix.

Multi-fluid approximations are not only capable of accurately describing the thermal and caloric properties in the homogeneous gas, liquid, and supercritical regions of multi-component mixtures (see Chap. 8), but also their phase behaviour. Figures 7.3 – 7.6 show pT plots of the phase boundaries of different synthetic natural gas mixtures including the recently measured dew point data of Mørch *et al.* (2006) (see Fig. 7.3), Avila *et al.* (2002a) (see Fig. 7.4), and Jarne *et al.* (2004a) (see Figs. 7.5 and 7.6). The compositions of these mixtures are given in Table 7.14. Aside from the two "dry" natural gases, Jarne *et al.* (2004a) measured dew points of mixtures of these gases with water. Selected results of these measurements are shown in Fig. 7.5 for 0.172% water and in Fig. 7.6 for 0.154% water in addition to the dry mixtures. The comparisons demonstrate that the new mixture model is able to accurately

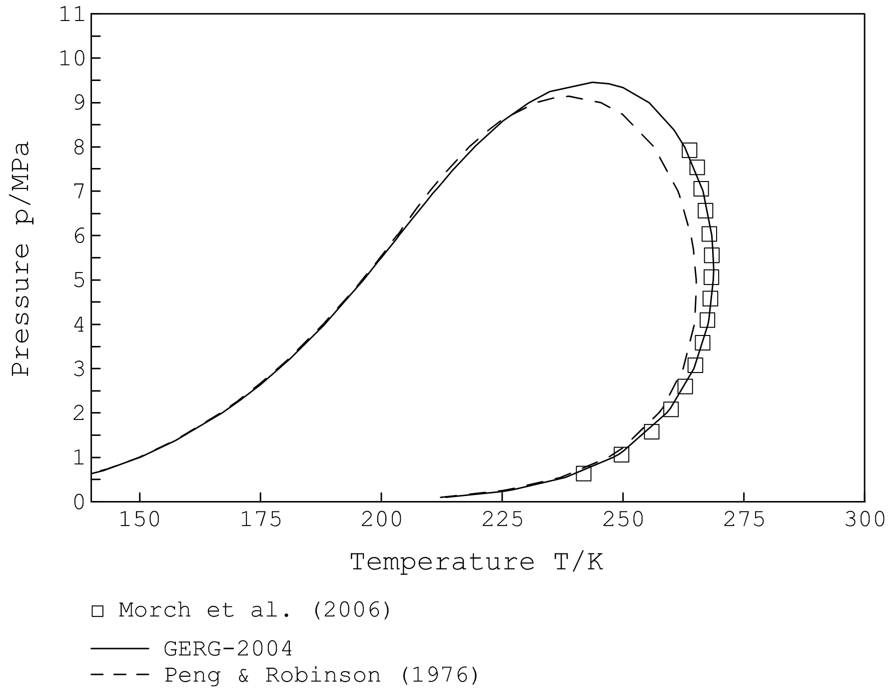

Fig. 7.3 Comparison of the vapour-liquid phase boundary of a four-component hydrocarbon mixture as calculated from the new equation of state (GERG-2004), Eqs. (7.1) – (7.10), and the cubic equation of state of Peng and Robinson (1976) with the corresponding experimental (dew point) data measured by Mørch *et al.* (2006); for the mixture composition see Table 7.14.

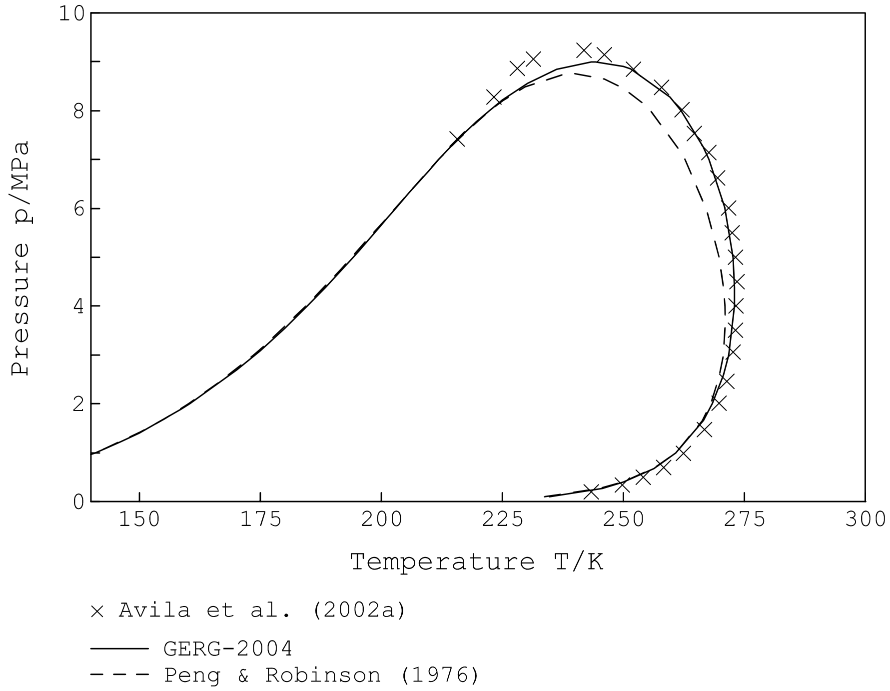

Fig. 7.4 Comparison of the vapour-liquid phase boundary of a 12-component synthetic natural gas as calculated from the new equation of state (GERG-2004), Eqs. (7.1) – (7.10), and the cubic equation of state of Peng and Robinson (1976) with the corresponding experimental (dew point) data measured by Avila *et al.* (2002a); for the mixture composition see Table 7.14.

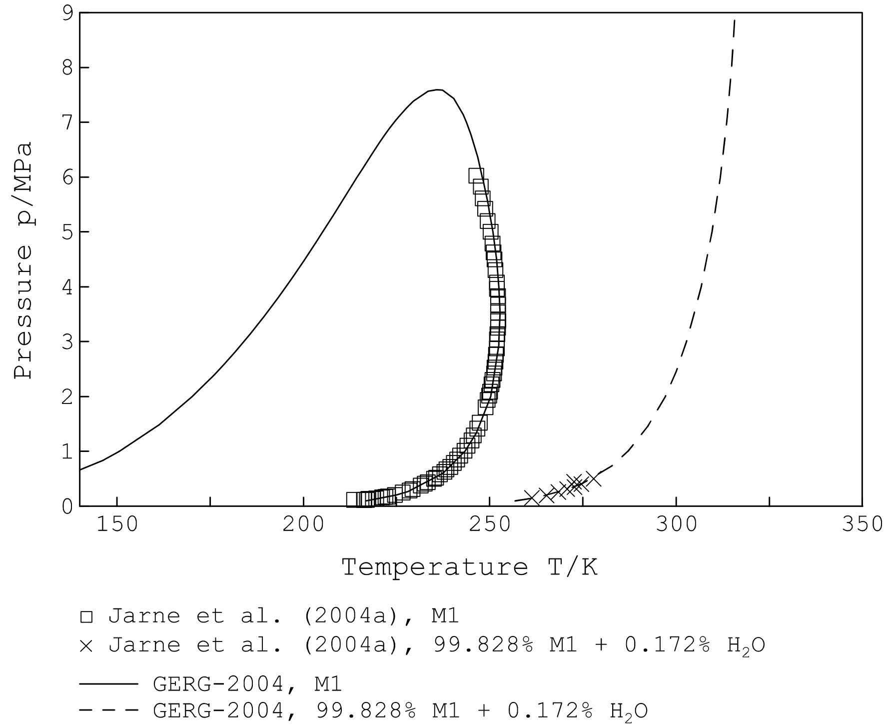

Fig. 7.5 Comparison of the vapour-liquid phase boundaries of a 10-component synthetic natural gas and its mixture with water as calculated from the new equation of state (GERG-2004), Eqs. (7.1) – (7.10), with the corresponding experimental (dew point) data measured by Jarne *et al.* (2004a); for the composition of the dry gas see Table 7.14.

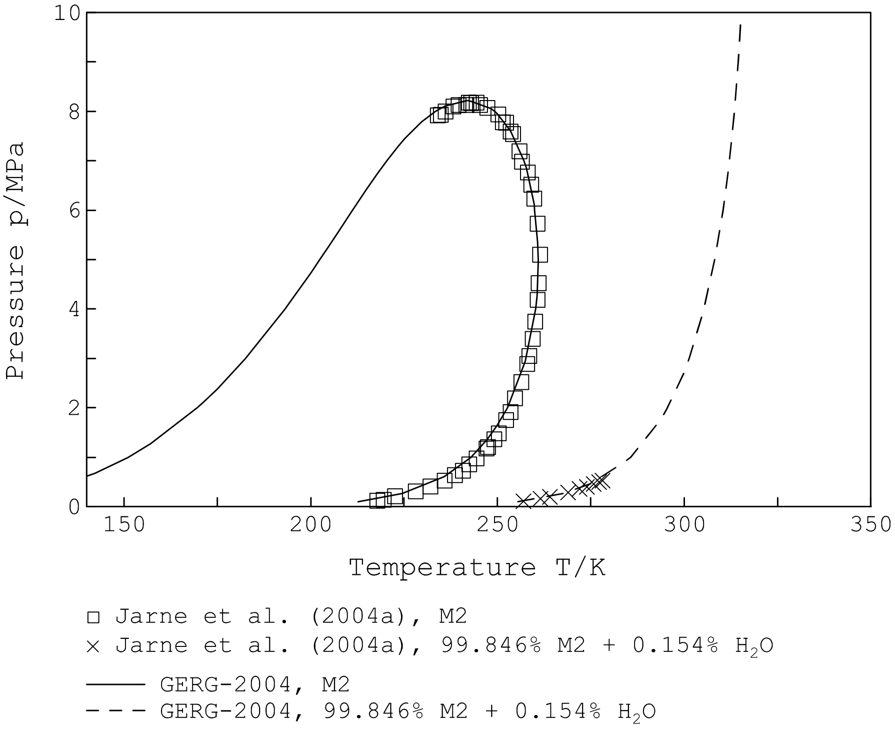

Fig. 7.6 Comparison of the vapour-liquid phase boundaries of a 10-component synthetic natural gas and its mixture with water as calculated from the new equation of state (GERG-2004), Eqs. (7.1) – (7.10), with the corresponding experimental (dew point) data measured by Jarne *et al.* (2004a); for the composition of the dry gas see Table 7.14.

predict the dew point conditions of different types of natural gases, even for mixtures containing, for example, about 26% of carbon dioxide (see Fig. 7.5).

As the phase behaviour of multi-component mixtures is considerably sensitive to errors in the mixture composition, especially when heavier hydrocarbons such as n-hexane or n-octane are involved, one has to be very careful in assessing the data and their representation by equations of state. Even small amounts of secondary or minor components frequently result in a significantly different phase behaviour. Comprehensive investigations have shown that the representation of multi-component dew point data by the GERG-2004 formulation yields, on average, similar or better results than other equations (e.g. cubic equations of state and their modifications) although the new equation of state was not fitted to any multi-component mixture data. Figures 7.3 and 7.4 show that the cubic equation of state of Peng and Robinson (1976) with binary interaction parameters taken from Knapp *et al.* (1982) deviates significantly from the experimental data, especially at elevated pressures. It is also interesting to note that none of the equations used by the different authors for comparisons are able to reproduce the measurements considerably better than the new equation of state, even if they are fitted to the data [see, for example, Mørch *et al.* (2006)].

Table 7.14 Molar compositions of selected synthetic natural gas mixtures

Component	Mixture composition (mole fractions)			
	Mørch *et al.* (2006)	Avila *et al.* (2002a)	Jarne *et al.* (2004a), M1	Jarne *et al.* (2004a), M2
Methane	0.966110	0.833482	0.691140	0.844460
Nitrogen	–	0.056510	0.015590	0.007720
Carbon dioxide	–	0.002840	0.259080	0.017000
Ethane	–	0.075260	0.026200	0.086830
Propane	–	0.020090	0.004230	0.032970
n-Butane	0.014750	0.005200	0.001040	0.005890
Isobutane	0.015270	0.003050	0.001050	0.002930
n-Pentane	0.003850	0.001440	0.000230	0.000860
Isopentane	–	0.001200	0.000340	0.000840
n-Hexane	–	0.000680	0.001100	0.000500
n-Heptane	–	0.000138	–	–
n-Octane	–	0.000110	–	–

Figure 7.7 displays an ordinary binary mixture phase behaviour exemplified for the methane–ethane system at about 15%, 50%, and 85% of ethane including selected experimental data reported by Bloomer *et al.* (1953) and Ellington *et al.* (1959) for the respective three mixture compositions. In addition, the vapour pressure curves of pure methane and pure ethane calculated from the new equation of state are shown along with the complete critical line of the binary system. The measured bubble and dew point pressures of the two authors are

reproduced by the new equation of state with average absolute deviations of less than 1.8% for the complete data set of Bloomer *et al.* (1953) and less than 1.5% for the measurements of Ellington *et al.* (1959), which is in agreement with the targeted uncertainty for the best measured vapour pressure data (see also Chaps. 6 and 8, and Table A2.1).

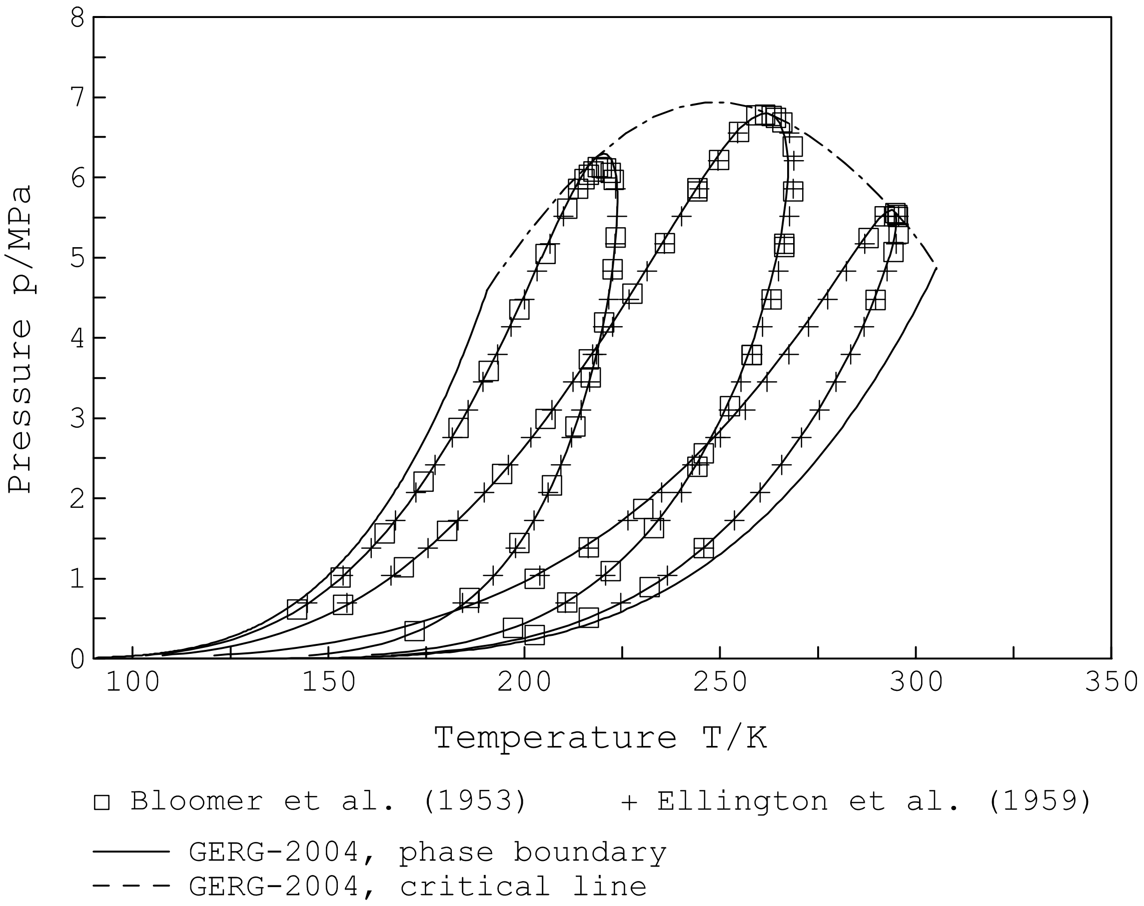

Fig. 7.7 Phase diagram for the methane–ethane binary mixture showing the vapour pressure curves of pure methane and pure ethane, the vapour-liquid phase boundaries at ethane mole fractions of about 15%, 50%, and 85%, and the critical line as calculated from the new equation of state (GERG-2004), Eqs. (7.1) – (7.10); the experimental data for the binary mixture are plotted for comparison.

Aside from this ordinary phase behaviour, other binary mixtures, such as the methane–n-butane system and the methane–helium system, displayed in Figs. 7.8 and 7.9, show a totally different behaviour. Although the methane–n-butane system containing 1% of n-butane (dashed line) shows very common phase behaviour, the mixture containing only 0.1% n-butane (solid line) shows two temperature maxima at 192.18 K and 191.84 K and a temperature minimum at 187.70 K is observed (see Fig. 7.8). Furthermore, two retrograde condensations occur for an isothermal expansion as the critical point is located at 191.64 K and 4.717 MPa, which is below the maximum temperatures. This behaviour is in agreement with the results obtained from other equations of state. Mixtures containing helium are

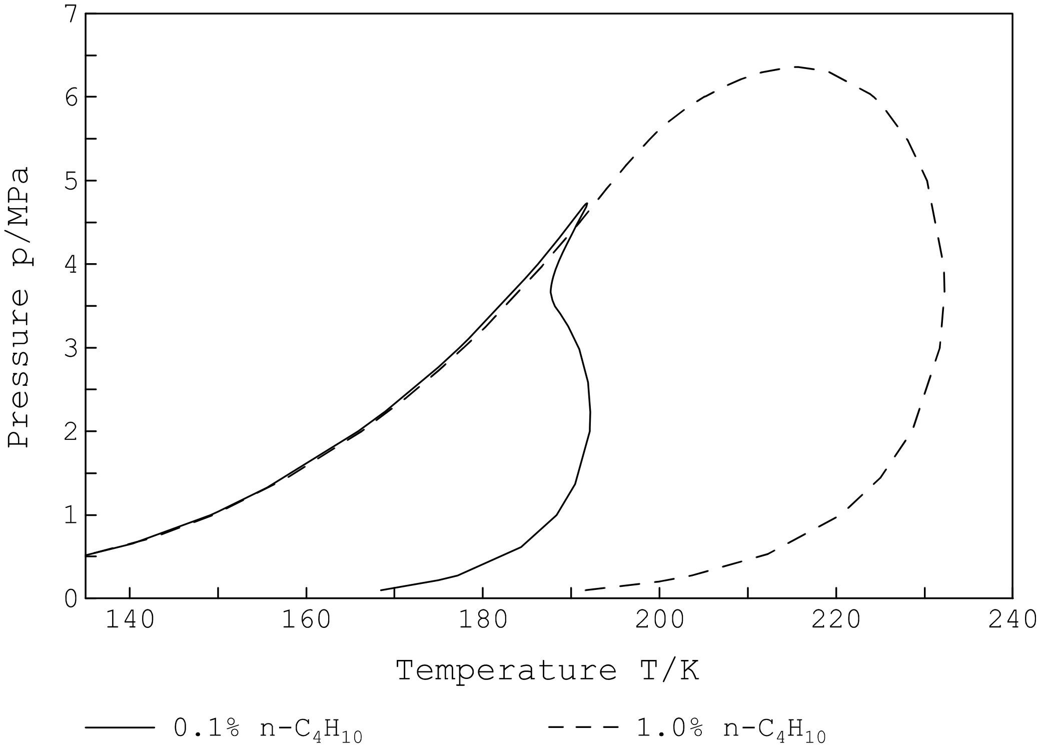

Fig. 7.8 Phase envelopes for the methane–n-butane binary mixture at n-butane mole fractions of 0.1% and 1% as calculated from the new equation of state (GERG-2004), Eqs. (7.1) – (7.10).

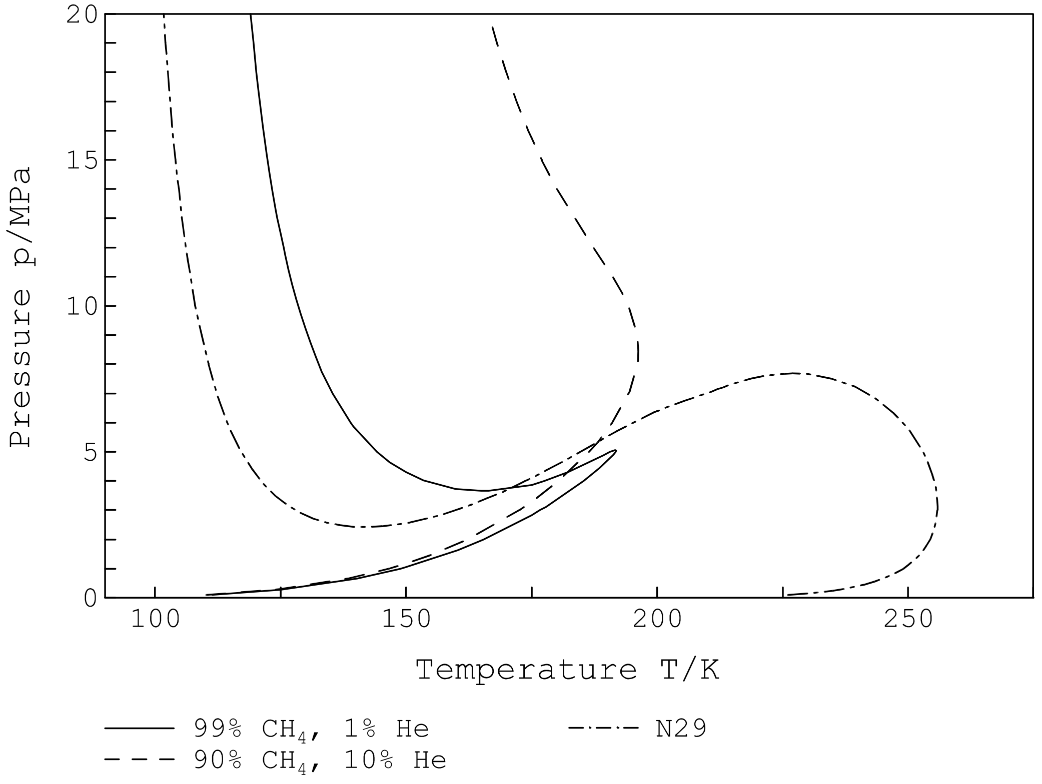

Fig. 7.9 Phase envelopes for the methane–helium binary mixture at helium mole fractions of 1% and 10% and the natural gas “N29” as calculated from the new equation of state (GERG-2004), Eqs. (7.1) – (7.10); for the composition of the natural gas mixture see Table 7.13.

characterised by a bubble point branch extending to infinity, where the phase boundary may have a pressure maximum and minimum similar to the methane–helium system containing 1% helium (solid line), or no pressure extrema such as the mixture containing 10% of helium (dashed line). Natural gases containing a small amount of helium show a phase behaviour similar to the one for the 13-component mixture "N29" (dot-dashed line) shown in Fig. 7.9, revealing that a small helium content has a pronounced influence on the phase behaviour of natural gases and related mixtures at low temperatures[63]; see also Gonzalez and Lee (1968), who illustrated the effect of helium on the phase behaviour of natural gases by measuring dew and bubble points for several simulated natural gas samples. Very similar phase behaviour is observed for hydrocarbon mixtures and natural gases containing hydrogen as compared to those shown in Fig. 7.9.

Frequently, the sequential construction of the phase envelope results in intersecting phase boundaries, similar to the one for the methane–ethane–n-octane ternary mixture shown in Fig. 7.10. This selected mixture consists of 72% methane, 20% ethane, and 8% n-octane. The phase envelope intersects itself in the low temperature region on the bubble point line at about 210.7 K and 5.93 MPa. At this point the coexistence of three phases, where the liquid phase of the overall mixture composition is in equilibrium with an incipient liquid and an incipient vapour phase of different compositions[64], is observed. The intersection part is shown in detail in Fig. 7.11, where the characteristic "swallowtail" pattern is evident. The branch from temperatures below 201 K up to the intersection point represents vapour-liquid equilibrium (with an incipient vapour phase). At approximately 210.7 K, the vapour-liquid equilibrium line crosses the two-phase boundary and becomes unstable (the swallowtail part is of no physical meaning). Following the swallowtail part of the curve, the incipient vapour phase gradually becomes closer and closer to the liquid in composition (the composition of the incipient phase changes continuously along the swallowtail part) until the intersection is reached again, where the incipient phase is now a liquid-like phase. The branch on the phase boundary extending from the three-phase point up to the critical point of the mixture represents liquid-liquid equilibrium. Further investigations will probably reveal a three-phase region extending from the three-phase point similar to the one shown by Michelsen (1986) for

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[63] Due to such a phase behaviour, it is recommended to always initiate the sequential construction of phase boundaries (or lines of constant vapour fraction) from the dew point line, i.e., for $\beta = 1$ (or $\beta \geq 0.5$), for which proper initial estimates are available at low pressures. Initial estimates for a low-temperature bubble point are not easy to generate for mixtures showing a strongly nonideal bubble point behaviour at low temperatures.

[64] The incipient phases are the coexisting equilibrium phases for a specified composition. For instance, on the vapour-liquid dew point line, the saturated vapour phase of a specified (overall) mixture composition is in equilibrium with an incipient liquid phase of different composition. On the vapour-liquid bubble point line, the saturated liquid phase of a specified (overall) mixture composition is in equilibrium with an incipient vapour phase of different composition. At the three-phase point, two incipient phases occur that are all in equilibrium with the specified composition.

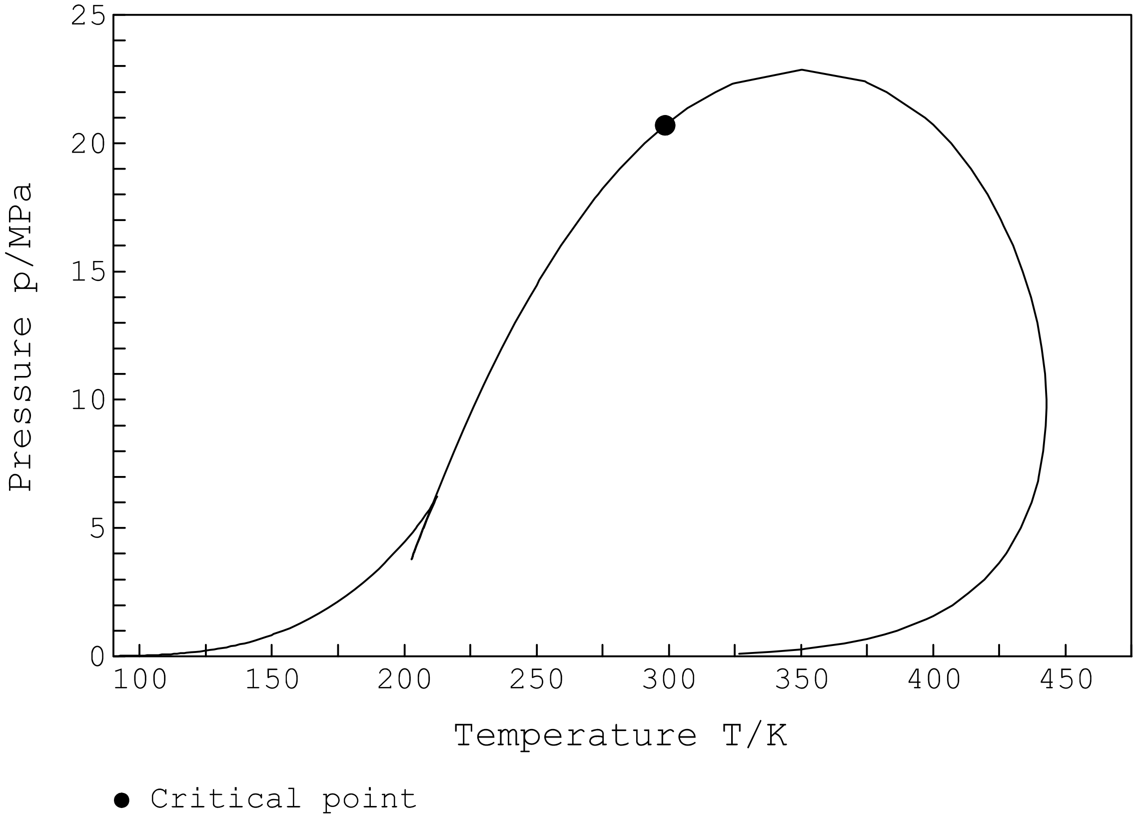

Fig. 7.10 Phase envelope for a ternary hydrocarbon mixture as calculated from the new equation of state (GERG-2004), Eqs. (7.1) – (7.10); the mixture composition is as follows: 72% CH_4, 20% C_2H_6, and 8% $n\text{-}C_8H_{18}$.

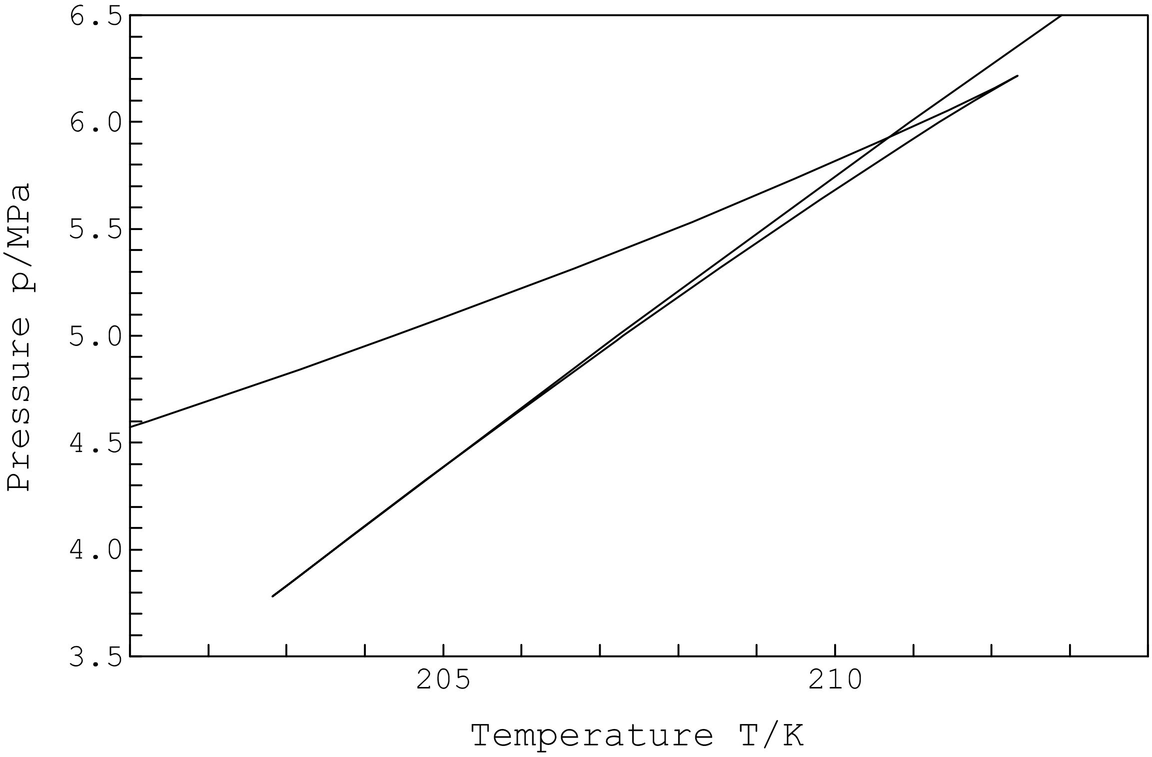

Fig. 7.11 Detail of the phase envelope for the methane–ethane–n-octane ternary mixture shown in Fig. 7.10.

a comparable mixture. The boundaries of this region cannot be calculated with a procedure limited to two coexisting phases. Nevertheless, the point of intersection provides an estimate of the phase compositions for a subsequent three-phase calculation or the construction of the boundaries of the three-phase region. Under certain conditions, the minimum of the swallowtail part can be located at a negative pressure. In such a case, the pressure-based algorithm is not able to construct the complete phase boundary in a single run (see also Sec. 7.7.2).

The principles used for calculating phase boundaries for the two-phase region can easily be extended to enable the calculation of the phase boundaries of three-phase regions (such as a three-phase bubble line where a light and a heavy liquid phase are in equilibrium with an incipient vapour phase, or a vapour-liquid-liquid three-phase boundary where one of the two liquid phases is the incipient phase) by introducing an additional set of K-factors and a phase fraction for the phase split between the two present phases as new variables [see Michelsen (1986) and Pedersen *et al.* (1996)]. This calculation, however, is not as easy to automate as with the two-phase boundary due to numerous additional complicating factors. One being that an initial estimate for the compositions of the two dense phases at liquid-liquid equilibrium is needed (see also Sec. 5.4.2). Even though the two-phase algorithms presented in the previous sections do not allow for quantitative information about the precise location of the three-phase region, it is worthwhile to note that many essential qualitative features of the phase diagram can be estimated purely from the false (unstable) two-phase calculation [see also Michelsen (1986)].

The three-phase behaviour of binary and multi-component mixtures will become an interesting issue when extending the current mixture model by further implementing the natural gas component hydrogen sulphide. Mixtures rich in hydrogen sulphide are of great importance in technical applications dealing with acid gases and raw natural gases (see also Chap. 9) and are capable of three-phase equilibrium [e.g. Ng *et al.* (1985); see also Heidemann and Khalil (1980) and Michelsen (1980), (1986)].

7.8 Development of a Proper Density Solver

As mentioned in the previous sections, the correct solution of the density from the mixture model developed here or any other equation of state for mixtures at a specified mixture temperature, pressure, and composition is extremely important for a successful implementation of such property calculation algorithms. The roots of cubic equations of state such as the equation of Peng and Robinson (1976) [see Sec. 2.1.2], a simple cubic polynomial, can be calculated explicitly using the cubic formula. The total number of roots is explicitly given by this closed-form solution with three as the maximum number of solutions. Furthermore, in the case of three density roots, the middle root is always the one corresponding to the largest value of the Gibbs free energy of all roots for the given mixture conditions (T, p, and $\bar{x}$). Thus, such an "unstable" root cannot only be identified by the fact that it is the middle root at which the derivative of pressure with respect to density, $\partial p/\partial \rho$, is negative (or $\partial p/\partial V$ is positive), but alternatively from the fact that it corresponds to a higher Gibbs free energy compared to the outer solutions. Since no (auxiliary) equations are available for accurately describing the saturated phase densities of any type of mixture, these techniques can be used for stability analysis procedures, phase equilibrium calculations, etc.

Using multi-parameter equations of state such as that used here requires an iterative calculation for the density at the specified mixture conditions. Unfortunately, for such empirical mixture models, the number of density solutions is not limited to three and, furthermore, not known explicitly[65]. A further complicating factor is that physically wrong solutions (resulting from multiple loops) do not necessarily correspond to higher values of the Gibbs free energy. Moreover, there are physically wrong solutions for which $\partial p/\partial \rho$ is positive (see also Fig. 7.12). Nevertheless, in the extended fluid region, only this type of an empirical equation of state, being a single and thus completely consistent model for the gas and liquid phases, the supercritical region, and the phase equilibrium, is able to represent state-of-the-art data for thermal and caloric properties of binary and multi-component mixtures within their experimental uncertainty.

As an example, the pressure-density plot given in Fig. 7.12 shows three isotherms for different mixture compositions calculated from the new mixture model at the same temperature of 200 K. The isotherm represented by the solid line corresponds to the (overall) composition of the mixture NIST2, which is a 10-component typical natural gas mixture (see also Table 7.13). The isotherm has a monotonically increasing shape and only one single density solution exists for any value of pressure. At a specified pressure of 4.5 MPa, the density amounts to $5.27\ \mathrm{mol \cdot dm^{-3}}$ and the molar Gibbs free energy of this particular point equals $4322.44\ \mathrm{J \cdot mol^{-1}}$. The stability condition derived in Sec. 7.5.1 is, however, not

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[65] The multiple density solutions result from the characteristics of the accurate multi-parameter pure substance equations of state (see Chap. 4) in the two-phase region. These equations form the basis of the multi-fluid mixture model. Additionally, the departure functions developed for some of the binary mixtures contribute to this behaviour to some extent. As mentioned in Sec. 4.6, Lemmon and Jacobsen (2005) developed a functional form enabling the elimination of such undesirable characteristics of modern multi-parameter pure substance equations of state and presented an equation of state for the pure fluid pentafluoroethane which exhibits a more fundamentally consistent behaviour in the two-phase region. Whether such a functional form also enables the highly accurate description of the properties of pure substances similar to that achieved by reference equations of state still needs to be investigated. It is furthermore not known whether multi-fluid mixture models based on such equations of state are able to accurately describe the thermodynamic properties of mixtures with the same quality as, for example, the new mixture model. As experienced in this work, the multiple density solutions can be handled in a quite efficient and reliable way, without any problems concerning the calculation of thermodynamic properties for the various types of mixtures investigated in this work.

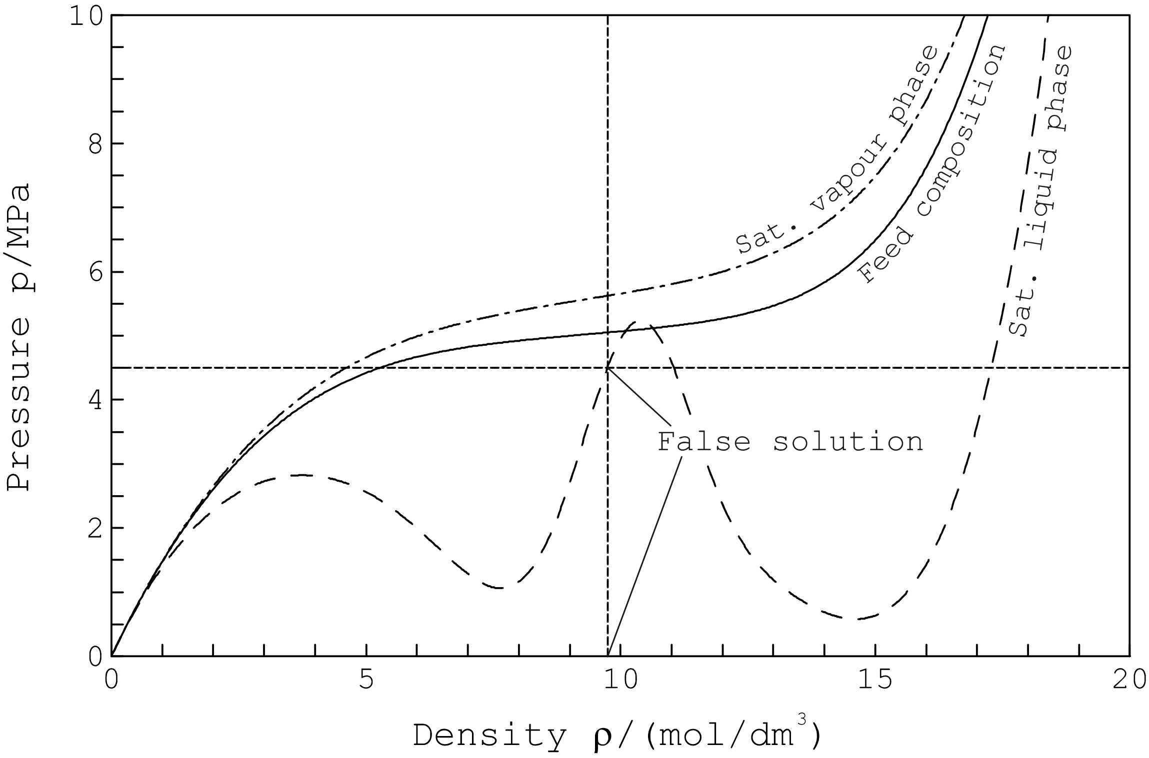

Fig. 7.12 Pressure-density diagram showing three isotherms for different mixture compositions calculated from the new mixture model at a temperature of 200 K. The isotherm represented by the solid line corresponds to the (overall) composition of the simulated natural gas "NIST2" (see Table 7.13). The isotherm indicated by the long-dashed line corresponds to the composition of the saturated liquid phase, and the dot-dashed line represents the isotherm for the composition of the saturated vapour phase, determined from a pT flash calculation for the overall mixture composition at a pressure of 4.5 MPa.

satisfied at this point and the stability analysis performed for the given mixture condition reveals a stable system for a vapour-liquid phase split at a given temperature, pressure, and overall mixture composition. The isotherm indicated by the long-dashed line corresponds to the liquid phase composition (rich in ethane, propane, and heavier alkanes) and the dot-dashed line represents the isotherm for the vapour phase composition (rich in methane) in equilibrium with the liquid phase determined from the flash calculation for the overall feed composition of the mixture. The molar Gibbs free energy of the resulting equilibrium system amounts to 4305.74 $\mathrm{J \cdot mol^{-1}}$ (which is lower than G of the unstable feed) calculated as the sum of the total Gibbs free energies of the two phases[66]. Although the dot-dashed isotherm shows a similar shape as compared to the isotherm of the feed composition, the one for the liquid phase composition shows the characteristic multiple loops. This is only one example of possible behaviour of a mixture at equilibrium. For instance, all of the isotherms for the feed

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[66] Note that the molar Gibbs free energy g of the overall equilibrium system is given by the sum of the molar Gibbs free energies g' and g'' of the equilibrium phases according to $g = (1-\beta)g' + \beta g''$. In the example, β = 0.853567, g' = 2921.08 $\mathrm{J \cdot mol^{-1}}$, and g'' = 4543.28 $\mathrm{J \cdot mol^{-1}}$ at saturated phase densities of 17.28 $\mathrm{mol \cdot dm^{-3}}$ and 4.61 $\mathrm{mol \cdot dm^{-3}}$.

and equilibrium compositions can show a continuously increasing shape or all can exhibit multiple loops with the possibility for very large positive or negative values for pressure. Under certain mixture conditions several other circumstances have to be taken into account as explained below.

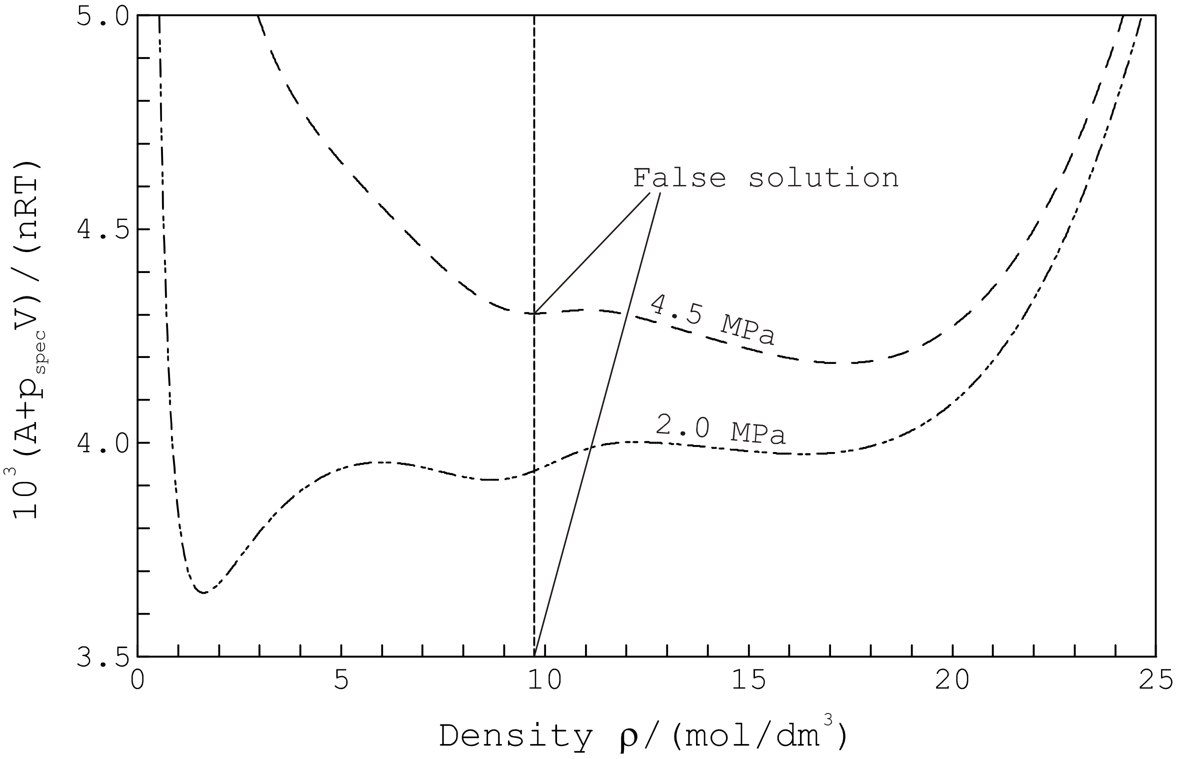

Fig. 7.13 Plot of the function given by Eq. (7.150) as calculated from the new mixture model for the composition of the saturated liquid phase of the example shown in Fig. 7.12 at pressures of 4.5 MPa (long-dashed line) and 2.0 MPa (dot-dot-dashed line), and at a temperature of 200 K.

When multiple loops occur, one of the outer roots might be a false (physically wrong) solution as shown in Fig. 7.12 for the isotherm corresponding to the liquid phase composition for a density value of $9.74\ \mathrm{mol\cdot dm^{-3}}$. The calculation of the Gibbs free energy of the outer solutions is, in general, of no help here, as the Gibbs free energy of the false solution might be lower than the one for the correct solution. In this case, the solution at the highest density is indeed the root with the lowest Gibbs free energy (see also Fig. 7.13). The limiting densities are those obtained at the outer local extrema of the pressure function. The valid density solutions are located below the outer local maximum of p for a gas-like root, and above the outer local minimum of p for a liquid-like root. Thus, only one solution is valid for the isotherm of the liquid-like composition shown in Fig. 7.12.

Assuming a pressure of 2.0 MPa for this isotherm, there are five solutions, and two outer "real" solutions exist. In this example, the outer gas-like root has a lower Gibbs free energy than the other solutions, but the middle root has a lower Gibbs free energy than the outer liquid-like root. This is shown in the plot of the function

$$q = \left(A + p_{\text{spec}} V\right) \big/ (nRT) \tag{7.150}$$

versus density in Fig. 7.13 calculated from the new mixture model for the liquid phase composition in the example shown in Fig. 7.12 at specified pressures p_{spec} of 4.5 MPa (long-dashed line) and 2.0 MPa (dot-dot-dashed line), and $T = T_{\text{spec}} = 200$ K. For such a formulation, the density roots of the equation of state are found at the local extrema of Eq. (7.150) in case of multiple solutions[67]. This enables the development of a density solver based on a minimisation procedure where the total volume V is chosen as the independent variable. The first derivative of this function with respect to total volume [i.e. the gradient of the objective function, Eq. (7.150)] is zero at the stationary points, and the second derivative equals $-\partial p/\partial V$ (divided by nRT), which is positive at the local minima and negative at the local maxima. The local maxima always indicate unstable density solutions, whereas the outer local minima correspond to "real" solutions when no points of inflexion are found at densities below the lowest root and above the highest root. Equation (7.150) equals the reduced (molar) Gibbs free energy $G/(nRT)$ at their local extrema. The points of inflexion can be determined by minimising (or maximising) $\partial q/\partial V$ in the vicinity of the local minima of Eq. (7.150). The use of a minimisation procedure to solve the equation of state for the proper density as described above generally gives additional safety as compared to the traditional root finding algorithms used in this work, but still requires a search for the (valid) solution with the minimum of the objective function.

The following cases should usually be considered when calculating the density for a specified mixture temperature, pressure, and molar composition:

- Only one density root exists. This is the common case for many mixture conditions and requires no additional effort. Note that a single solution does not imply that the system is stable in terms of a homogeneous mixture (the same is valid for all other cases).
- Multiple roots exist, and two outer "real" roots were determined. The root that corresponds to the lower Gibbs free energy is taken since this is the most "promising" solution (but should not be confused with a stability analysis which determines whether the mixture is stable or unstable at the specified conditions). For (pressure-based) phase envelope calculations, however, the algorithm must be supplied with either the vapour-like or liquid-like solution even though this might not be the one with the lowest Gibbs free energy. The selection of an "unstable" root which is closest to the root of the previous step (of the stepwise phase envelope construction) often allows calculations through an unstable part of the phase diagram (see Figs. 7.10 and 7.11). Choosing the "stable" root itself

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[67] The existence of only one density solution is the equivalent of the existence of only one minimum of Eq. (7.150).

(corresponding to the lowest Gibbs free energy) could imply that the calculation is unable to proceed.

- Multiple roots exist, and two outer roots were determined. The outer local extrema of the pressure function testify that one of these roots is a physically wrong solution resulting from the multiple loops. The one "real" root is taken as the solution.

Tracing the isotherm for the roots of $-p+p_{\text{spec}}$ and local extrema in p starting from a very low and a very high density is a safe but not very efficient method for deciding whether an iterated density corresponds to a physically reasonable solution. In this work, the density solutions explicitly obtained from the cubic equation of state of Peng and Robinson (1976) are used as initial estimates for the iterative calculation and the number of solutions obtained from the cubic formula are taken as a "hint" of the number of "real" roots that have to be solved from the multi-fluid mixture model. In general, it is very likely that only one correct solution will exist for the multi-fluid mixture model if the cubic solution reveals only one solution. Nevertheless, as the cubic root might deviate significantly, i.e. ±(5 – 8)% for gas-like densities and ±(10 – 15)% for liquid-like densities, from the solution obtained from the multi-fluid mixture model (see also Sec. 2.1.2 and Chap. 8), the iteration has to be controlled at least for unstable branches where $\partial p/\partial \rho$ is negative. If the density solver fails to find a density for some reason, the property interface switches to a subsequent root checker which analyses $\partial p/\partial \rho$ along the isotherm starting from a very low density and from a very high density. The reciprocal of the molar co-volume b [see Eq. (2.3)], which is available from the cubic solution at the current mixture composition, is a good upper boundary for the calculations at the higher densities. If two density solutions are found (the maximum number of solutions is two because the search is started from the outer limits of the isotherm), they should be analysed and the one with the lowest Gibbs free energy or the solution demanded by the property calculation algorithm will be chosen.

7.9 Minimisation (or Maximisation) of Helmholtz Free Energy Based Flash Formulations

As described in Secs. 7.5.1 and 7.6, the algorithms used for stability analysis and pT flash calculations are based on the minimisation of the Gibbs free energy. The importance of G derives from the fact that its natural variables are temperature, pressure, and composition, which are the variables most accessible to measure and control in the laboratory. Moreover, these are the independent variables favoured by engineers in the design of chemical processes. Many models based on the excess Gibbs free energy have been developed, which are frequently used along with simple equations of state in hybrid models to describe the phase equilibrium of mixtures (see also Chap. 2 and Sec. 7.4). As described in the previous section, the use of algorithms based on the minimisation of the Gibbs free energy requires, however, the (iterative) calculation of the density from equations of state for mixtures for the given set of values for T, p, and $\bar{x}$ (or $\bar{n}$). Although this can be handled in a quite efficient and reliable way, algorithms based on the minimisation of flash formulations using the Helmholtz free energy A (depending on its natural variables temperature, total volume, and composition) are advantageous in itself for critical point calculations and in connection with state-of-the-art multi-fluid mixture models explicit in the reduced Helmholtz free energy, for which it is difficult to solve for the correct density (see Sec. 7.8). For this, the traditional calculation of thermodynamic properties at a specified temperature, pressure, and composition is abandoned in favour of a calculation at a specified temperature, total volume, and composition (see also Sec. 7.7.2).

As mentioned in Sec. 5.4.4, all of the flash calculations for the different specifications listed in Table 5.4 can be formulated as minimisation (or maximisation) problems using the Helmholtz free energy as the core function as will be briefly described in the following subsections. For simplicity, a feed of $n = 1$ mole of composition $\bar{x}$ is considered in all cases.

7.9.1 Solution to the *pT* Flash Using Volume-Based Variables

The pT flash calculation can also be carried out using unconstrained minimisation with "volume-based" thermodynamics by formulating the objective function

$$Q = A + p_{\text{spec}}\,V, \tag{7.151}$$

where the total phase volumes V' and V'', and the vapour flows $\bar{v}$ are chosen as the independent variables[68] [see Michelsen (1999) and Nagarajan *et al.* (1991), who primarily proposed and investigated the volume-based pT flash]. Equation (7.151) satisfies the equilibrium conditions at its stationary point according to:

$$\frac{\partial Q}{\partial v_i} = \mu_i'' - \mu_i', \quad i = 1, 2, ..., N, \tag{7.152}$$

$$\frac{\partial Q}{\partial V''} = -p'' + p_{\text{spec}}, \tag{7.153}$$

$$\frac{\partial Q}{\partial V'} = -p' + p_{\text{spec}}, \tag{7.154}$$

and in addition, the second derivatives of Q with respect to V', V'', and v_i have the correct sign (> 0) as is evident from the following relations:

$$\frac{\partial^2 Q}{\partial v_i^2} = \frac{\partial \mu_i''}{\partial v_i} + \frac{\partial \mu_i'}{\partial l_i} > 0, \quad \frac{\partial^2 Q}{\partial V''^2} = -\frac{\partial p''}{\partial V''} > 0, \quad \frac{\partial^2 Q}{\partial V'^2} = -\frac{\partial p'}{\partial V'} > 0. \tag{7.155}$$

Thus, the solution to the pT flash problem is found at the minimum of Q [Eq. (7.151)].

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[68] The liquid flows were eliminated since $\bar{l} = \bar{x} - \bar{v}$ for the specified overall mixture composition $\bar{x}$ (see also Sec. 5.4.4).

Note that Eq. (7.152) can also be written in terms of fugacity coefficients [see Eq. (7.27)]

$$\frac{\partial Q}{\partial v_i} = RT\left[\ln\frac{v_i}{\beta} + \ln p'' + \ln\varphi_i'' - \ln\frac{l_i}{1-\beta} - \ln p' - \ln\varphi_i'\right], \quad i = 1, 2, ..., N, \tag{7.156}$$

or in terms of the component fugacity over mole number ratios [see Eq. (7.34)] according to

$$\frac{\partial Q}{\partial v_i} = RT\left[\ln(f_i''/n_i'') - \ln(f_i'/n_i') + \ln v_i - \ln l_i\right], \quad i = 1, 2, ..., N. \tag{7.157}$$

Aside from the gradient vector of Q, the Hessian matrix, which comprises all second derivatives of Q with respect to all independent variables, is required for the minimisation [see also Eqs. (7.104) and (7.105)]. Since the total phase volumes are used as independent variables, Eq. (7.157) is advantageous, and the derivatives of the logarithm of the component fugacity over mole number ratios with respect to V', V'', and v_i are given by or can easily be obtained from the respective derivatives derived in Sec. 7.3 [see Eqs. (7.37) and (7.38)]. Nevertheless, Eq. (7.156) can also be used, but this requires the derivatives of $\ln\varphi_i$ with respect to total volume or with respect to mole numbers at constant total volume (not at constant pressure), which can, however, be easily derived from Eqs. (7.30) and (7.31) and the derivatives of pressure with respect to total volume and with respect to mole numbers according to Eqs. (7.62) and (7.63). The same pressure derivatives are required for the derivatives of Eqs. (7.153) and (7.154) with respect to V', V'', and v_i.

7.9.2 Solution to the *TV* Flash Using Volume-Based Variables

The *TV* flash can be solved as an unconstrained minimisation of the Helmholtz free energy (i.e. $Q = A$). For the two-phase *TV* flash, the desired molar flows $\bar{v}$ and $\bar{l}$ are found as the solution to

$$\min A\left(T, V'', V', \bar{v}, \bar{l}\right) \tag{7.158}$$

subject to the constraints

$$T = T_{\text{spec}}, \quad V' + V'' = V = V_{\text{spec}}, \quad \text{and} \quad \bar{l} + \bar{v} = \bar{x}. \tag{7.159}$$

With the elimination of the liquid flows and $V' = V_{\text{spec}} - V''$, Eq. (7.158) is reduced to the unconstrained minimisation problem

$$\min A\left(T_{\text{spec}}, V'', V_{\text{spec}} - V'', \bar{v}, \bar{x} - \bar{v}\right) \tag{7.160}$$

with V'' and $\bar{v}$ as the chosen independent variables. Equation (7.160) satisfies the equilibrium conditions at its minimum since the derivatives of A with respect to the independent variables (i.e. the gradient vector) are given by

$$\frac{\partial A}{\partial V''} = -p'' + p' \quad \text{and} \quad \frac{\partial A}{\partial v_i} = \mu_i'' - \mu_i', \quad i = 1, 2, ..., N. \tag{7.161}$$

7.9.3 Solution to Other Flash Specifications Using Volume-Based Variables

Q-functions for the remaining specifications (see Table 5.4) with the Helmholtz free energy as the core function, i.e. based on temperature, total volume, and composition as the independent variables, can be formulated similar to Eq. (7.151) as outlined by Michelsen (1999). Table 7.15 summarises such Q-functions corresponding to the different flash specifications listed in Table 5.4 using A or G as the core functions. Note that only for the specifications of T and p, and of T and V, the solution corresponds to a minimum of Q.

Table 7.15 Q-functions for state function based specifications

Specification	Q-function using A	Q-function using G
$p, T, \bar{n}$	$A + p_{\text{spec}} V$	G
$p, H, \bar{n}$	$(A + p_{\text{spec}} V - H_{\text{spec}})/T$	$(G - H_{\text{spec}})/T$
$p, S, \bar{n}$	$A + T S_{\text{spec}} + p_{\text{spec}} V$	$G + T S_{\text{spec}}$
$T, V, \bar{n}$	A	$G - p V_{\text{spec}}$
$U, V, \bar{n}$	$(A - U_{\text{spec}})/T$	$(G - U_{\text{spec}} - p V_{\text{spec}})/T$
$S, V, \bar{n}$	$A + T S_{\text{spec}}$	$G + T S_{\text{spec}} - p V_{\text{spec}}$

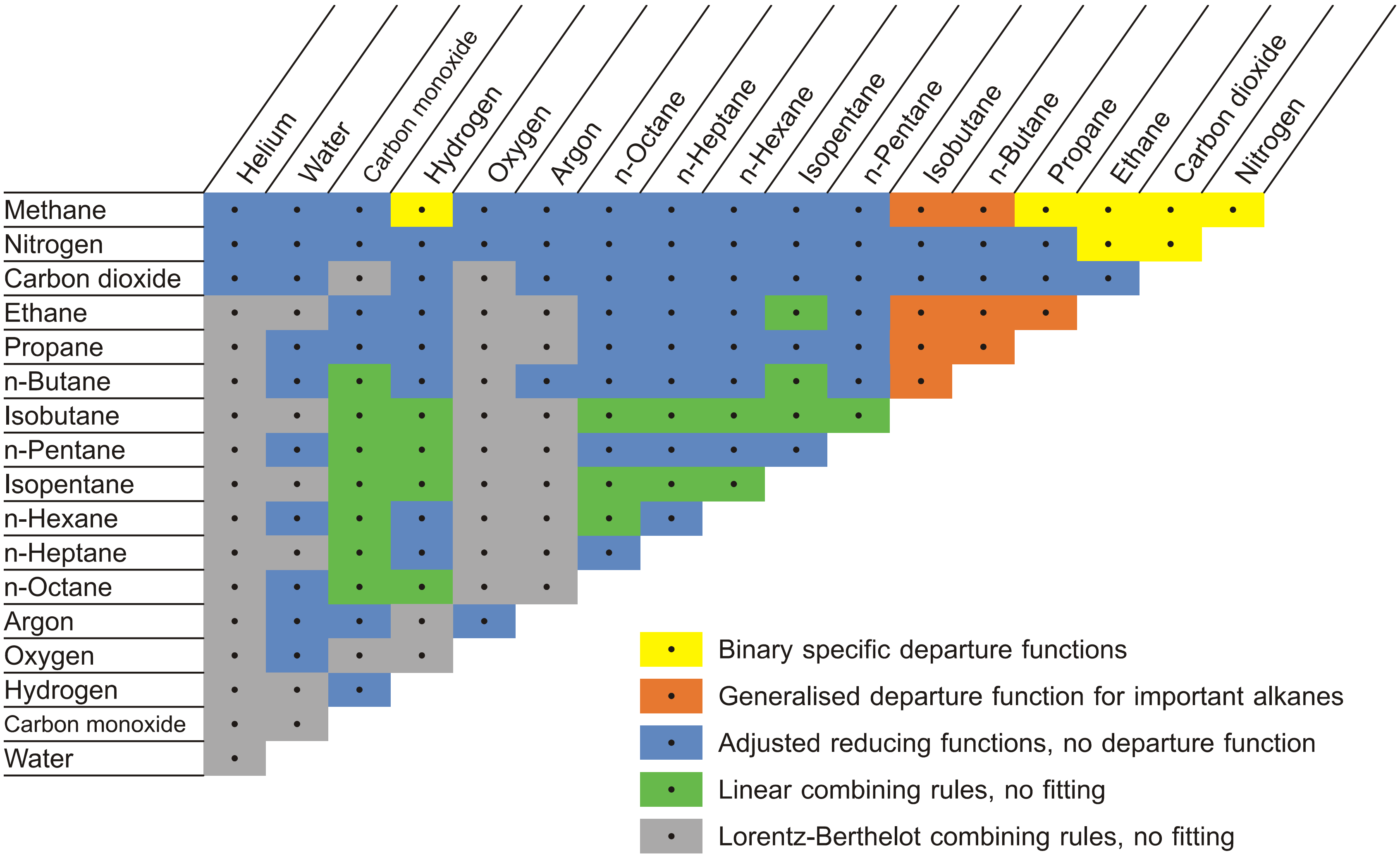
For those Q-functions where the solution does not correspond to a minimum of Q (but to a saddle point), Michelsen (1999) presented a formal framework using G as the core function which enables the formulation of the phase equilibrium problems as unconstrained maximisation problems, combined with an inner loop minimisation of the Gibbs free energy at the current T and p, i.e. an inner loop pT flash calculation. As an alternative, a Newton-Raphson based approach, capable of handling all of the specifications listed in Table 7.15 with a common Jacobian matrix, was derived for G enabling the simultaneous convergence of all independent variables (with presumed good initial estimates available).

With regard to modern mixture models based on multi-fluid approximations explicit in the reduced Helmholtz free energy, and aside from the Gibbs free energy based approaches, the development of similar procedures using the Helmholtz free energy as the core function seems to be worthwhile to solve all of the above listed calculation problems. The basis for such formulations are derivatives of $\ln \varphi_i$, $\ln(f_i/n_i)$, or μ_i with respect to the independent variables. These were derived from α by means of the systematic approach presented in Sec. 7.3. The interesting part of the development of Helmholtz free energy based flash algorithms concerning multi-fluid mixture models seems to be the influence of the special characteristics of α on the minimisation process and how false solutions, which might result from this, can be avoided by a proper solution strategy.

7.10 Development of the Different Binary Equations of State of the New Mixture Model

The new equation of state for the thermodynamic properties of natural gases, similar gases, and other mixtures, Eqs. (7.1) – (7.10), describes multi-component mixtures based only on formulations developed for the binary mixtures of the components in the model. Figure 7.14 gives an overview of the 153 binary combinations that result from the 18 natural gas components studied in this work (see Table 4.2). This figure shows that most of the binary systems are taken into account by only using adjusted reducing functions for density and temperature [see Eqs. (7.9) and (7.10)]. The binary mixtures for which in addition binary specific departure functions or a generalised departure function were developed are listed separately in Table 7.16. Binary mixtures characterised by poor data, neither allowing for the development of a departure function nor the fitting of the parameters of the reducing functions, are taken into account by setting the parameters of the reducing functions to unity or using linear combining rules (instead of the combining rules of Lorentz and Berthelot) for the critical parameters of the respective pure components as described in Sec. 5.2. The linear combining rules are used for binary mixtures composed of secondary alkanes, and for binary mixtures consisting of secondary alkanes and either hydrogen or carbon monoxide as the second component as displayed in Fig. 7.14. The remaining subsystems again characterised by poor data are taken into account by using the combining rules of Lorentz and Berthelot (which is the default when setting the parameters of the reducing functions to unity). The use of different combining rules is immaterial when data are used to adjust the binary parameters of the reducing functions (see Sec. 5.2).

For the binary mixtures consisting of methane with the primary natural gas components nitrogen, carbon dioxide, ethane, and propane, as well as for the binary systems methane–hydrogen, nitrogen–carbon dioxide, and nitrogen–ethane, the data situation is quite satisfactory (see also Table 6.4) and binary specific departure functions were developed. The most accurate (and also most extensive) data sets available are those for the binary mixtures methane–nitrogen and methane–ethane. The binary equations developed for these systems have a strong influence on the description of the thermodynamic properties of natural gases and similar multi-component mixtures, and they reproduce the available data to within the very low experimental uncertainties of the most accurate measurements (see Table 6.2 and also Sec. 8.1). In order to develop a mixture model which is able to accurately describe the properties of a variety of natural gases (of typical and unusual composition), a generalised departure function was developed for binary mixtures of important secondary alkanes. The data for these mixtures do not allow for the development of binary specific departure functions. For the development of the generalised departure function for secondary alkanes, selected data for the well-measured binary alkane mixtures methane–ethane and methane–propane were also used.



	Helium	Water	Carbon monoxide	Hydrogen	Oxygen	Argon	n-Octane	n-Heptane	n-Hexane	Isopentane	n-Pentane	Isobutane	n-Butane	Propane	Ethane	Carbon dioxide	Nitrogen
Methane	🟦	🟦	🟦	🟨	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟧	🟧	🟨	🟨	🟨	🟨
Nitrogen	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟨	🟨	
Carbon dioxide	🟦	🟦	⬜	🟦	⬜	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦		
Ethane	⬜	⬜	🟦	🟦	⬜	⬜	🟦	🟦	🟦	🟩	🟦	🟧	🟧	🟧			
Propane	⬜	🟦	🟦	🟦	⬜	⬜	🟦	🟦	🟦	🟦	🟦	🟧	🟧				
n-Butane	⬜	🟦	🟩	🟦	⬜	🟦	🟦	🟦	🟦	🟩	🟦	🟧					
Isobutane	⬜	⬜	🟩	🟩	⬜	⬜	🟩	🟩	🟩	🟩	🟩						
n-Pentane	⬜	🟦	🟩	🟩	⬜	⬜	🟦	🟦	🟦	🟦							
Isopentane	⬜	⬜	🟩	🟩	⬜	⬜	🟩	🟩	🟩								
n-Hexane	⬜	🟦	🟩	🟦	⬜	⬜	🟩	🟦									
n-Heptane	⬜	⬜	🟩	🟦	⬜	⬜	🟦										
n-Octane	⬜	🟦	🟩	🟩	⬜	⬜											
Argon	⬜	🟦	🟦	⬜	🟦												
Oxygen	⬜	🟦	⬜	⬜													
Hydrogen	⬜	⬜	🟦														
Carbon monoxide	⬜	⬜															
Water	⬜																

🟨 Binary specific departure functions
🟧 Generalised departure function for important alkanes
🟦 Adjusted reducing functions, no departure function
🟩 Linear combining rules, no fitting
⬜ Lorentz-Berthelot combining rules, no fitting

Fig. 7.14 Overview of the 153 binary combinations that result from the 18 natural gas components considered for the development of the new equation of state (GERG-2004), Eqs. (7.1) – (7.10). The diagram shows the different formulations developed for the binary mixtures.

Table 7.16 List of the binary mixtures taken into account by the binary specific departure functions and the generalised departure function for secondary alkanes developed in this work

Binary mixture	Type of departure function	Number of terms	Type of terms[a]
Methane–Nitrogen	binary specific	9	P (2), E (7)
Methane–Carbon dioxide	binary specific	6	P (3), E (3)
Methane–Ethane	binary specific	12	P (2), E (10)
Methane–Propane	binary specific	9	P (5), E (4)
Methane–n-Butane	generalised	10	P
Methane–Isobutane	generalised	10	P
Methane–Hydrogen	binary specific	4	P
Nitrogen–Carbon dioxide	binary specific	6	P (2), E (4)
Nitrogen–Ethane	binary specific	6	P (3), E (3)
Ethane–Propane	generalised	10	P
Ethane–n-Butane	generalised	10	P
Ethane–Isobutane	generalised	10	P
Propane–n-Butane	generalised	10	P
Propane–Isobutane	generalised	10	P
n-Butane–Isobutane	generalised	10	P

[a] ”P” indicates polynomial terms according to Eq. (4.24), and “E” indicates the new exponential terms composed of a polynomial and the modified exponential expression according to Eq. (7.163). The numbers in parentheses indicate the respective number of terms.

The development of the various binary equations is based on the binary data for the thermal and caloric properties presented in Sec. 6.1. In the first step, the binary parameters of the reducing functions for density and temperature were fitted to selected data. Subsequently, departure functions consisting of 4 to 12 individual terms were developed. For the optimisation of the structure of the departure functions, linearised data were used as required by the linear optimisation procedure (see Sec. 4.4.2). The data sets used for fitting and structure optimisation are indicated as “used data” in Table A2.1 of the appendix. All other data were used for comparisons only.

The development of departure functions involves considerable but worthwhile effort. The pursued basic strategy for this development is described in the following. Details concerning the development of a new functional form and the different banks of terms used for the development of the different binary departure functions are given in Sec. 7.11.

7.10.1 Fitting of the Reducing Functions for Density and Temperature

For all of the considered binary mixtures, the parameters of the reducing functions in Eqs. (7.9) and (7.10) were firstly adjusted without the use of a departure function. The fitting of the parameters to the different linear and nonlinear data types was, in general, performed using nonlinear fitting procedures as described in Sec. 5.5. For phase equilibrium properties, linearised VLE data were used in the initial cycles of the iterative fitting process (see Sec. 5.5.3). Subsequently, direct (nonlinear) fitting to VLE data was applied as described in Sec. 5.5.4. Since the reducing functions only depend on the mixture composition, the use of VLE data which uniformly cover large composition ranges proved to be advantageous.

Since a multi-fluid approximation without a departure function is in general not able to reproduce the most accurate data to within their (low) experimental uncertainties, e.g. gas phase densities and gas phase speeds of sound at low temperatures and elevated pressures measured using state-of-the-art measuring techniques (see Chap. 6), the data were weighted in a reasonable manner (with comparatively low weights). With this, the limited abilities of a simple multi-fluid approximation based only on adjusted reducing functions for the description of thermodynamic properties were taken into account.

For the initial estimates, the binary parameters $\gamma_{v,ij}$, $\beta_{v,ij}$, $\gamma_{T,ij}$, and $\beta_{T,ij}$ of Eqs. (7.9) and (7.10) were set to unity. Thus, the reducing functions for density and temperature reduce to simple quadratic mixing rules using combining rules for the component critical parameters. In general, it is advantageous to retain the asymmetric binary parameters $\beta_{v,ij}$ and $\beta_{T,ij}$ in the initial fitting cycles, prior to the simultaneous fitting of all parameters to obtain the final set of coefficients.

The data sets for several binary mixtures consisting of secondary and minor components are either limited with respect to the covered temperature, pressure, and composition ranges, or the number of available data (see Table 6.4). The development of equations for these systems was carried out carefully, and occasionally only the (symmetric) parameters $\gamma_{v,ij}$ and $\gamma_{T,ij}$ were fitted to the data in order to avoid unreasonable behaviour in regions not covered by data. Thus, the parameters $\beta_{v,ij}$ and $\beta_{T,ij}$ remain unity for these systems.

7.10.2 Development of Binary Specific Departure Functions

After the parameters of the reducing functions have been determined, the development of a departure function for a binary mixture using the structure optimisation method described in Sec. 4.4 can be performed. This optimisation procedure determines the structure of the part of the departure function which depends only on the reduced density δ and the inverse reduced temperature τ. For the development of any equation for a binary mixture based on a multi-fluid approximation, it is important to examine the ranges of the reduced mixture properties δ and τ covered by the data (not the absolute temperature, pressure, and composition ranges)[69]

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[69] For instance, the reduced temperature $T/T_\mathrm{r} = 1/\tau$ for a methane–nitrogen mixture containing 10% nitrogen amounts to about 1.20 at 220 K, whereas it approximately equals 1.25 for 20% nitrogen at

in order to reasonably weight all data as desired for the range of most interest for the multi-component mixture (see also Sec. 4.8).

In order to consider nonlinear data for the homogeneous region (e.g. speed of sound data) in the linear structure optimisation procedure, the required precorrelation factors were calculated from a preliminary equation (see also Sec. 4.4.2). To meet the requirements for the description of phase equilibrium properties, linearised VLE data were considered in the optimisation process in addition to linear and linearised homogeneous properties. The often missing saturated phase densities of the selected *pTxy*-data were also calculated from a preliminary equation to provide complete equilibrium information. For this, the phase densities were calculated as described in Sec. 5.4.1 by solving the preliminary equation for the densities at the given (experimental) values of saturation temperature, vapour pressure, and phase compositions, rather than solving the equilibrium conditions from the equation. Thus, the values for the *pTxy*-data remain unchanged and are simply supplemented by the precorrelated phase densities.

The structure optimisation of the departure function was carried out based on the method of Setzmann and Wagner (1989) described in Sec. 4.4.2 using the linear and linearised mixture properties. The coefficients of the resulting structure-optimised equation were then redetermined form direct (nonlinear) fitting to the selected linear and nonlinear binary data. For direct fitting of vapour-liquid equilibrium properties, measured vapour pressures and vapour phase compositions at the given saturation temperature and liquid phase composition were usually used. Furthermore, data for saturated liquid densities at a given temperature and composition were additionally used when available. Due to the linearisation of the nonlinear binary data, the entire process of optimising the structure of a departure function is a recursive process. Therefore, the most recently determined departure function is used at each step to first relinearise the nonlinear data for both the homogeneous region and for phase equilibrium. Then the next linear structure optimisation begins. This iterative process, composed of the linearisation of the data, the linear structure optimisation, and the nonlinear fitting of the coefficients, is repeated until convergence is obtained. For certain binary mixtures, such as the binary systems methane–carbon dioxide and methane–ethane, it was advantageous to repeatedly determine the parameters of the reducing functions with subsequent fitting. This can be done separately or simultaneously together with the coefficients of the departure function. Using the iterative optimisation and fitting process as described above, a new departure function was finally determined based on the improved reducing functions.

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the same temperature. For the methane–ethane mixture, however, a reduced temperature of about 1.19 is obtained at 250 K and 15% ethane, and also at 270 K and 30% ethane.

7.10.3 Development of a Generalised Departure Function

Because the data situation for binary mixtures consisting of alkanes is limited, binary specific departure functions can only be developed for the binary systems methane–ethane and methane–propane. Since methane is the dominant component in virtually all natural gases, it is necessary to account for at least the binary mixtures methane–n-butane and methane–isobutane by using departure functions to obtain a sufficiently accurate description of the thermodynamic properties of natural gas mixtures. In order to achieve an accurate description for these and other binary alkane mixtures characterised by limited data, a generalised departure function for the eight binary alkane mixtures listed in Table 7.16 was developed. Data for the well-measured binary mixtures methane–ethane and methane–propane were used along with the limited data sets to develop an accurate description of binary alkane mixtures such as ethane–propane.

The development of this generalised departure function was carried out in several steps. The starting point was the binary specific departure function for the methane–ethane system with the respective reducing functions for density and temperature. The binary mixture methane–propane was then considered as additional system. Selected data for this mixture and the initial binary specific departure function for methane–ethane were used to fit the binary parameters of the reducing functions and the binary specific parameter F_{ij} according to Eq. (7.3) for the methane–propane mixture. This produced reducing functions and a parameter F_{ij} that result in a reasonable description of the properties of the system methane–propane using the structure of the departure function determined for the methane–ethane mixture. Then, the selected data for both binary mixtures were used to develop a departure function (at fixed reducing functions and F_{ij} parameters) that best describes the properties of both mixtures using a simultaneously determined single structure. Similar to the development of the binary specific departure functions described in the previous section, the basic iterative procedure of the linearisation of the data, the linear optimisation of the structure of the departure function, and the subsequent nonlinear fitting of its coefficients to the selected linear and nonlinear data were carried out. In between this iterative process, the parameters of the reducing functions and the F_{ij} parameters of both binary mixtures were refitted to obtain reducing functions which are best suited for the description of the thermodynamic properties of binary mixtures with the generalised departure function. After the whole process of developing the generalised departure function for the binary mixtures methane–ethane and methane–propane converged satisfyingly, additional binary mixtures were added in a similar manner to that for the methane–propane mixture, beginning with the system methane–n-butane. In intermediate optimisation steps, selected data for the binary systems ethane–propane and propane–n-butane were also used, although they have only a minor influence on the structure of the equation due to their limited data (this is also true for the other secondary alkane mixtures).

The final structure of the generalised departure function for secondary binary alkane mixtures is almost completely based on the accurate and comprehensive data sets for the three binary systems methane–ethane, methane–propane, and methane–n-butane, with more than 6,200 selected data points used. For additional binary alkane mixtures, the parameters of the reducing functions and the F_{ij} parameter of each binary equation were fitted to selected data for the binary mixture using the final generalised departure function. Thus, the data for these binary mixtures did not contribute in the optimisation of the structure of the generalised departure function.

7.11 Development of New Terms and the Different Banks of Terms

As described in Sec. 5.3.4, two different types of terms, namely the polynomial terms and polynomial terms in combination with exponential terms (for simplicity, referred to in the following as exponential terms) according to Eqs. (4.24) and (4.25), form the structure of the departure functions used in the multi-fluid mixture models reported in the literature (see Table 5.2). The departure functions developed by Klimeck (2000) for selected binary mixtures of seven main and secondary natural gas components are composed of both functional forms [see Eq. (5.24)], and these forms are the basis of many formulations for the residual Helmholtz free energy of modern wide-range pure substance equations of state. The bank of terms used initially in this study is very similar to the one used for optimising the structure of the new class of pure substance equations of state for the main natural gas components developed by Klimeck (2000) (see Sec. 4.8). Although the resulting binary equations achieved a very accurate description of the thermal and caloric properties of binary and multi-component mixtures, physically wrong behaviour in vapour-liquid equilibrium properties, indicated by "bumps" in the vapour-liquid phase boundary of binary mixtures (see Figs. 7.16 – 7.18), was observed after finishing the development of the binary equations. In this section the solution to the problem of the appearance of the bumps in the phase boundary is described.

The results of the extensive investigations concerning the bumps in the phase boundary carried out in this work can be summarised as follows:

- The undesirable bumps appeared in every binary equation developed by Klimeck (2000) which used a departure function to accurately describe the thermal and caloric properties of binary mixtures. Thus, the problem existed in all of the 14 binary equations containing a binary specific (six binary mixtures) or a generalised departure function (eight binary mixtures).
- The bumps are not due to the special characteristics (i.e. the multiple loops described in Sec. 7.8) of the multi-parameter equations of state used for the pure components.

- Potential errors in the density solver or the fitting and structure optimisation routines were excluded by verifying the computer code.
- The bumps are associated with the use of exponential expressions in the departure functions. The appearance of the bumps is even more likely when using values for density exponents $c_{ij,k} \geq 3$ in the argument of the exponential expression [see Eq. (7.162)]. Equations developed without a departure function or departure functions that consist of only polynomial terms do not show any wrong physical behaviour.
- The use of exponential terms (including those with $c_{ij,k} \geq 3$) in the departure function of binary mixtures is necessary to be able to represent the available accurate speed of sound data to within their (usually very low) experimental uncertainty. Without these exponential expressions (i.e. using a structure consisting of only polynomial terms), the description of the speed of sound data of binary mixtures and also of natural gases at lower temperatures is less accurate (and not within the experimental uncertainty of the data).
- Aside from the low quality of most VLE data (see Chap. 6), additional difficulties arise because of the lack of data for vapour-liquid equilibrium properties particularly in the mixture critical region and the poor data for thermal and caloric properties in the homogeneous region close to the mixture critical region. This contributes to the wrong physical behaviour since the structure of a departure function using exponential expressions with density exponents $c_{ij,k}$ up to 6 is far too flexible for use in a multi-fluid mixture model.
- The use of artificial VLE data calculated from equations that are developed only for phase equilibrium, providing a more consistent and extensive data set, usually complicates the development of departure functions for binary mixtures. Such an approach is not recommended and often adversely effects the description of the available thermal and caloric properties in the homogeneous region.

7.11.1 Development of a New Functional Form

The solution to this problem was the development of a new functional form, suitable for the structure of the departure functions of binary mixtures, that replaced the ordinary exponential terms. Although this solution appears to be fairly reasonable, its realisation is not a trivial task. Furthermore, the investigations of the bumps in the phase boundary revealed that the new binary equations had to achieve at least the same accurate description of the thermal and caloric properties of binary mixtures in the homogeneous region as compared to those developed by Klimeck (2000) in order to meet the requirements on the new mixture model concerning the accuracy in the description of the thermodynamic properties of natural gases (see Chap. 3).

In the beginning of the departure function development, different modifications of the ordinary exponential term

$$\alpha_{ij,k}^{\mathrm{r}} = n_{ij,k}\,\delta^{d_{ij,k}}\,\tau^{t_{ij,k}}\,e^{-\delta^{c_{ij,k}}}, \tag{7.162}$$

such as terms using the inverse reduced mixture temperature τ in the argument of the exponential function instead of δ, or combinations of exponential functions depending on both δ and τ, were used for selected binary mixtures. Further theoretical considerations resulted in rather unusual functional forms such as an integrated exponential term for which the first derivative with respect to δ equals Eq. (7.162). Furthermore, formulations using an inverse tangent function in δ instead of the exponential expression were tested. Each of these tests required full implementation of the functional form into the structure optimisation and fitting routines, and the property calculation programs as well. Nevertheless, either the modified equations showed similar or even worse behaviour (e.g. with the combined exponential functions in δ and τ) than with the ordinary exponential functions, or the equations did not achieve the required high accuracy in the description of the thermal and caloric properties of binary (and consequently of multi-component) mixtures.

As mentioned before, extensive investigations showed that certain characteristics of the ordinary exponential terms are particularly useful for the accurate description of speed of sound data in the gas phase at lower temperatures. Therefore, a functional form was finally designed which uses a modified exponential expression for the reduced mixture density δ. As shown in Sec. 5.3.4 [see Eq. (5.25)], the resulting new exponential term can be written as

$$\alpha_{ij,k}^{\mathrm{r}} = n_{ij,k}\,\delta^{d_{ij,k}}\,\tau^{t_{ij,k}}\,e^{-\eta_{ij,k}\left(\delta-\varepsilon_{ij,k}\right)^{2}-\beta_{ij,k}\left(\delta-\gamma_{ij,k}\right)}, \tag{7.163}$$

where $\eta_{ij,k}$, $\varepsilon_{ij,k}$, $\beta_{ij,k}$, and $\gamma_{ij,k}$ are adjustable parameters. Together with the density exponent $d_{ij,k}$, the parameters are used to (manually) model certain shapes of the departure function with respect to δ. A plot of such different shapes is displayed in Fig. 7.15. The parameters are chosen in such a way that the maximum of the term is located between values for the reduced mixture density δ of 0.5 and 1. Furthermore, the parameters are used to control the gradients of the term on both sides of the maximum (usually, the gradient of an ordinary exponential term is too steep on both sides of the maximum). By limiting the structure optimisation procedure to use certain predefined exponential terms reduces the flexibility of the structure of the departure function to be developed, even though the exponential characteristic required for the accurate description of speed of sound data is maintained.

The new functional form should not be confused with the modified Gaussian bell-shaped terms introduced by Setzmann and Wagner (1991) for the improved description of the thermal and caloric properties of pure substances in the vicinity of the critical point. These terms are currently used in the bank of terms for the α^{r} equation of highly accurate equations of state for pure substances (see Sec. 4.6) and have the following structure:

$$\alpha_k^{\mathrm{r}} = n_k\,\delta^{d_k}\,\tau^{t_k}\,e^{-\eta_k(\delta-\varepsilon_k)^2-\beta_k(\tau-\gamma_k)^2}\,. \tag{7.164}$$

Similar to the new functional form, the adjustable parameters η_k, ε_k, β_k, and γ_k are not automatically determined in the optimisation and nonlinear fitting process, but based on comprehensive precalculations. The influence of these terms (in normal use) on the description of thermodynamic properties is, however, limited to a somewhat narrow range in the critical region, whereas the new term behaves similar to an ordinary exponential term with density exponents $c_{ij,k}$ of 1 and 2.

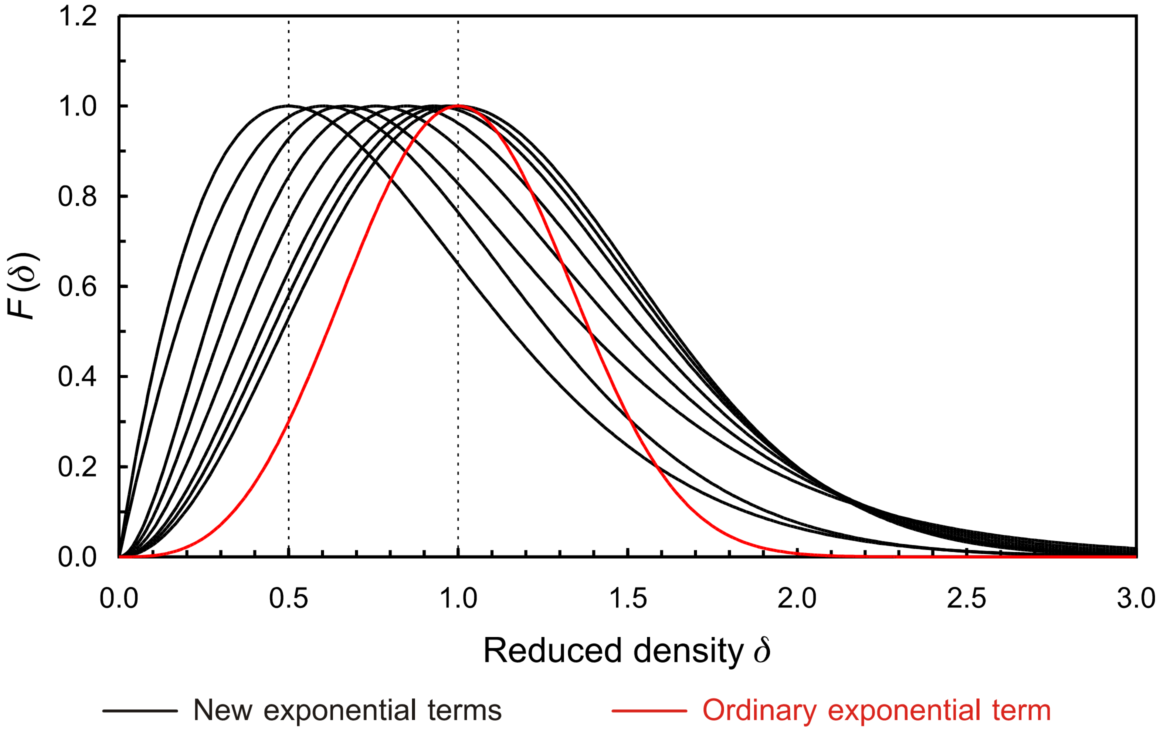

Fig. 7.15 Different shapes of the new term given by Eq. (7.163) for selected values of the density exponent $d_{ij,k}$ and the parameters $\eta_{ij,k}$, $\varepsilon_{ij,k}$, $\beta_{ij,k}$, and $\gamma_{ij,k}$; the shape of an ordinary exponential term given by Eq. (7.162) is plotted for comparison.

The new functional form enables the description of the thermodynamic properties of binary mixtures in the homogeneous gas, liquid, and supercritical regions with the same high accuracy as with the ordinary exponential form, while demonstrating physically correct behaviour along the phase boundary. Equations developed using the new terms in the right way show no bumps and are as accurate or even more accurate than the equations developed by Klimeck (2000), especially for the accurate speed of sound measurements at lower temperatures. Furthermore, the equations developed using the new terms show better behaviour with regards to the composition dependence in the description of binary mixture data. Reducing the step size of the temperature exponent $t_{ij,k}$ from 0.125 to 0.050 in the bank of terms significantly improved the quality of the equations and the convergence behaviour of the iterative structure optimisation process. A drawback of such a reduction is the large amount of terms that have to be handled by the structure optimisation procedure and the resulting increase in computing time. The banks of terms used to develop the different binary equations consisted of up to 1,612 terms.

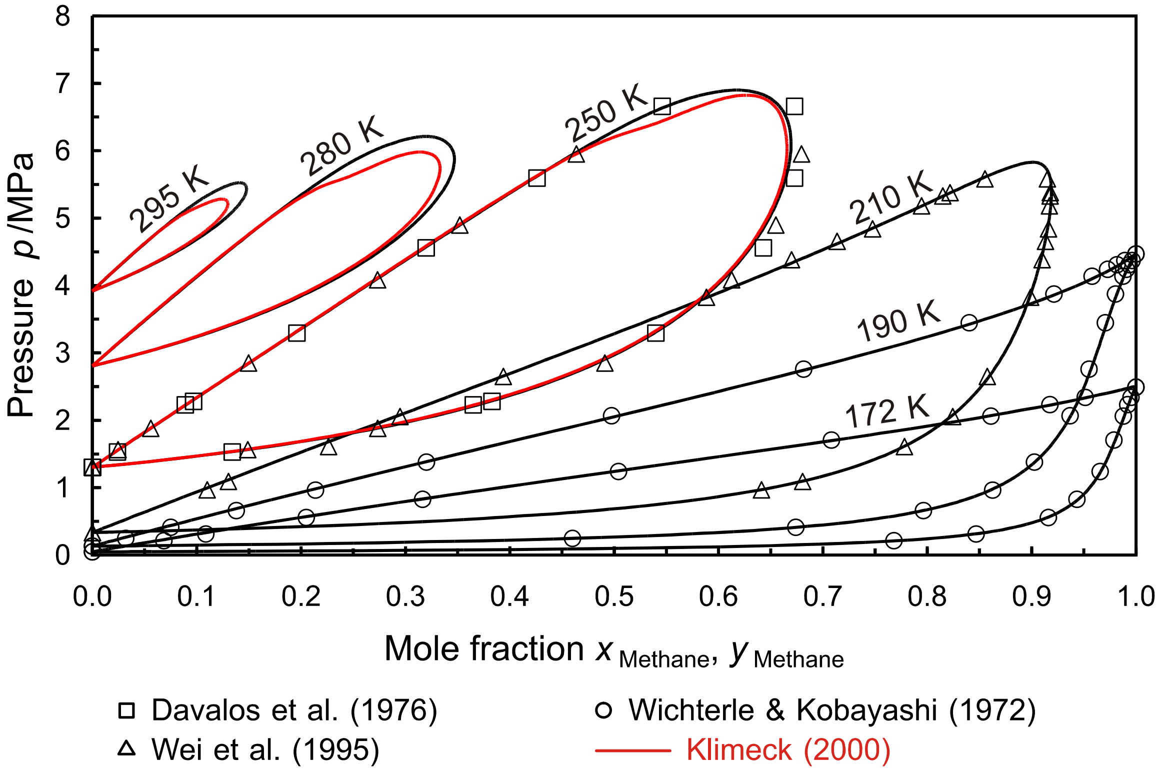

Fig. 7.16 Pressure-composition diagram for the methane–ethane binary mixture showing the vapour-liquid phase boundaries at temperatures ranging from 172 K to 295 K as calculated from the new equation of state (GERG-2004), Eqs. (7.1) – (7.10), and the mixture model of Klimeck (2000); the experimental data for the binary mixture are plotted for comparison.

As an example, Fig. 7.16 shows a pressure-composition diagram for the binary mixture methane–ethane at temperatures ranging from 172 K to 295 K. The solid lines represent the bubble and dew point lines calculated from the new equation of state developed using the new exponential terms according to Eq. (7.163). The red color lines correspond to the bubble and dew point lines calculated from the equation of state of Klimeck (2000) developed using the ordinary exponential terms according to Eq. (7.162). Both equations of state describe the accurate vapour pressure data of Wichterle and Kobayashi (1972a), Davalos *et al.* (1976), and Wei *et al.* (1995) with deviations of less than ±(1 – 3)%, which is in agreement with the experimental uncertainty of the data. The equation of Klimeck (2000) shows the characteristic "bumps" for the isotherms in the critical region of the mixture at elevated pressures, whereas the new equation of state developed in this work shows physically correct behaviour. More obvious unphysical behaviour in the equation of state of Klimeck (2000) occurs for the pressure-composition diagram of the binary mixture methane–carbon dioxide displayed in Fig. 7.17, or the density-composition diagram of the methane–n-butane mixture shown in Fig. 7.18. The use of ordinary exponential terms results in a completely wrong description of the phase boundary of the methane–carbon dioxide mixture at elevated pressures over wide ranges of temperature, exemplified in Fig. 7.17 by the two isotherms at 230 K and 293 K, whereas Fig. 7.18 displays the characteristic "bumps" obtained at higher temperatures in the critical region of the methane–n-butane mixture resulting from the use of ordinary exponential terms in the generalised departure function developed by Klimeck (2000) for secondary alkanes. For both examples, however, the new equation of state shows physically correct behaviour on the phase boundary.

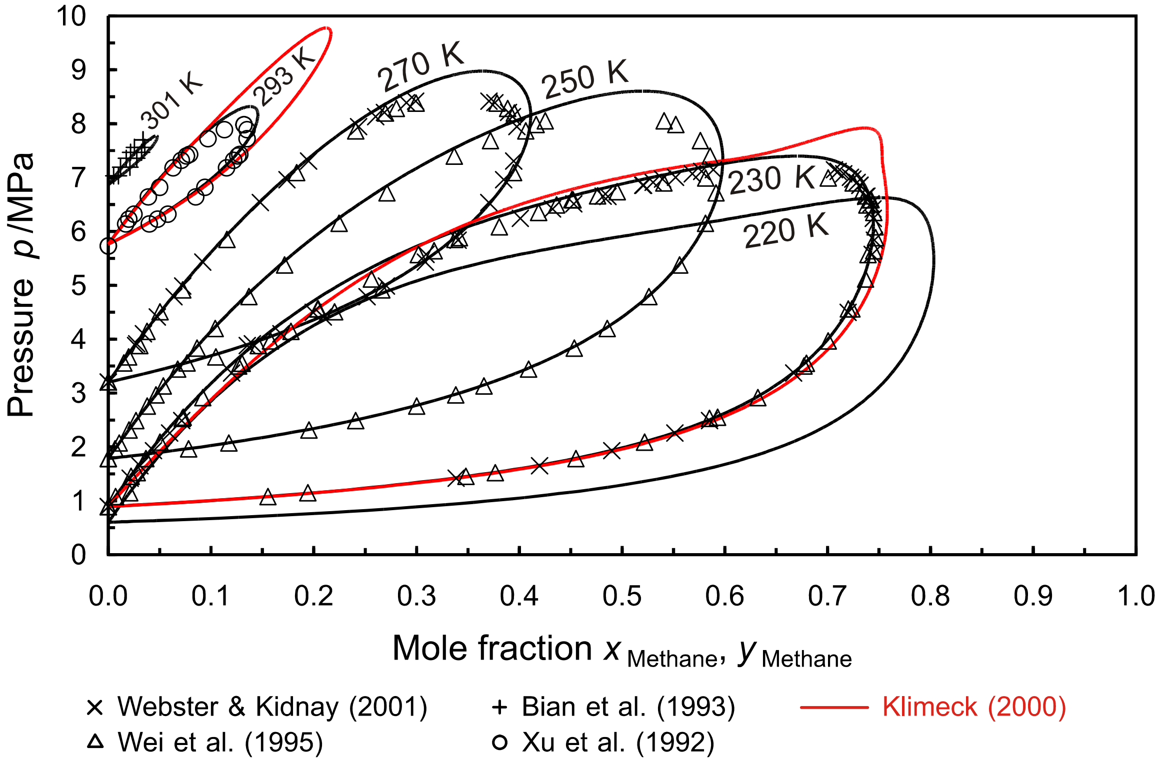

Fig. 7.17 Pressure-composition diagram for the methane–carbon dioxide binary mixture showing the vapour-liquid phase boundaries at temperatures ranging from 220 K to 301 K as calculated from the new equation of state (GERG-2004), Eqs. (7.1) – (7.10), and the mixture model of Klimeck (2000); the experimental data for the binary mixture are plotted for comparison.

The development of departure functions for binary mixtures based on the new functional form is associated with considerable additional effort since the phase behaviour has to be analysed over the whole mixture critical region for the selected bank of terms. However, in this way, departure functions for binary mixtures can be developed which allow for a very accurate description of the thermal and caloric properties of binary mixtures along with an accurate and physically reasonable description of the mixture phase behaviour (even in regions characterised by poor data).

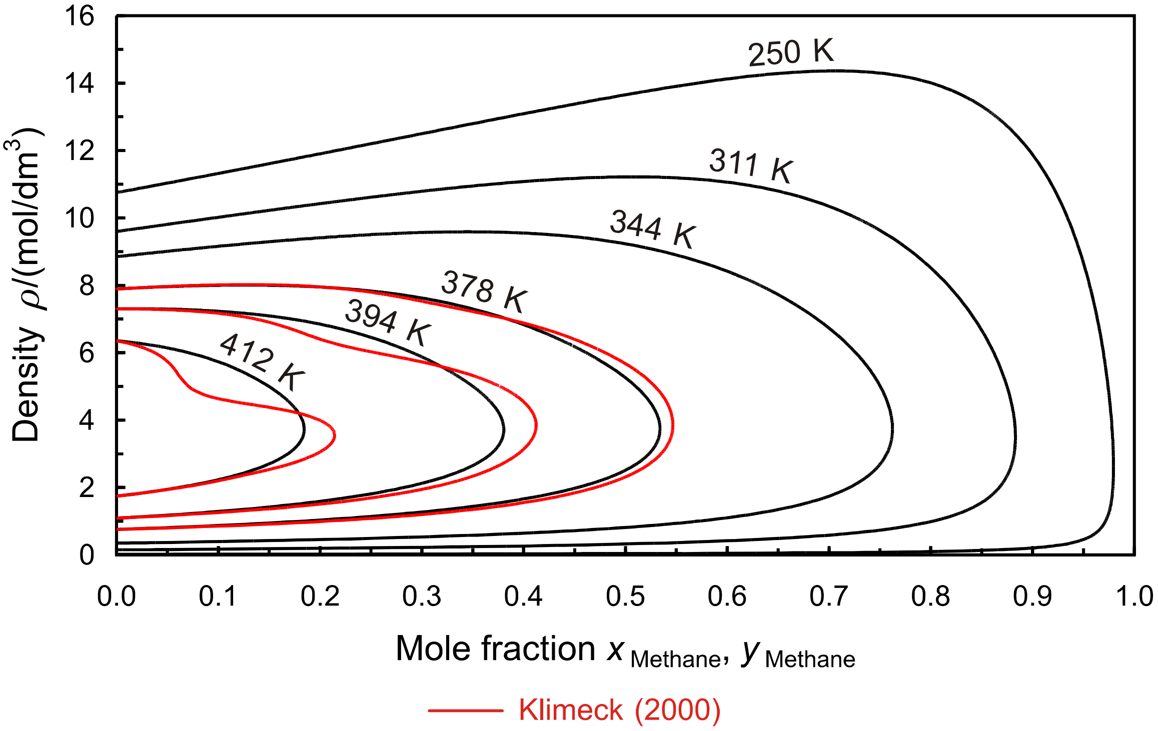

Fig. 7.18 Density-composition diagram for the methane–n-butane binary mixture showing the vapour-liquid phase boundaries at temperatures ranging from 250 K to 412 K as calculated from the new equation of state (GERG-2004), Eqs. (7.1) – (7.10), and the mixture model of Klimeck (2000).

7.11.2 The Different Banks of Terms

Based on the ordinary polynomial terms and the new mixture term, binary specific departure functions were developed for the binary mixtures methane–nitrogen, methane–carbon dioxide, methane–ethane, methane–propane, nitrogen–carbon dioxide, and nitrogen–ethane as described in Sec. 7.10.2 (see also Table 7.16). Different banks of terms were used for the different types of mixtures. A general formulation of these banks of terms can be expressed as follows:

$$\alpha_{ij}^{\mathrm{r}} = \sum_{k=1}^{4}\sum_{l=0}^{80} n_{kl}\,\delta^{k}\tau^{l/20} + \sum_{k=1}^{K_{ij}}\sum_{l=0}^{160} n_{kl}\,\delta^{d_{ij,k}}\tau^{l/20} e^{-\eta_{ij,k}\left(\delta-\varepsilon_{ij,k}\right)^2-\beta_{ij,k}\left(\delta-\gamma_{ij,k}\right)}, \tag{7.165}$$

where K_{ij} is the maximum number of new terms used. The parameters $d_{ij,k}$, $\eta_{ij,k}$, $\varepsilon_{ij,k}$, $\beta_{ij,k}$, and $\gamma_{ij,k}$ are listed in Table 7.17, representing the parameter sets which yield the most suitable functional form for each binary mixture resulting from comprehensive tests concerning various parameter combinations.

Table 7.17 Parameters of the new exponential terms according to Eq. (7.163) contained in the different banks of terms, Eq. (7.165), for the respective binary mixtures

k	$d_{ij,k}$	$\eta_{ij,k}$	$\varepsilon_{ij,k}$	$\beta_{ij,k}$	$\gamma_{ij,k}$
		CH_4–N_2, CH_4–CO_2, CH_4–C_2H_6, N_2–C_2H_6			
1	1	1.000	0.500	1.000	0.500
2	2	1.000	0.500	1.000	0.500
3	2	0.875	0.500	1.250	0.500
4	2	0.750	0.500	1.500	0.500
5	2	0.500	0.500	2.000	0.500
6	2	0.250	0.500	2.500	0.500
7	2	0.000	0.500	3.000	0.500
8	3	0.000	0.500	3.000	0.500
			CH_4–C_3H_8		
1	1	0.250	0.500	0.750	0.500
2	1	0.250	0.500	1.000	0.500
3	1	0.000	0.500	2.000	0.500
4	2	0.000	0.500	2.000	0.500
5	2	0.000	0.500	3.000	0.500
6	2	0.000	0.500	4.000	0.500
			N_2–CO_2		
1	1	0.250	0.500	0.750	0.500
2	1	0.125	0.500	0.875	0.500
3	1	0.250	0.500	1.000	0.500
4	1	0.000	0.500	2.000	0.500
5	2	0.000	0.500	2.000	0.500
6	2	0.000	0.500	3.000	0.500
7	2	0.000	0.500	4.000	0.500

The data situation for the methane–hydrogen mixture does not require the use of functional forms which exhibit an exponential behaviour. Therefore, the following bank of terms consisting only of polynomial terms was used:

$$\alpha_{ij}^{\mathrm{r}} = \sum_{k=1}^{4} \sum_{l=-20}^{40} n_{kl}\, \delta^{k} \tau^{l/20} . \tag{7.166}$$

The use of the new functional forms for the development of the generalised departure function for secondary alkanes was also investigated. As the data situation for the secondary alkane mixtures does not require the use of the new terms, and in order to be able to extend the generalised formulation to further binary alkane mixtures, it was decided to use a formulation which consisted of only polynomial terms. The corresponding bank of terms used to develop the final generalised equation can be written as

$$\alpha_{ij}^{\mathrm{r}} = \sum_{k=1}^{4}\sum_{l=0}^{160} n_{kl}\,\delta^{k}\tau^{l/20}\,. \tag{7.167}$$

7.12 The Alternative (Invariant) Equation of State

To investigate the problem of invariance (see Sec. 5.2.1) and the predictive capabilities of a mixture model that uses invariant reducing functions for the description of the thermodynamic properties of multi-component mixtures, an alternative equation of state based on the multi-fluid mixture model presented in Sec. 7.1 was developed using the invariant reducing functions described below.

7.12.1 The Invariant Reducing Functions

The alternative equation of state uses the invariant reducing functions for density and temperature that are based on a mixing rule suggested by Mathias *et al.* (1991) as described in Sec. 5.2.1 [see Eq. (5.18)]:

$$\frac{1}{\rho_{\mathrm{r}}(\bar{x})} = \sum_{i=1}^{N}\sum_{j=1}^{N} x_i x_j\,\phi_{v,ij}\,\frac{1}{\rho_{\mathrm{c},ij}} + \sum_{i=1}^{N} x_i \left(\sum_{j=1}^{N} x_j\,\lambda_{v,ij}^{1/3}\,\frac{1}{\rho_{\mathrm{c},ij}^{1/3}}\right)^{3} \tag{7.168}$$

and

$$T_{\mathrm{r}}(\bar{x}) = \sum_{i=1}^{N}\sum_{j=1}^{N} x_i x_j\,\phi_{T,ij}\,T_{\mathrm{c},ij} + \sum_{i=1}^{N} x_i \left(\sum_{j=1}^{N} x_j\,\lambda_{T,ij}^{1/3}\,T_{\mathrm{c},ij}^{1/3}\right)^{3}, \tag{7.169}$$

where the Lorentz-Berthelot combining rules according to Eqs. (5.14) and (5.15) are used for $1/\rho_{\mathrm{c},ij}$ and $T_{\mathrm{c},ij}$ similar to that for Eqs. (7.9) and (7.10). Although the mathematical structure of Eqs. (7.168) and (7.169) appears to be comparatively complex, the reducing functions and their derivatives with respect to mole fractions listed in Table 7.18 can be coded very efficiently (only requiring about $N^2/2$ loops for the calculation of ρ_{r} and T_{r} and their mole fraction derivatives at a given mixture composition).

Similar to Eqs. (7.9) and (7.10), two adjustable parameters are used each of the invariant formulations, namely $\phi_{v,ij}$ and $\lambda_{v,ij}$, and $\phi_{T,ij}$ and $\lambda_{T,ij}$. For the symmetric numbering of mole fractions

$$\phi_{v,ij} = \phi_{v,ji},\quad \phi_{T,ij} = \phi_{T,ji},\quad \lambda_{v,ij} = -\lambda_{v,ji},\quad \text{and}\quad \lambda_{T,ij} = -\lambda_{T,ji}, \tag{7.170}$$

and for $j = i$ $\phi_{v,ii} = \phi_{T,ii} = 1$ and $\lambda_{v,ii} = \lambda_{T,ii} = 0$. Equations (7.168) and (7.169) reduce to simple quadratic mixing rules when $\phi_{v,ij} = \phi_{T,ij} = 1$ and $\lambda_{v,ij} = \lambda_{T,ij} = 0$, with the respective combining rules according to Eqs. (5.14) and (5.15) for the critical parameters of the pure components. Furthermore, for binary mixtures (i.e. $N = 2$), Eqs. (7.168) and (7.169) reduce to a much more simple form given by

$$Y_{\mathrm{r}}(\bar{x}) = \sum_{i=1}^{N} \sum_{j=1}^{N} x_i x_j \left(\phi_{Y,ij} + x_j\, \lambda_{Y,ij}\right) Y_{\mathrm{c},ij}\,, \tag{7.171}$$

where Y corresponds to either the molar volume v or the temperature T. The mathematical structure of the formulation according to Eq. (7.171) was originally suggested by Panagiotopoulos and Reid (1986) for a mixing rule for the parameter a of cubic equations of state [see, for example, Eq. (2.3)] to improve the description of the VLE properties of strongly polar, asymmetric mixtures. Unlike that for Eqs. (7.168) and (7.169), the invariance condition (see Sec. 5.2.1) is, however, not fulfilled for the reducing functions according to Eq. (7.171).

Table 7.18 The invariant reducing functions for mixture density $1/\rho_{\mathrm{r}}(\bar{x})$ and temperature $T_{\mathrm{r}}(\bar{x})$ and their derivatives with respect to the mole fractions x_i

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Reducing function for density $1/\rho_{\mathrm{r}}$ $(Y = v)$ and temperature T_{r} $(Y = T)$[a]

$$Y_{\mathrm{r}} = Y_{\mathrm{r}}(\bar{x}) = \sum_{i=1}^{N} x_i \sum_{j=1}^{N} x_j\, \phi_{Y,ij}\, Y_{\mathrm{c},ij} + \sum_{i=1}^{N} x_i \left(\sum_{j=1}^{N} x_j\, \lambda_{Y,ij}^{1/3}\, Y_{\mathrm{c},ij}^{1/3} \right)^3$$

Combining rules for $Y_{\mathrm{c},ij} = Y_{\mathrm{c},ji}$

$$\frac{1}{\rho_{\mathrm{c},ij}} = \frac{1}{8}\left(\frac{1}{\rho_{\mathrm{c},i}^{1/3}} + \frac{1}{\rho_{\mathrm{c},j}^{1/3}} \right)^3 \text{ for } Y = v \text{ and } T_{\mathrm{c},ij} = \left(T_{\mathrm{c},i} \cdot T_{\mathrm{c},j}\right)^{0.5} \text{ for } Y = T$$

Derivatives of $Y_{\mathrm{r}} = Y_{\mathrm{r}}(\bar{x})$ with respect to x_i

$$\left(\frac{\partial Y_{\mathrm{r}}}{\partial x_k}\right)_{x_l} = 2x_k\, Y_{\mathrm{c},k} + 2\sum_{\substack{i=1\\ i\neq k}}^{N} x_i\, \phi_{Y,ki}\, Y_{\mathrm{c},ki} + \left(\sum_{\substack{j=1\\ j\neq k}}^{N} x_j\, \lambda_{Y,kj}^{1/3}\, Y_{\mathrm{c},kj}^{1/3} \right)^3 + 3\sum_{\substack{i=1\\ i\neq k}}^{N} x_i\, \lambda_{Y,ik}^{1/3}\, Y_{\mathrm{c},ik}^{1/3} \left(\sum_{\substack{j=1\\ j\neq i}}^{N} x_j\, \lambda_{Y,ij}^{1/3}\, Y_{\mathrm{c},ij}^{1/3} \right)^2$$

$$\left(\frac{\partial^2 Y_{\mathrm{r}}}{\partial x_k^2}\right)_{x_l} = 2\, Y_{\mathrm{c},k} + 6\sum_{\substack{i=1\\ i\neq k}}^{N} x_i\, \lambda_{Y,ik}^{2/3}\, Y_{\mathrm{c},ik}^{2/3} \left(\sum_{\substack{j=1\\ j\neq i}}^{N} x_j\, \lambda_{Y,ij}^{1/3}\, Y_{\mathrm{c},ij}^{1/3} \right)$$

$$\left(\frac{\partial^2 Y_{\mathrm{r}}}{\partial x_k\, \partial x_l}\right)_{k\neq l} = 2\, \phi_{Y,kl}\, Y_{\mathrm{c},kl} + 3\, \lambda_{Y,kl}^{1/3}\, Y_{\mathrm{c},kl}^{1/3} \left(\sum_{\substack{j=1\\ j\neq k}}^{N} x_j\, \lambda_{Y,kj}^{1/3}\, Y_{\mathrm{c},kj}^{1/3} \right)^2 + 3\, \lambda_{Y,lk}^{1/3}\, Y_{\mathrm{c},lk}^{1/3} \left(\sum_{\substack{j=1\\ j\neq l}}^{N} x_j\, \lambda_{Y,lj}^{1/3}\, Y_{\mathrm{c},lj}^{1/3} \right)^2$$

$$+ 6\sum_{\substack{i=1\\ i\neq k\\ i\neq l}}^{N} x_i\, \lambda_{Y,ik}^{1/3}\, Y_{\mathrm{c},ik}^{1/3}\, \lambda_{Y,il}^{1/3}\, Y_{\mathrm{c},il}^{1/3} \left(\sum_{\substack{j=1\\ j\neq i}}^{N} x_j\, \lambda_{Y,ij}^{1/3}\, Y_{\mathrm{c},ij}^{1/3} \right)$$

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[a] $\phi_{Y,ij} = \phi_{Y,ji}$ and $\lambda_{Y,ij} = -\lambda_{Y,ji}$ for the symmetric numbering of mole fractions.

The two binary parameters ϕ and λ [$\phi_{v,ij}$ and $\lambda_{v,ij}$ in Eq. (7.168) and $\phi_{T,ij}$ and $\lambda_{T,ij}$ in Eq. (7.169)] allow for arbitrary symmetric and asymmetric shapes of the invariant reducing functions concerning equimolar composition similar to γ and β in Eqs. (7.9) and (7.10). Figure 7.19 exemplifies different shapes of the expression

$$x_i x_j \left(\phi_{ij} + x_j \lambda_{ij}\right) \tag{7.172}$$

plotted over mole fraction x_i of component i for selected values of the binary parameters ϕ_{ij} and λ_{ij}. Comparisons of these with the different shapes plotted for the expression

$$x_i x_j \beta_{ij} \gamma_{ij} \frac{x_i + x_j}{\beta_{ij}^2 x_i + x_j} \tag{7.173}$$

in Fig. 5.1 show a higher flexibility of the invariant reducing functions than Eqs. (7.9) and (7.10) since Eq. (7.172) allows for shapes that intersect the abscissa for $0 < x_i < 1$ (see the curve plotted for $\phi_{ij} = -0.5$ and $\lambda_{ij} = 0.75$ in Fig. 7.19).

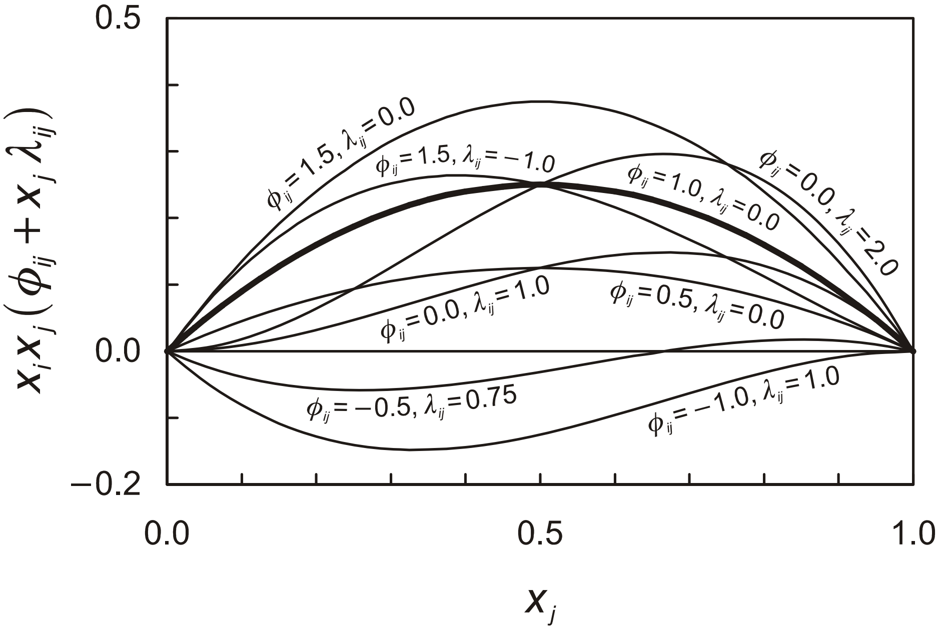

Fig. 7.19 Different symmetric and asymmetric shapes respecting equimolar composition of the invariant reducing functions used for the alternative mixture model for selected values of the binary parameters ϕ and λ in Eqs. (7.168) and (7.169).

7.12.2 The Dilution Effect

Aside from the invariance condition, the so-called "dilution" effect [see Michelsen and Kistenmacher (1990)] is an additional problem that affects the suitability of the mathematical structure of reducing functions for the extension from binary to multi-component mixtures. The terms in Eqs. (7.168), (7.169), and (7.171) with the binary parameter λ included are calculated in a double summation, but contain products of more than two mole fractions, e.g.

$x_i x_j^2$ and $x_i x_j^3$. This implies that as the number of components in the mixture increases, the influence of these terms becomes smaller or entirely vanishes. This deficiency to some extent concerns, for example, the calculation of properties of natural gases containing small amounts of secondary and minor components such as higher alkanes, which have a considerable influence on the real mixture behaviour, especially for VLE conditions. The effect increases with the exponent of the mole fractions and can be decreased by dividing these terms by $x_i + x_j$. In this context it should be noted that the reducing functions according to Eqs. (7.9) and (7.10) do not suffer from this defect.

7.12.3 Fitting the Binary Parameters of the Invariant Reducing Functions

Instead of developing binary equations by fitting the adjustable binary parameters of the invariant reducing functions for density and temperature [Eqs. (7.168) and (7.169)] to experimental data for thermal and caloric properties for the respective binary mixtures as described in Sec. 7.10, the alternative mixture model was developed by substituting the reducing functions of the original mixture model and maintaining its optimised departure functions [see Eqs. (7.1) – (7.10)] by Eqs. (7.168) and (7.169). Therefore, the invariant reducing functions[70] with their respective binary parameters ϕ and λ were directly fitted to values of $\rho_{\mathrm{r}}(\bar{x})$ and $T_{\mathrm{r}}(\bar{x})$ calculated for several discrete mixture compositions from the original reducing functions developed using experimental data[71]. This procedure ensures that the invariant reducing functions result in (virtually) the same values for the reduced mixture variables δ and τ as obtained from the original formulations[72]. Hence, the binary equations of both mixture models behave in a nearly identical manner and achieve the same accuracy in the description of the thermal and caloric properties of the different binary mixtures. The difference in the description of multi-component mixtures then results purely from the

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[70] Instead of fitting the adjustable parameters of Eqs. (7.168) and (7.169), those of the reduced formulations given in Eq. (7.171) were fitted. The simplification of Eqs. (7.168) and (7.169) to Eq. (7.171) for $N = 2$ enables the formation of another alternative (but not invariant) equation of state which behaves completely identical for binary mixtures, but different for multi-component systems.

[71] For the binary mixtures methane–nitrogen, methane–ethane, and methane–propane, equations based on the invariant reducing functions (and the binary specific departure functions previously optimised based on the original reducing functions) were developed by fitting the parameters of Eqs. (7.168) and (7.169) to experimental data for thermal and caloric properties of the respective binary mixtures. The binary equations developed in this way yield very similar results compared to those developed using Eqs. (7.9) and (7.10). Whether the apparently very flexible mathematical structure of the invariant reducing functions is advantageous or not for other binary systems or what the outcome is by starting the fitting and optimisation process from the beginning (without information from an existing departure function) still needs to be investigated.

[72] Fitting the binary parameters to experimental data might lead to noticeable deviations in the description of the properties of binary mixtures due to the different mathematical structures of the reducing functions. The degree of change in the description of the properties of multi-component mixtures caused by this additional influence would not be known without an isolated investigation of the predictive capabilities of an alternative mixture model using invariant reducing functions.

different mathematical structures of the respective reducing functions for the extension from binary to multi-component mixtures. In reality, the deviations between the reducing functions are in general negligible, and the differences in the description of multi-component mixtures can be attributed to the different structure of the reducing functions. A list of the parameters ϕ and λ determined in this way is given in Table A4.1 of the appendix. Note that $\phi_{Y,ij} = \gamma_{Y,ij}$ and $\lambda_{Y,ij} = 0$ if $\beta_{Y,ij} = 1$, where Y corresponds to either v or T.

7.12.4 Results of the Investigations Concerning the Problem of Invariance and the Description of Thermodynamic Properties Using the Alternative Equation of State

Whether the theoretical considerations concerning the structure of the reducing functions of the multi-fluid mixture model are of practical relevance or not was investigated in this work. As mentioned in Sec. 5.2.1, the invariance condition is neither fulfilled for the reducing functions used in the new mixture model [see Eqs. (7.9) and (7.10)] nor for those of other existing models based on multi-fluid approximations containing expressions to model asymmetric shapes respecting equimolar composition [e.g. Lemmon and Jacobsen (1999); see also Sec. 5.2]. Figure 7.20 shows that the violation of the invariance condition causes significant deviations in calculated mixture properties, exemplified here for the density, when dividing a component into several identical pseudo-components. The plot displays percentage density deviations calculated from the new mixture model [Eqs. (7.1) – (7.10)] and the one developed by Lemmon and Jacobsen (1999) for a mixture consisting of 95% of methane and 5% of propane. The mixture is investigated in different ways, namely as a binary mixture and as a multi-component mixture consisting of several identical pseudo-components. The baseline of the deviation plot corresponds to the respective density values calculated for the binary mixture from the new mixture model and from the mixture model of Lemmon and Jacobsen (1999). For the multi-component mixture, the amount of methane was divided into four pseudo-components with concentrations of 80% for one of them, and 5% for the other three. The dashed and dot-dashed lines represent the deviations which occur for the calculations with the partitioned system. From a logical point of view, the equations of state should yield identical results without any deviations compared to the binary mixture calculations. The plotted deviations do not, however, verify this assumption. Density values calculated from the mixture model of Lemmon and Jacobsen (1999) deviate for the two types of mixtures by up to 0.2%, whereas the deviations calculated from the new mixture model are less than 0.04%, and thus less severe. Nevertheless, a deviation in density of ±0.04% resulting from the violation of the invariance condition cannot be neglected when aiming for a targeted uncertainty of $\Delta\rho/\rho \leq 0.1\%$ (see Chap. 3). The magnitude of the resulting deviations between the considered binary mixture and the partitioned system basically depends on temperature, pressure (or density), the type of thermodynamic property, the number of pseudo-components introduced, the way of partitioning a component into two or more identical pseudo-components, and the differences in the critical properties of the components. Note that no deviations occur for any partitioning when the alternative equation of state using the invariant reducing functions according to Eqs. (7.168) and (7.169) is applied.

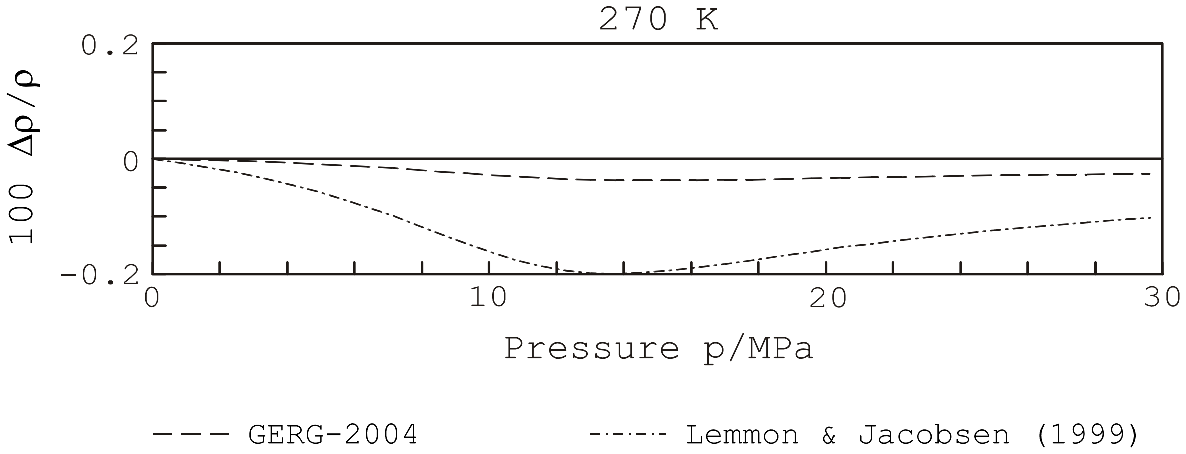

Fig. 7.20 Percentage density deviations $100\Delta\rho/\rho = 100(\rho_{\text{exp}} - \rho_{\text{calc}})/\rho_{\text{exp}}$ resulting from the violation of the invariance condition of the asymmetric reducing functions used for mixture models based on a multi-fluid approximation. The baseline corresponds to the density values calculated from the respective equation for the original (binary) mixture, i.e. without dividing a component into several identical pseudo-components.

Instead of dividing a mixture component into several identical pseudo-components (which is merely of academic interest), grouping of similar components (e.g. the heavy fraction of a hydrocarbon phase) to represent the mixture by a (smaller) number of discrete components can be regarded as the inverse of the partitioning described above. Clearly, with more components, their individual mole fractions become smaller, and different results are obtained (when the reducing functions do not fulfil the invariance condition). Since similar components in general do not behave identical, it is, however, difficult to ascertain whether the deviations between the properties of the original mixture and those of the grouped system result from the unfulfilled invariance condition or their different behaviour.

Since the new mixture model was developed to describe the thermodynamic properties of mixtures based on a defined (and limited) number of distinct components, problems do not occur when the model is used in the way it was designed for, or, in other words, when components are distinct, the problem of invariance is not severe. Problems may exist when a description may vary, i.e. when a characterisation is used to describe several similar mixture components.

Investigations concerning the description of the thermodynamic properties of multi-component mixtures using the new mixture model and the alternative (invariant) equation of state revealed that the structure of the reducing functions is of considerable importance. To determine the differences in the quality of the two equations, their description of the experimental data for thermal and caloric properties of natural gases and other mixtures presented in Chap. 6 was compared. The results can be summarised as follows:

- The alternative equation of state describes most of the available thermal and caloric properties of natural gases, similar gases, and other mixtures (see Sec. 6.2) in the homogeneous region very similar to the new mixture model (see Sec. 8.4). For instance, the majority of the available most accurate gas phase $p\rho T$-data for natural gases and similar gases is described with density deviations of less than ±0.1%, which is in agreement with the uncertainty of the data. Furthermore, no decisive differences were observed for the available saturated liquid densities.
- Aside from a differing description observed for the available $p\rho T$-data of rich natural gases (containing comparatively large amounts of hydrocarbons from ethane to n-hexane), considerable differences were observed for natural gas mixtures rich in carbon dioxide. Here, the alternative equation of state deviates from the measured density data by more than 0.1% at lower temperatures. This weakness is very likely due to the structure of the invariant reducing functions, which seems to be less suited for certain types of mixtures.
- In addition, the alternative mixture model is less accurate in the description of dew point data for natural gases as exemplified by the pressure-temperature plot displayed in Fig. 7.21. In contrast to the new mixture model, the alternative equation of state using the invariant reducing functions according to Eqs. (7.168) and (7.169) considerably deviates from the measurements of Avila *et al.* (2002a) at elevated pressures. The deficiency of the invariant reducing functions concerning the previously described dilution effect might be responsible for the less accurate description since the 12-component mixture contains small amounts of the heavier alkanes n-heptane (0.014%) and n-octane (0.011%) (see also Table 7.14). Similar behaviour as shown in Fig. 7.21 is also observed for other mixtures.

The results of the comprehensive comparisons prove that the reducing functions according to Eqs. (7.9) and (7.10) used in the new mixture model are of considerable advantage for the description of, for example, carbon dioxide rich natural gases and natural gas dew points. Their deficiency caused from the problem of invariance seems to be of minor importance and does not affect the accuracy in the description of the available data for the thermal and caloric properties of multi-component mixtures[73]. The investigations have shown that the differences

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[73] Most of the natural gas mixtures listed in the GERG TM7 (see Chap. 6) under “N-file” (see also Tables A2.2 and A2.3 of the appendix) originally contained small amounts (less than 0.01% up to 0.07%) of the minor components neopentane, benzene, and toluene, which are not included in the new mixture model. A few of those mixtures also contain a number of trace components, such as cyclopentane, cyclohexane, isohexane, and 1-butene, with amounts of in general less than 0.01%. The mole fractions of these components that were added to those of similar substances were in general considered in the new mixture model according to ISO 12213 [ISO (1997)]. Aside from these minor and trace components, a few mixtures contain considerable amounts of ethylene and propylene as additional components of up to 0.31% for ethylene and up to 0.37% for propylene. Whether the noticeable but minor differences in the description of the respective $p\rho T$-data between

between the new mixture model and the alternative invariant version are small for most of the available data, except for a few mixtures. In reality, the new mixture model using the reducing functions according to Eqs. (7.9) and (7.10) is slightly advantageous concerning the temperature and pressure dependence of the percentage deviations. When a mixture contains considerable amounts of components that are not considered in the new mixture model, but are added to a similar existing component, the invariant version might yield more accurate results. Nevertheless, an extension of the new mixture model to incorporate these further components as distinct components is always preferable for a more accurate description of the mixture properties. The invariant reducing functions are, however, of interest when a multi-fluid mixture model is developed using a varying characterisation. Potential modifications of the invariant reducing functions according to Eqs. (7.168) and (7.169) to reduce the influence of the dilution effect still need to be investigated as well as the development of binary equations based on fitting the adjustable parameters of the invariant reducing functions to experimental data.

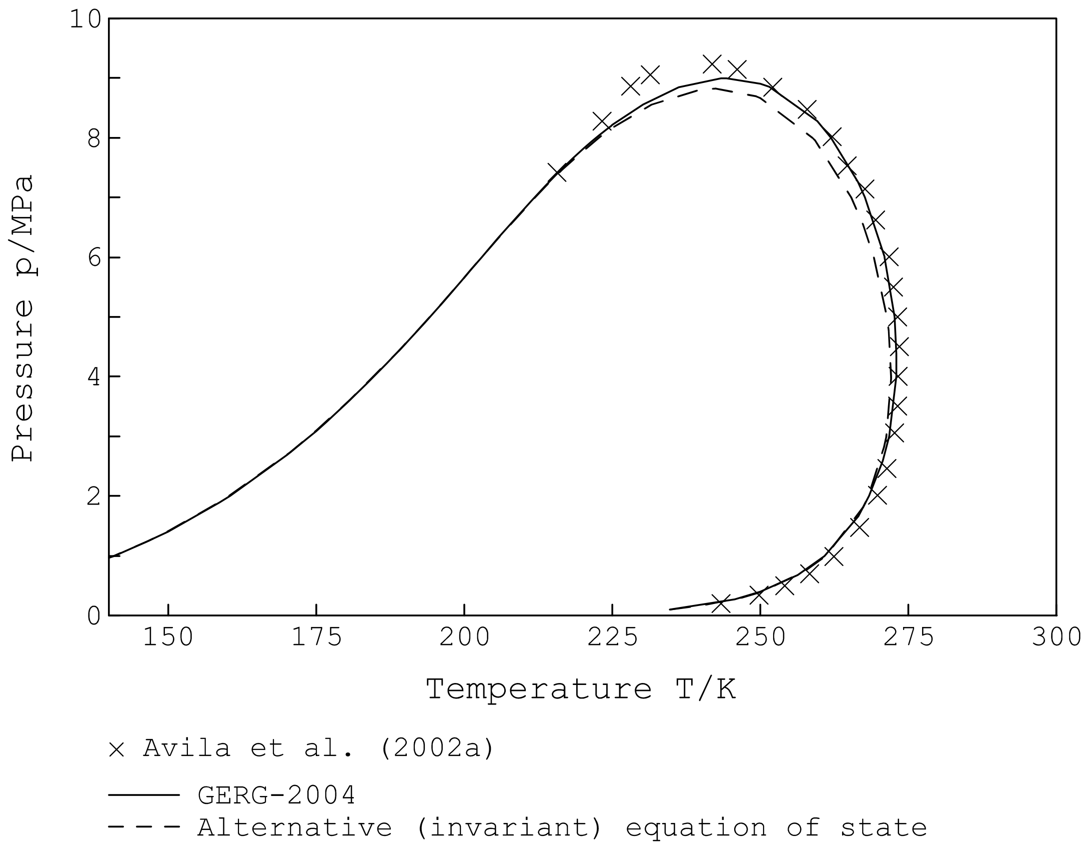

Fig. 7.21 Comparison of the vapour-liquid phase boundary of a 12-component synthetic natural gas as calculated from the new equation of state (GERG-2004), Eqs. (7.1) – (7.10), and the alternative (invariant) equation of state with the corresponding experimental (dew point) data measured by Avila *et al.* (2002a); for the mixture composition see Table 7.14.

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the new mixture model and the alternative invariant version are due to the invariance problem or not remains to be investigated. Such an investigation would require the extension of the mixture model to, for example, ethylene or propylene as an additional component.

7.13 Range of Validity and Estimates of Uncertainty

The new wide-range equation of state (GERG-2004), Eqs. (7.1) – (7.10), for natural gases, similar gases, and other (multi-component and binary) mixtures consisting of the 18 natural gas components listed in Table 4.2, is valid in the gas phase, in the liquid phase, for vapour-liquid equilibrium, and in the supercritical region. The entire range of validity concerning the calculation of thermal and caloric properties of mixtures is divided into three different parts, namely the normal range, the extended range, and the range beyond the extended range. The conservatively estimated uncertainties for the different ranges of validity, as described below, are based on the representation of the available experimental data (see Chap. 6) of various thermodynamic properties of binary and multi-component mixtures by the new equation of state.

Due to the vast amount of experimental data for the different binary and multi-component mixtures, and the varying real mixture behaviour, which strongly depends on temperature, pressure, and composition, it is impossible to discuss each of the different binary and multi-component systems separately at this point. Therefore, only the most important statements on both the range of validity and estimated uncertainties of the new equation of state are given in this section. The given statements are focussed on the use of the equation in standard and advanced technical applications using natural gases and similar mixtures. In general, there are no restrictions concerning the composition range of binary and multi-component mixtures. But, since the estimated uncertainty of the new equation of state is based on the experimental data used for the development and evaluation of the equation, the uncertainty is mostly unknown for the composition ranges not covered by the data. The data situation only allows for a well-founded uncertainty estimation for selected properties and parts of the fluid surface.

Further details and comparisons of the new mixture model with selected experimental data and other equations of state are the subject of Chap. 8. A detailed statistical analysis using all of the available data presented in Chap. 6 is given in the appendix (see Tables A2.1, A2.2, and A2.4).

7.13.1 The Normal Range of Validity

The normal range of validity covers temperatures of $90\ \mathrm{K} \leq T \leq 450\ \mathrm{K}$ and pressures of $p \leq 35\ \mathrm{MPa}$. This range corresponds to the use of the equation in both standard and advanced technical applications using natural gases and similar mixtures, e.g. pipeline transport, natural gas storage, and improved processes with liquefied natural gas (see also Chap. 3).

The uncertainty of the equation in gas phase density is less than 0.1% in density over the temperature range from 250 K to 450 K at pressures up to 35 MPa. This uncertainty estimate is valid for various types of natural gases[74], including, for example, natural gases rich in nitrogen, rich in carbon dioxide, rich in ethane, rich in hydrogen (natural gas–hydrogen mixtures), and natural gases containing comparatively high or considerable amounts of propane and heavier alkanes, carbon monoxide, or oxygen, as well as for many other mixtures (e.g. coke-oven gases) consisting of the 18 natural gas components covered by the new equation of state. The great majority of experimental densities for various rich natural gases, containing comparatively large amounts of carbon dioxide (up to 20%), ethane (up to 18%), propane (up to 14%), n-butane (up to 6%), n-pentane (0.5%), and n-hexane (0.2%), are reproduced by the new equation of state to within ±(0.1 – 0.3)% over the measured temperature (280 K to 350 K) and pressure ranges (up to 30 MPa). For rich natural gases with carbon dioxide mole fractions of 14% and more, systematic deviations exceeding 0.3% are observed (see also Sec. 8.4.1).

The uncertainty in gas phase speeds of sound of common natural gases and similar gases is less than 0.1% in the temperature range from 270 K to 450 K at pressures up to 20 MPa, and in the temperature range from 250 K to 270 K at pressures up to 12 MPa. At higher pressures, the data situation does not, in general, allow for a well-founded uncertainty estimation for multi-component as well as binary mixtures. Therefore, an increased uncertainty of less than (0.2 – 0.3)% is assumed at higher pressures. The uncertainty in speed of sound for some important binary mixtures, such as methane–nitrogen and methane–ethane, amounts to less than (0.05 – 0.1)% over wide temperature, pressure, and composition ranges down to temperatures of 220 K (and below) and at pressures up to 30 MPa (e.g. for the methane–nitrogen system). Furthermore, the new equation represents accurate data for isobaric enthalpy differences of binary and multi-component mixtures to within their experimental uncertainty, which is less than (0.2 – 0.5)%.

Measured isobaric and isochoric heat capacities in the homogeneous gas, liquid, and supercritical regions for binary and multi-component mixtures are accurately described by the new model to within ±(1 – 2)%, which is in agreement with the experimental uncertainty of the available data. Experimental liquid phase isobaric enthalpy differences are represented to within ±(0.5 – 1)%.

In the liquid phase of many binary and multi-component mixtures, including LNG-like mixtures and mixtures of light or heavier hydrocarbons, the uncertainty of the equation in density amounts to approximately (0.1 – 0.5)% at pressures up to 40 MPa, which is in agreement with the experimental uncertainty. A similar uncertainty is estimated for saturated liquid densities of different binary and multi-component LNG-like mixtures in the temperature range from 100 K to 140 K, which is of considerable importance for processes with liquefied natural gas. In this temperature range, comparisons with experimental liquid

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[74] This applies to almost every natural gas mixture included in the GERG TM7 (see Sec. 6.2).

phase and saturated liquid densities show that the uncertainty is less than (0.1 – 0.3)% for many mixtures.

The *pTxy* relation of binary and multi-component mixtures as well as the dew points of natural gases and hydrocarbon mixtures are accurately described as well. The most accurate vapour pressure data for binary and ternary mixtures, consisting of the natural gas main components (see Table 4.2), as well as propane, n-butane, and isobutane, are reproduced by the equation to within their experimental uncertainty, which is approximately (1 – 3)% (see also Table 6.2). Certain other mixtures have higher uncertainties of up to 5% (or more). This is due to the poor data situation. The comparatively high experimental uncertainty of the data only allows for a representation of the vapour-liquid equilibrium with reasonable accuracy. In this context, it should be again noted that the phase behaviour of many mixtures is considerably sensitive to errors in the mixture composition. The poor data situation requires a very careful assessment of the data and their representation by equations of state. Accurate experimental vapour phase compositions are described to within ±(0.5 – 1) mole-%, which is well within the uncertainty of the measurements.

7.13.2 The Extended Range of Validity and the Calculation of Properties Beyond this Range

The extended range of validity covers temperatures of $60\ \text{K} \leq T \leq 700\ \text{K}$ and pressures of $p \leq 70\ \text{MPa}$. The uncertainty of the equation in gas phase density at temperatures and pressures outside the normal range of validity is roughly estimated to be (0.2 – 0.5)%. For certain mixtures, the extended range of validity covers temperatures of $T > 700\ \text{K}$ and pressures of $p > 70\ \text{MPa}$. For example, the equation accurately describes gas phase density data of air to within ±(0.1 – 0.2)% at temperatures up to 900 K and pressures up to 90 MPa. The present data situation outside the normal range of validity does not, in general, allow for well-founded estimates of uncertainty concerning other thermodynamic properties (see Tables A2.1, A2.2, and A2.4 for further details respecting the description of different properties for individual mixtures).

When larger uncertainties are acceptable, tests have shown that the equation can be reasonably used outside the extended range of validity. For example, density data (frequently of questionable and low accuracy outside the extended range of validity) of certain binary mixtures are described to within ±(0.5 – 1)% at pressures up to 100 MPa and more.

7.13.3 Some General Statements on the Uncertainty in Calculated Properties for Binary Mixtures

The new mixture model basically allows for the calculation of thermodynamic properties of a total of 153 binary mixtures of arbitrary composition. These binary systems strongly differ in their real mixture behaviour and the quality and extent of the available experimental data (see Table 6.4). Therefore, it is not possible to give individual statements on the uncertainty in the description of the thermodynamic properties for each of the binary mixtures at this point. To provide at least some general statements on the uncertainty of the new equation of state in the description of the different binary mixtures, the classifications according to Table 7.19 are made. Firstly, the quality in the calculation of thermodynamic properties can be distinguished according to the criterion of whether a departure function (binary specific or generalised) was developed, only the reducing functions were adjusted, or different combining rules were used (without fitting the parameters of the reducing functions) to take into account the respective binary system (see also Fig. 7.14). The second classification concerns the description of several thermodynamic properties for the different fluid regions.

Table 7.19 Conservative estimates of the uncertainty of the new equation of state (GERG-2004), Eqs. (7.1) – (7.10), in the description of selected thermal and caloric properties[a] of different binary mixtures by using adjusted reducing functions and a binary specific departure function, adjusted reducing functions and a generalised departure function, or only adjusted reducing functions (without a departure function)

Mixture region	Adjusted reducing functions and binary specific departure function	Adjusted reducing functions and generalised departure function	Only adjusted reducing functions (no departure function)
Gas phase 0 – 30 MPa $1.2 \le T/T_\mathrm{r} \le 1.4$	$\frac{\Delta\rho}{\rho} \le 0.1\%$	$\frac{\Delta\rho}{\rho} \le (0.1 - 0.2)\%$	$\frac{\Delta\rho}{\rho} \le (0.5 - 1)\%$
Gas phase 0 – 30 MPa $1.4 \le T/T_\mathrm{r} \le 2.0$	$\frac{\Delta\rho}{\rho} \le 0.1\%$	$\frac{\Delta\rho}{\rho} \le 0.1\%$	$\frac{\Delta\rho}{\rho} \le (0.3 - 0.5)\%$
Gas phase 0 – 20 MPa $1.2 \le T/T_\mathrm{r} \le 1.4$	$\frac{\Delta w}{w} \le 0.1\%$	$\frac{\Delta w}{w} \le 0.5\%$	$\frac{\Delta w}{w} \le 1\%$
Gas phase 0 – 20 MPa $1.4 \le T/T_\mathrm{r} \le 2.0$	$\frac{\Delta w}{w} \le 0.1\%$	$\frac{\Delta w}{w} \le 0.3\%$	$\frac{\Delta w}{w} \le 0.5\%$
Phase equilibrium $100\ \mathrm{K} \le T \le 140\ \mathrm{K}$	$\frac{\Delta\rho'}{\rho'} \le (0.1 - 0.2)\%$	$\frac{\Delta\rho'}{\rho'} \le (0.2 - 0.5)\%$	$\frac{\Delta\rho'}{\rho'} \le (0.5 - 1)\%$
Phase equilibrium	$\frac{\Delta p_\mathrm{s}}{p_\mathrm{s}} \le (1 - 3)\%$	$\frac{\Delta p_\mathrm{s}}{p_\mathrm{s}} \le (1 - 5)\%$	$\frac{\Delta p_\mathrm{s}}{p_\mathrm{s}} \le 5\%$
Liquid phase 0 – 40 MPa $T/T_\mathrm{r} \le 0.7$	$\frac{\Delta\rho}{\rho} \le (0.1 - 0.3)\%$	$\frac{\Delta\rho}{\rho} \le (0.2 - 0.5)\%$	$\frac{\Delta\rho}{\rho} \le (0.5 - 1)\%$

[a] The relative uncertainty in isobaric and isochoric heat capacity is estimated to be less than (1 – 2)% in the homogeneous gas, liquid, and supercritical regions independent of the type of developed binary equation (see also the statements given in Sec. 7.13.1).

Table 7.19 summarises the roughly estimated uncertainties of the different binary equations in the selected thermodynamic properties and for the different regions of the fluid surface for those mixtures for which a binary specific or generalised departure function was developed, or only adjusted reducing functions were used[75]. The given general statements result from conservative estimations. For many individual mixtures, properties, or compositions, the uncertainty is often well below the maximum values given in Table 7.19. This concerns, for example, the uncertainty in liquid phase density and in vapour pressure of binary mixtures composed of very similar alkanes for which a generalised departure function is used, such as ethane–propane, propane–n-butane, propane–isobutane, or n-butane–isobutane, which is often within the range given for mixtures for which a binary specific departure function was developed. The same is valid for other binary mixtures composed of similar (or similar behaving) components taken into account only by adjusted reducing functions (or even without any fitting), such as methane–argon, nitrogen–oxygen, nitrogen–argon, carbon dioxide–ethane, n-heptane–n-octane, oxygen–argon, etc. Liquid phase densities of mixtures consisting of heavier hydrocarbons, such as n-pentane–n-hexane, n-pentane–n-heptane, or n-hexane–n-heptane, are reproduced to within ±(0.2 – 0.5)%.

The uncertainty statements listed in Table 7.19 may be exceeded when mixtures show a comparatively strong real mixture behaviour. The difference between the critical temperatures of the pure components can be used as a very simplified indication of the extent of the real behaviour. When the critical temperatures differ by more than 150 K, increased uncertainties may have to be expected, especially affecting the uncertainty in vapour pressure.

It is very difficult to give a general statement on the accuracy achieved for binary mixtures which are taken into account by using only reducing functions with different combining rules (no fitting). For binary mixtures composed of similar behaving components, e.g. similar alkanes, comparable uncertainties may be expected as for the mixtures using adjusted reducing functions. But because data are not available in most of these cases, the uncertainty is basically considered to be unknown.

The development of the new equation of state and the estimates of uncertainty are based on experimental data, which (at least for the properties in the homogeneous region) often do not cover the entire composition range (see Table 6.4). Therefore, the uncertainty also depends on the composition. One exception of considerable importance for natural gases is the binary mixture methane–nitrogen. Here, the uncertainty statements given in Table 7.19 are approximately valid over the entire composition range. Further details on the temperature, pressure, and composition ranges covered by the available experimental data for binary mixtures are given in Table 6.4 (see also Tables A2.1, A2.6, and A2.7 of the appendix).

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[75] Reduced temperature ranges are used for a general classification. Normally, this requires the determination of $T_{\mathrm{r}}(\bar{x})$ according to Eq. (7.10). An estimate for T_{r} depending on the mixture composition can be obtained from a linear combination of the critical temperatures of the two components according to $T_{\mathrm{r}} = x_1\, T_{\mathrm{c},1} + x_2\, T_{\mathrm{c},2}$.

7.14 The Developed Property Calculation Software

Based on the tangent-plane stability analysis and the *pT* flash and phase envelope algorithms described in Secs. 7.5.1, 7.6, 7.7.1, and 7.7.2, a comprehensive software package was developed enabling the calculation of a number of thermodynamic properties from the new mixture model. The stability analysis allows for “blind” property calculations for any binary and multi-component mixture consisting of the 18 natural-gas components listed in Table 4.2. The software enables the calculation of thermodynamic properties in the homogeneous gas, liquid, and supercritical regions, and allows extensive VLE calculations, including *pT* flash, phase envelope, dew point, and bubble point calculations at arbitrary mixture conditions without any user-provided initial estimates.

The software package contains an executable Fortran program, a dynamic link library (DLL), and a Microsoft Excel Add-in. The executable Fortran program basically enables the same type of calculations as provided by the exported DLL functions and subroutines (depending on the input variables temperature, pressure, and overall mixture composition; see Table 7.20), but uses a fixed format for the output of the calculations. With the Excel Add-in, the property functions and subroutines exported by the DLL can be added to the standard function volume of Microsoft Excel, and thus can be used as easily as standard Excel functions and array formulas. Aside from single flash calculations, saturation points, phase envelopes, and lines of constant vapour fraction can be calculated and displayed directly from within an Excel spreadsheet using either the pressure-based or the volume-based phase envelope algorithm (see Secs. 7.7.1 and 7.7.2). Furthermore, the DLL can easily be integrated into programs developed by the user.

Along with the density (and the saturated phase densities in case the mixture is split in two phases) at a given temperature, pressure, and overall mixture composition, almost all of the thermal and caloric properties listed in Table 7.1 and selected derivatives of those given in Table 7.2 can be calculated from the software. The output of the functions can be in either molar or specific units. In addition, the fugacity and fugacity coefficient of each mixture component [see Eqs. (5.42) and (5.43); see also Table 7.3 and Sec. 7.3], the vapour fraction β [see Eq. (5.54)], and the *K*-factors [see Eq. (5.41)] and phase compositions in case of a phase split can be obtained. A list of the calculable thermodynamic properties and their respective functions and subroutines depending on the different combinations of the input variables is given in Table 7.20. The property functions and subroutines will return defined negative values if an input or internal error occurs. Furthermore, defined negative values are returned to indicate certain conflicts concerning the calculation of properties at the specified overall mixture conditions (e.g. the speed of sound can be calculated for each of the equilibrium phases in case of a phase split, but not for the overall equilibrium system). Further details are provided in the manual of the software package [see Kunz and Wagner (2006)].

Table 7.20 List of the calculable thermodynamic properties and their respective functions and subroutines developed for single property calculations from the dynamic link library

Property	Symbol	Function or subroutine depending on	
		T, p, and $\bar{x}$	T, ρ, and $\bar{x}$
	Functions		
Pressure	p	–	POTDX
Density	ρ	DOTPX	–
Compression factor	Z	ZOTPX	ZOTDX
Enthalpy	h	HOTPX	HOTDX
Entropy	s	SOTPX	SOTDX
Isobaric heat capacity	c_p	CPOTPX	CPOTDX
Isochoric heat capacity	c_v	CVOTPX	CVOTDX
Speed of sound	w	WOTPX	WOTDX
Isentropic exponent	κ	CAPOTPX	CAPOTDX
Joule-Thomson coefficient	μ_{JT}	RJTOTPX	RJTOTDX
Internal energy	u	UOTPX	UOTDX
Gibbs free energy	g	GOTPX	GOTDX
Helmholtz free energy	a	AOTPX	AOTDX
Derivative of p with respect to T	$(\partial p/\partial T)_{\rho,\bar{x}}$	DPDTOTPX	DPDTOTDX
Derivative of p with respect to ρ	$(\partial p/\partial \rho)_{T,\bar{x}}$	DPDDOTPX	DPDDOTDX
Derivative of ρ with respect to T	$(\partial \rho/\partial T)_{p,\bar{x}}$	DDDTOTPX	DDDTOTDX
Derivative of p with respect to V	$n(\partial p/\partial V)_{T,\bar{n}}$	DPDVOTPX	DPDVOTDX
Derivative of V with respect to T	$(1/n)(\partial V/\partial T)_{p,\bar{n}}$	DVDTOTPX	DVDTOTDX
Vapour fraction	β	FRACOTPX	–
	Subroutines[a]		
Fugacity	f_i	SFUGOTPX	–
Fugacity coefficient	φ_i	SPHIOTPX	–
Phase compositions	x_i', x_i''	SXFLOTPX	–
Natural logarithm of K-factors	$\ln K_i$	SLNKOTPX	–

Property	Symbol	Function depending on T and $\bar{x}$
Second thermal virial coefficient	B	BOTX
Third thermal virial coefficient	C	COTX

[a] The subroutines return the respective mixture properties for each component i, with $i = 1, 2, ..., N$.

The property functions and subroutines depending on temperature, pressure, and molar composition listed in Table 7.20 allow for "blind" single-phase and two-phase calculations, i.e. the number of phases does not have to be known in advance[76]. A phase type variable

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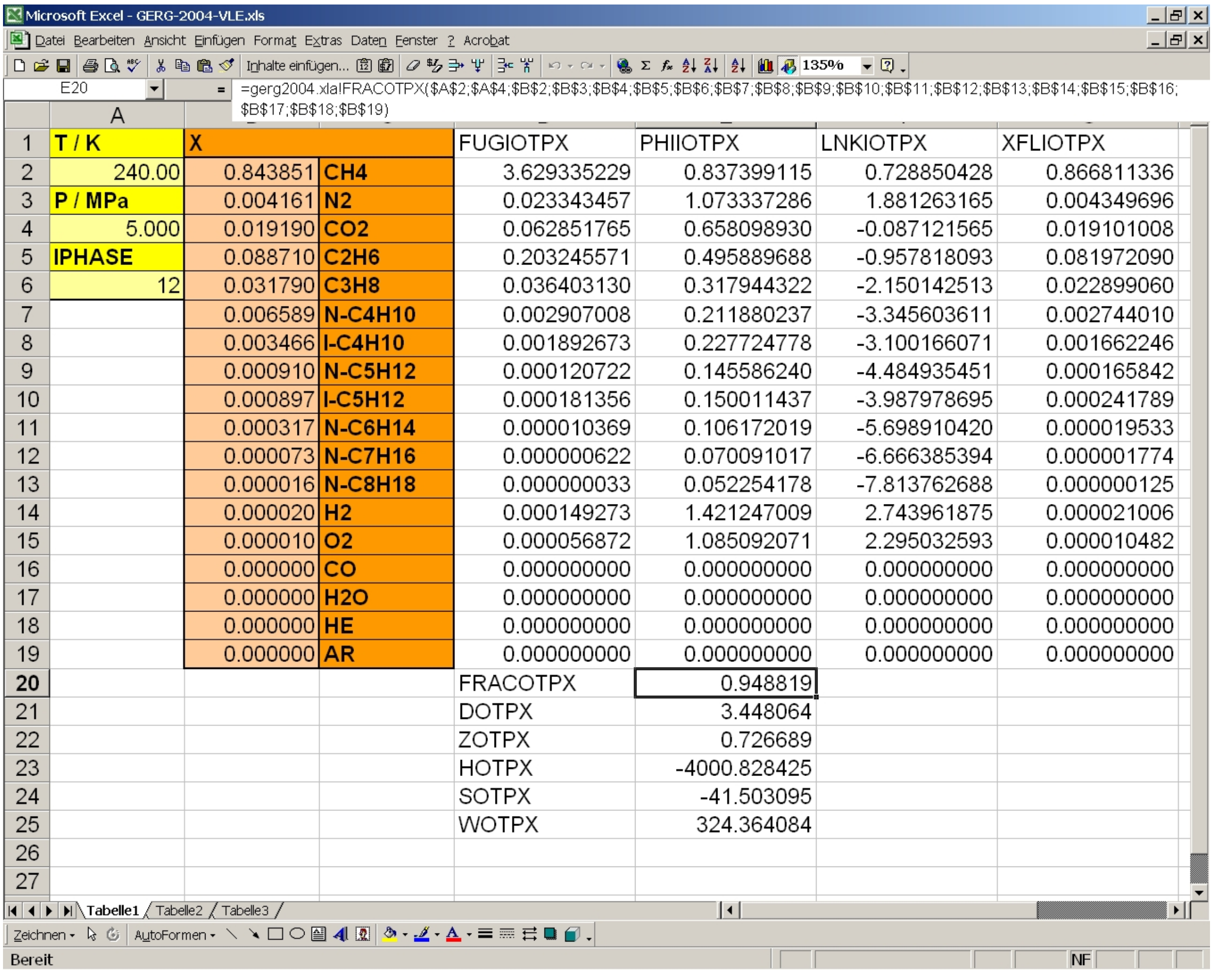
[76] The property functions depending on temperature, density, and composition listed in Table 7.16 do not allow for "blind" calculations. To be able to perform such "blind" calculations similar to that

which can be specified by the user enables, among others, the choice of the output of the functions and subroutines in case of a phase split (e.g. property of the overall equilibrium system, saturated liquid property, or saturated vapour property) when using the property functions and subroutines from within an Excel spreadsheet.



E20 = =gerg2004.xla!FRACOTPX(A2;A4;B2;B3;B4;B5;B6;B7;B8;B9;B10;B11;B12;B13;B14;B15;B16;B17;B18;B19)

	A						
1	**T / K**	X		FUGIOTPX	PHIIOTPX	LNKIOTPX	XFLIOTPX
2	240.00	0.843851	**CH4**	3.629335229	0.837399115	0.728850428	0.866811336
3	**P / MPa**	0.004161	**N2**	0.023343457	1.073337286	1.881263165	0.004349696
4	5.000	0.019190	**CO2**	0.062851765	0.658098930	-0.087121565	0.019101008
5	**IPHASE**	0.088710	**C2H6**	0.203245571	0.495889688	-0.957818093	0.081972090
6	12	0.031790	**C3H8**	0.036403130	0.317944322	-2.150142513	0.022899060
7		0.006589	**N-C4H10**	0.002907008	0.211880237	-3.345603611	0.002744010
8		0.003466	**I-C4H10**	0.001892673	0.227724778	-3.100166071	0.001662246
9		0.000910	**N-C5H12**	0.000120722	0.145586240	-4.484935451	0.000165842
10		0.000897	**I-C5H12**	0.000181356	0.150011437	-3.987978695	0.000241789
11		0.000317	**N-C6H14**	0.000010369	0.106172019	-5.698910420	0.000019533
12		0.000073	**N-C7H16**	0.000000622	0.070091017	-6.666385394	0.000001774
13		0.000016	**N-C8H18**	0.000000033	0.052254178	-7.813762688	0.000000125
14		0.000020	**H2**	0.000149273	1.421247009	2.743961875	0.000021006
15		0.000010	**O2**	0.000056872	1.085092071	2.295032593	0.000010482
16		0.000000	**CO**	0.000000000	0.000000000	0.000000000	0.000000000
17		0.000000	**H2O**	0.000000000	0.000000000	0.000000000	0.000000000
18		0.000000	**HE**	0.000000000	0.000000000	0.000000000	0.000000000
19		0.000000	**AR**	0.000000000	0.000000000	0.000000000	0.000000000
20				FRACOTPX	0.948819		
21				DOTPX	3.448064		
22				ZOTPX	0.726689		
23				HOTPX	-4000.828425		
24				SOTPX	-41.503095		
25				WOTPX	324.364084		
26							
27							

Fig. 7.22 Example screenshot demonstrating the calculation of selected thermodynamic properties of a 14-component natural gas mixture under VLE conditions using the functions and subroutines exported by the GERG-2004 dynamic link library from within an Excel spreadsheet.

The phase envelope routines automatically calculate (and indicate) critical points as well as maxima and minima in temperature and pressure (if it exists for the specified vapour fraction and mixture composition) as described in Sec. 7.7.1. Aside from the saturation temperature and pressure, the output of the phase envelope routines includes the composition of the incipient phase (or of the equilibrium phases in case $0 < \beta < 1$) and the K-factors of all components at each calculated point. Moreover, the volume-based phase envelope routine

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using inputs of temperature, pressure, and composition, the development of a *TV* flash routine (see Sec. 7.9.2) is required.

yields the compressibility factors of the phase boundary (or of the line of constant vapour fraction) and of the incipient (or equilibrium) phase.

Figures 7.22 – 7.24 show example screenshots of calculations carried out with the general software package described above. The calculation of selected thermodynamic properties of a 14-component natural gas mixture under VLE conditions using the functions and subroutines exported by the DLL from within an Excel spreadsheet is shown in Fig. 7.22. The Excel plot in Fig. 7.23 displays the phase boundary of the same 14-component natural gas mixture. The plot was calculated from the new equation of state using the pressure-based phase envelope routine directly from within the Excel table. Figure 7.24 exemplifies a phase boundary calculation of a four-component natural gas mixture using the pressure-based phase envelope routine in the executable Fortran program.

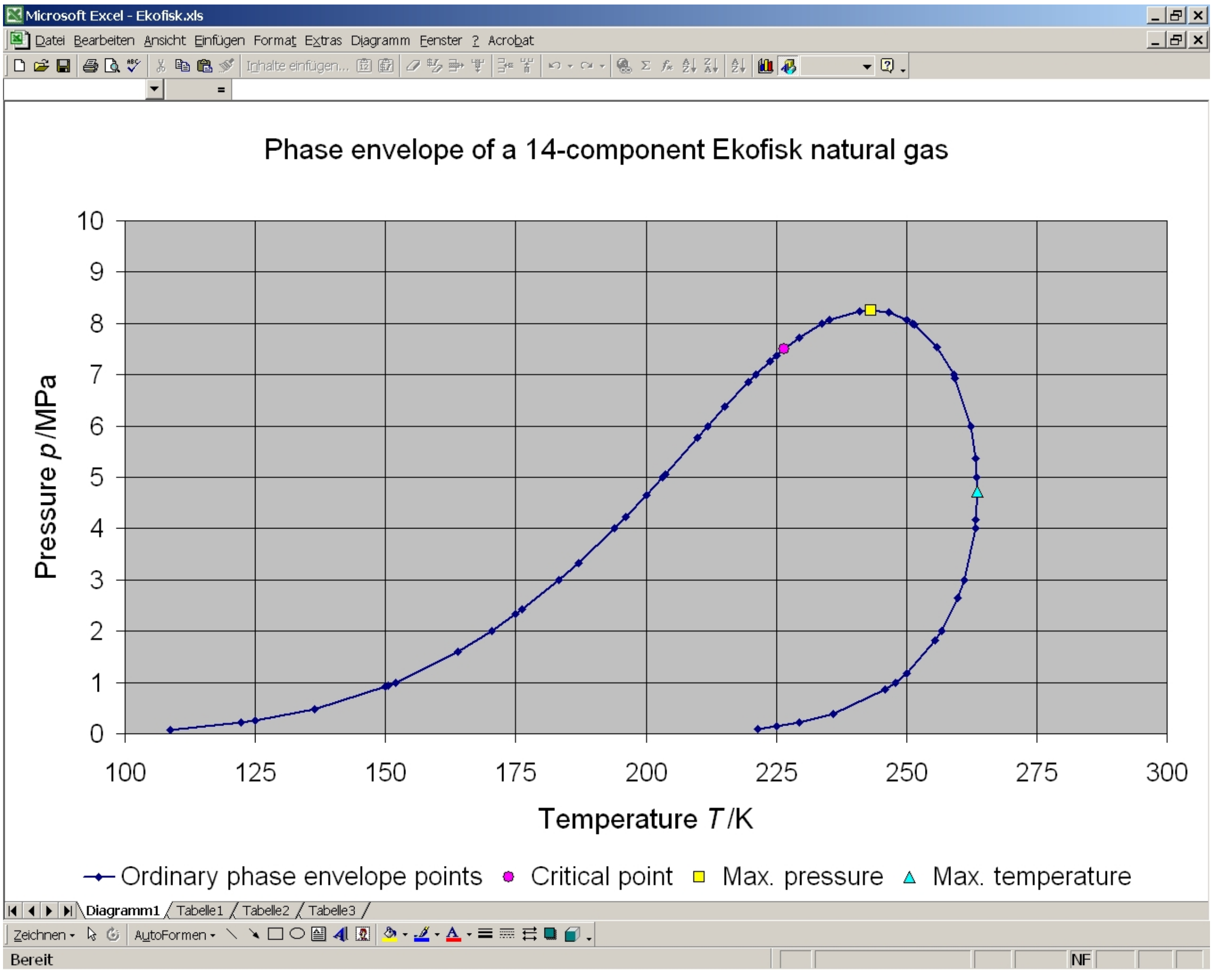
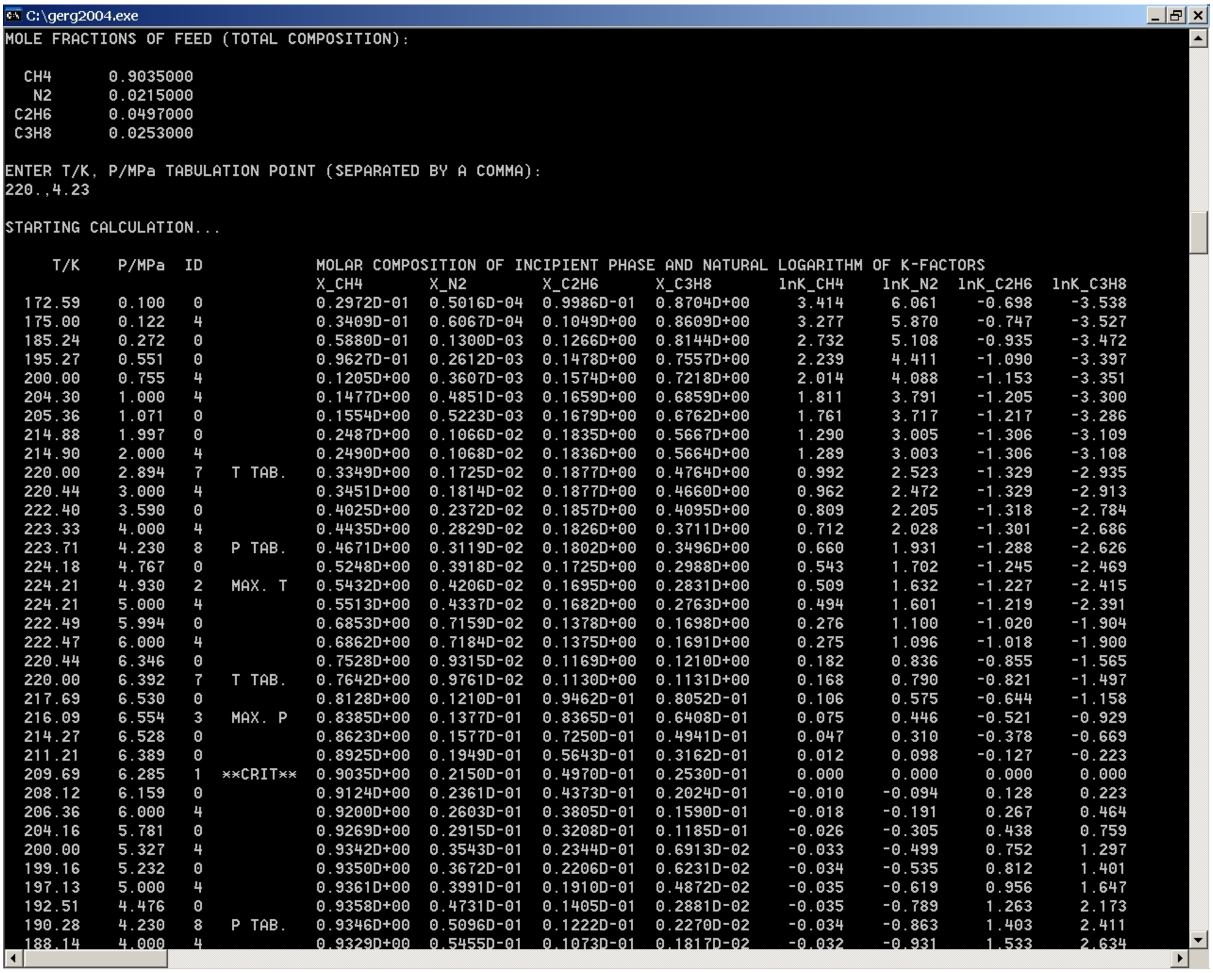


Fig. 7.23 Example screenshot of an Excel plot showing the phase envelope for a 14-component natural gas mixture as calculated from the new equation of state (GERG-2004), Eqs. (7.1) – (7.10), using the pressure-based phase envelope routine exported by the GERG-2004 dynamic link library from within the Excel spreadsheet.



```
MOLE FRACTIONS OF FEED (TOTAL COMPOSITION):

  CH4      0.9035000
   N2      0.0215000
 C2H6      0.0497000
 C3H8      0.0253000

ENTER T/K, P/MPa TABULATION POINT (SEPARATED BY A COMMA):
220.,4.23

STARTING CALCULATION...

     T/K    P/MPa  ID           MOLAR COMPOSITION OF INCIPIENT PHASE AND NATURAL LOGARITHM OF K-FACTORS
                                X_CH4       X_N2        X_C2H6      X_C3H8       lnK_CH4    lnK_N2  lnK_C2H6  lnK_C3H8
  172.59    0.100   0           0.2972D-01  0.5016D-04  0.9986D-01  0.8704D+00     3.414     6.061    -0.698    -3.538
  175.00    0.122   4           0.3409D-01  0.6067D-04  0.1049D+00  0.8609D+00     3.277     5.870    -0.747    -3.527
  185.24    0.272   0           0.5880D-01  0.1300D-03  0.1266D+00  0.8144D+00     2.732     5.108    -0.935    -3.472
  195.27    0.551   0           0.9627D-01  0.2612D-03  0.1478D+00  0.7557D+00     2.239     4.411    -1.090    -3.397
  200.00    0.755   4           0.1205D+00  0.3607D-03  0.1574D+00  0.7218D+00     2.014     4.088    -1.153    -3.351
  204.30    1.000   4           0.1477D+00  0.4851D-03  0.1659D+00  0.6859D+00     1.811     3.791    -1.205    -3.300
  205.36    1.071   0           0.1554D+00  0.5223D-03  0.1679D+00  0.6762D+00     1.761     3.717    -1.217    -3.286
  214.88    1.997   0           0.2487D+00  0.1066D-02  0.1835D+00  0.5667D+00     1.290     3.005    -1.306    -3.109
  214.90    2.000   4           0.2490D+00  0.1068D-02  0.1836D+00  0.5664D+00     1.289     3.003    -1.306    -3.108
  220.00    2.894   7   T TAB.  0.3349D+00  0.1725D-02  0.1877D+00  0.4764D+00     0.992     2.523    -1.329    -2.935
  220.44    3.000   4           0.3451D+00  0.1814D-02  0.1877D+00  0.4660D+00     0.962     2.472    -1.329    -2.913
  222.40    3.590   0           0.4025D+00  0.2372D-02  0.1857D+00  0.4095D+00     0.809     2.205    -1.318    -2.784
  223.33    4.000   4           0.4435D+00  0.2829D-02  0.1826D+00  0.3711D+00     0.712     2.028    -1.301    -2.686
  223.71    4.230   8   P TAB.  0.4671D+00  0.3119D-02  0.1802D+00  0.3496D+00     0.660     1.931    -1.288    -2.626
  224.18    4.767   0           0.5248D+00  0.3918D-02  0.1725D+00  0.2988D+00     0.543     1.702    -1.245    -2.469
  224.21    4.930   2   MAX. T  0.5432D+00  0.4206D-02  0.1695D+00  0.2831D+00     0.509     1.632    -1.227    -2.415
  224.21    5.000   4           0.5513D+00  0.4337D-02  0.1682D+00  0.2763D+00     0.494     1.601    -1.219    -2.391
  222.49    5.994   0           0.6853D+00  0.7159D-02  0.1378D+00  0.1698D+00     0.276     1.100    -1.020    -1.904
  222.47    6.000   4           0.6862D+00  0.7184D-02  0.1375D+00  0.1691D+00     0.275     1.096    -1.018    -1.900
  220.44    6.346   0           0.7528D+00  0.9315D-02  0.1169D+00  0.1210D+00     0.182     0.836    -0.855    -1.565
  220.00    6.392   7   T TAB.  0.7642D+00  0.9761D-02  0.1130D+00  0.1131D+00     0.168     0.790    -0.821    -1.497
  217.69    6.530   0           0.8128D+00  0.1210D-01  0.9462D-01  0.8052D-01     0.106     0.575    -0.644    -1.158
  216.09    6.554   3   MAX. P  0.8385D+00  0.1377D-01  0.8365D-01  0.6408D-01     0.075     0.446    -0.521    -0.929
  214.27    6.528   0           0.8623D+00  0.1577D-01  0.7250D-01  0.4941D-01     0.047     0.310    -0.378    -0.669
  211.21    6.389   0           0.8925D+00  0.1949D-01  0.5643D-01  0.3162D-01     0.012     0.098    -0.127    -0.223
  209.69    6.285   1  **CRIT** 0.9035D+00  0.2150D-01  0.4970D-01  0.2530D-01     0.000     0.000     0.000     0.000
  208.12    6.159   0           0.9124D+00  0.2361D-01  0.4373D-01  0.2024D-01    -0.010    -0.094     0.128     0.223
  206.36    6.000   4           0.9200D+00  0.2603D-01  0.3805D-01  0.1590D-01    -0.018    -0.191     0.267     0.464
  204.16    5.781   0           0.9269D+00  0.2915D-01  0.3208D-01  0.1185D-01    -0.026    -0.305     0.438     0.759
  200.00    5.327   4           0.9342D+00  0.3543D-01  0.2344D-01  0.6913D-02    -0.033    -0.499     0.752     1.297
  199.16    5.232   0           0.9350D+00  0.3672D-01  0.2206D-01  0.6231D-02    -0.034    -0.535     0.812     1.401
  197.13    5.000   4           0.9361D+00  0.3991D-01  0.1910D-01  0.4872D-02    -0.035    -0.619     0.956     1.647
  192.51    4.476   0           0.9358D+00  0.4731D-01  0.1405D-01  0.2881D-02    -0.035    -0.789     1.263     2.173
  190.28    4.230   8   P TAB.  0.9346D+00  0.5096D-01  0.1222D-01  0.2270D-02    -0.034    -0.863     1.403     2.411
  188.14    4.000   4           0.9329D+00  0.5455D-01  0.1073D-01  0.1817D-02    -0.032    -0.931     1.533     2.634
```

Fig. 7.24 Example screenshot demonstrating a phase envelope calculation for a four-component natural gas mixture using the pressure-based phase envelope routine in the executable Fortran program.

8 Comparison of the New Equation of State (GERG-2004) with Experimental Data and Values from Other Equations of State

In this chapter, the quality of the new wide-range equation of state (GERG-2004 formulation or GERG-2004 for short), Eqs. (7.1) – (7.10), is discussed based on comparisons with selected experimental data used in the development of the mixture model and with further experimental data used for the validation of the equation (see Chap. 6). Many figures also show results of the AGA8-DC92 equation of state of Starling and Savidge (1992), which is the current, internationally accepted standard for the calculation of compression factors in the gas phase. Since the AGA8-DC92 equation was developed on the IPTS-68 temperature scale, all temperatures were converted to the IPTS-68 scale before values were calculated from this equation. Values calculated from the cubic equation of state of Peng and Robinson (1976) using binary interaction parameters taken from Knapp *et al.* (1982) are also included in several figures showing comparisons with liquid phase properties, saturated liquid densities, and other vapour-liquid equilibrium properties. For a brief description of these two equations, see Secs. 2.1.1 and 2.1.2. The multi-fluid mixture models developed by Lemmon and Jacobsen (1999), Lemmon *et al.* (2000), Klimeck (2000), and Miyamoto and Watanabe (2003), which are all limited to a smaller number of natural gas components than considered in this work (see Table 5.1), are used for comparison as well.

The GERG-2004 formulation considers mixtures consisting of the 18 natural gas components listed in Table 4.2. The collected experimental data for binary mixtures composed of these components cover a total of 98 binary systems (see Table 6.4). The corresponding huge number of data for the various thermal and caloric properties measured for wide ranges of temperature, pressure, and composition do not allow for a detailed graphical comparison of the new equation of state with all of the available experimental information. Therefore, the representation of data for binary mixtures by the GERG-2004 formulation is exemplified by deviation plots for selected binary systems (limited to certain ranges of temperature, pressure, and composition). The selected data represent, in general, the most accurate measurements available for the respective mixture property. In this context, it should be noted that the actual number of data used for the development and evaluation of the new equation of state far exceeds the selected experimental information shown in the figures in this chapter.

The discussion concerning properties of binary mixtures is divided into three different parts. Section 8.1 focuses on the description of thermal and caloric properties of binary mixtures of methane with the further main natural gas constituents nitrogen, carbon dioxide, and ethane, and the secondary alkanes propane and n-butane. These binary systems are of considerable importance for the description of the thermal and caloric properties of various types of natural gases and similar mixtures. Additional comments and comparisons are given for other binary mixtures consisting of these important natural gas components. Section 8.2 summarises the representation of binary data of mixtures composed of the hydrocarbons ethane, propane, n-butane, isobutane, n-pentane, isopentane, n-hexane, n-heptane, and n-octane. The accurate description of the properties of binary hydrocarbon mixtures is of particular importance in the treatment of liquefied petroleum gas (LPG), the production and refining of light oil, and processes using mixtures of hydrocarbons as alternative refrigerants. Furthermore, the accurate description of binary mixtures consisting of such hydrocarbons also improves the description of rich natural gases and other uncommon mixtures related to natural gases. A collection of other binary systems of the 18 components listed in Table 4.2 that also includes binary mixtures which contain or which are purely composed of hydrogen, oxygen, carbon monoxide, water, helium, and argon is given in Sec. 8.3. For instance, this section includes comparisons with binary data of hydrogen–hydrocarbon mixtures, mixtures of the air components nitrogen, oxygen, and argon, mixtures containing water, and other systems.

Finally, the quality of the new equation of state in the description of various types of natural gases, similar gases, and other multi-component mixtures is discussed in Sec. 8.4.

A statistical comparison of the new equation of state with all of the collected experimental data and values calculated from other equations of state is given in Tables A2.1, A2.2, and A2.4 of the appendix. The values for the statistical quantities are determined by comparisons of property values calculated from the respective equation of state to experimental data. The percentage deviation in any property z is defined here according to

$$\Delta z_m = \left[\frac{z_{\text{exp}} - z_{\text{calc}}}{z_{\text{exp}}} \right]_m , \tag{8.1}$$

and the average absolute deviation can be written as

$$\text{AAD} = \frac{1}{M} \sum_{m=1}^{M} \left| \Delta z_m \right| , \tag{8.2}$$

where M is the number of data points. The definitions of the further statistical quantities used in this work, along with further information on the calculation of these values, are given in the appendix [see Eqs. (A2.3) – (A2.5)].

Statistical comparisons only provide averaged information on the quality of an equation of state regardless of the temperature, pressure, density, or composition dependence of the deviations. Therefore, the graphical comparison of deviations between experimental data and values calculated from an equation of state along isotherms, isobars, isochores, or isopleths is always preferable for the assessment of the quality of an equation in the description of thermodynamic properties. The baseline in all of the following deviation plots is the new equation of state, GERG-2004, unless otherwise explicitly stated. When values calculated from other equations of state are additionally displayed (together with the experimental data and the new equation of state as the baseline), they are calculated for the lowest temperature written at the top of each small plot, unless otherwise indicated. Data points shown at the upper or lower vertical limits of the graph indicate that the points are off scale. In the following text, absolute values of the deviations are used in the discussions of maximum errors or systematic offsets.

In order to retain a certain level of transparency, the comparisons in the homogeneous region of binary mixtures, showing deviations of values calculated from other equations of state together with the experimental data and the new equation of state as the baseline, are limited to a number of selected mixture compositions. Detailed statistical comparisons for distinct binary mixture compositions of homogeneous properties are given in Table A2.1 of the appendix.

8.1 The Representation of Thermal and Caloric Properties of Selected Binary Mixtures of the Natural Gas Main Constituents

As described in Sec. 7.10, the properties of binary mixtures of methane with the additional main natural gas components nitrogen, carbon dioxide, and ethane, or with the secondary alkanes propane and n-butane, are described by using adjusted reducing functions along with binary specific or generalised departure functions. The same is true for other important binary mixtures consisting of the main natural gas components nitrogen, carbon dioxide, and ethane, and the secondary alkanes propane, n-butane, and isobutane as summarised in Table 7.16. The comparatively complex development of these equations enables the representation of even the best measurements to within their low experimental uncertainty (see Table 6.2). The resulting accuracy of the binary equations for the description of thermal and caloric properties for different fluid regions is described in the following subsections.

8.1.1 The $p\rho T$ Relation in the Homogeneous Region

To fulfil the high demands on the accuracy in the description of the $p\rho T$ relation of natural gases and similar mixtures in standard natural gas applications (gas metering, transmission, and storage; see Chap. 3), the accurate representation of binary $p\rho T$ data at supercritical temperatures by the new equation of state is of considerable importance. Advanced natural gas applications dealing, for example, with liquefied natural gas (LNG) require in addition the accurate description of the $p\rho T$ relation in the liquid phase of binary and multi-component mixtures of the natural gas main constituents (and further hydrocarbon components; see also Secs. 8.2.1 and 8.4.3). Improvements achieved for binary mixtures, in general, also result in an improved description of the properties of natural gases, similar gases, and other multi-component mixtures (compared to the previous equations of state) as will be shown in Sec. 8.4.

Methane–Nitrogen and Methane–Ethane

Experimental measurements of gas phase densities for the binary mixture methane–nitrogen and their percentage deviations from the GERG-2004 formulation are shown in Fig. 8.1 for temperatures ranging from 240 K to 400 K. The selected data cover a large range of molar concentrations from 10% to 75% of nitrogen. The $p\rho T$ data recently published by Chamorro *et al.* (2006) for 10% and 20% nitrogen represent the most accurate measurements in the gas phase. The data were measured using a single-sinker densimeter and their uncertainty is estimated to be $\Delta\rho/\rho \leq 0.03\%$. The uncertainty in density of the measurements of Jaeschke and Hinze (1991), covering molar concentrations from 20% to 75% of nitrogen and temperatures ranging from 270 K to 353 K, amounts to approximately less than 0.07%. For the data of Haynes and McCarty (1983) and Straty and Diller (1980), the uncertainty in density is assumed to be about (0.1 – 0.2)%. The deviation plots clearly demonstrate that the new equation of state is able to represent all of the data to within their experimental uncertainty for all temperatures and at pressures up to 30 MPa[77], independently of the mixture composition. Important improvements compared to the AGA8-DC92 equation of state and the multi-fluid mixture model of Lemmon and Jacobsen (1999) are achieved at temperatures below 275 K. At 240 K, the deviations of values calculated from the AGA8-DC92 equation for nitrogen concentrations of 10% (dashed line), 20% (dot-dashed line), and 68% (dot-dot-dashed line) clearly exceed the uncertainty of the measurements with deviations of up to 0.14% (10% nitrogen), up to 0.15% (20% nitrogen), and more than 0.2% (68% nitrogen, $p > 30$ MPa). Even at pipeline conditions (for pressures below 12 MPa) the deviations amount to more than 0.1% for the AGA8-DC92 equation of state. At 270 K, the AGA8-DC92 equation is also not able to represent the different data sets as accurately as the GERG-2004 formulation. The composition dependence of the deviations is particularly of concern. Values calculated from the AGA8-DC92 equation for the mixture containing 68% of nitrogen deviate by more than 0.1% from the corresponding measurements of Straty and Diller (1980) at elevated pressures, and values calculated for the mixtures containing 10% and 20% of nitrogen do not agree within the experimental uncertainty of the very accurate data of Chamorro *et al.* (2006). This is also true for the multi-fluid mixture model of Lemmon and Jacobsen (1999) as shown for the mixture containing 20% of nitrogen (dot-dot-dashed-dot-dashed line). It should be noted, however, here (and also for other comparisons shown in the following) that the recent measurements of Chamorro *et al.* (2006) were not available at the time the previous equations were developed (preliminary measurements on 20% nitrogen were used for the development of the new equation of state, and the results on 10% nitrogen were available prior to the publication of the data, but only used for comparison). At higher temperatures of 350 K and above, all equations yield quite similar results.

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[77] Data measured by Straty and Diller (1980) at pressures above 30 MPa are described by the new equation of state within the experimental uncertainty as well.

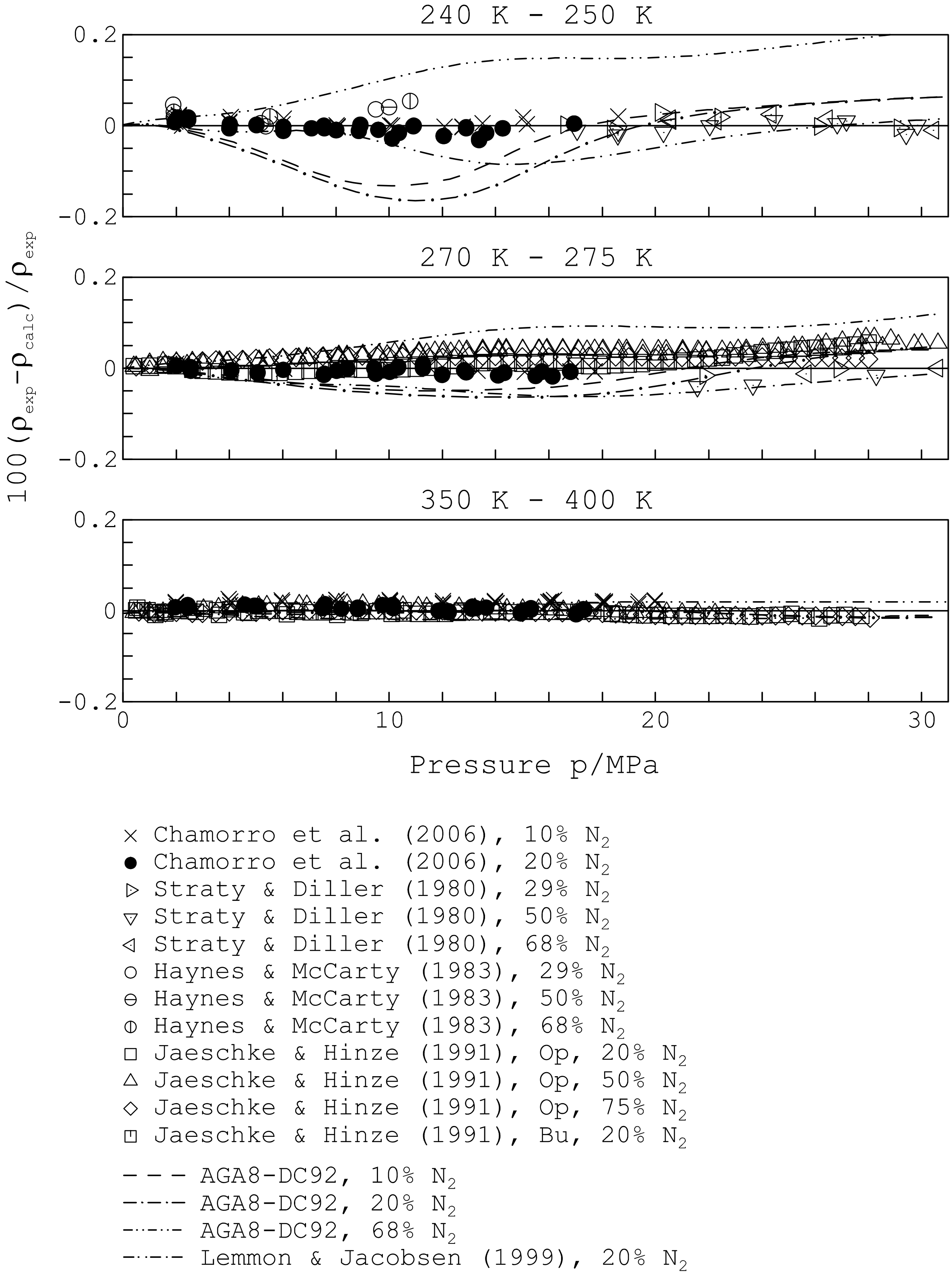

Fig. 8.1 Percentage density deviations of selected experimental $p\rho T$ data for the methane–nitrogen binary mixture from values calculated from the new equation of state (GERG-2004), Eqs. (7.1) – (7.10). Values calculated from the AGA8-DC92 equation of Starling and Savidge (1992) and the mixture model of Lemmon and Jacobsen (1999) are plotted for comparison. Bu: Burnett apparatus, Op: optical interferometry method.

Experimental $p\rho T$ data for the binary mixture methane–ethane are displayed in the deviation plots of Figs. 8.2 and 8.3 for temperatures ranging from 233 K to 350 K, pressures up to 30 MPa, and ethane concentrations of 4% to 30%. The data measured by Ruhrgas (1990) using an optical interferometry method (Op) and a Burnett apparatus (Bu) cover temperatures from 270 K to 350 K. The uncertainty in density of these measurements amounts to $\Delta\rho/\rho \leq 0.07\%$, similar to the data of Jaeschke and Hinze (1991) for the methane–nitrogen binary mixture using the same experimental equipment. The recent measurements of Wöll and El Hawary (2003) cover temperatures down to 233 K at ethane concentrations of 8% and 15%. The data were measured using a combined viscometer-densimeter apparatus. The uncertainty in density of these measurements is estimated to be $(0.05 - 0.1)\%$ with an increased uncertainty at pressures below 5 MPa. Except for the $p\rho T$ data measured by Wöll and El Hawary (2003) for the mixture containing 15% of ethane at the 233 K isotherm and pressures above 10 MPa (see Fig. 8.3), all of the measurements are represented by the GERG-2004 formulation well within their experimental uncertainty. This also includes the data of Ruhrgas (1990) for the mixture containing 30% of ethane for which the AGA8-DC92 equation yields a maximum deviation of 0.3% (see Table A2.1 of the appendix). The reduced temperature T/T_r for the mixture containing 30% of ethane at 270 K amounts to 1.19, which is actually in agreement with (slightly below) the lower limit of the reduced temperature range important in standard natural gas applications (see also Sec. 4.8). Considerably lower values of reduced temperatures are obtained for the data of Wöll and El Hawary (2003) at 233 K for the mixtures containing 8% ($T/T_\mathrm{r} = 1.16$) and 15% ($T/T_\mathrm{r} = 1.11$) of ethane. As no other accurate experimental information is available at this low reduced temperature, the representation of the 15% ethane data at 233 K with deviations of up to 0.15% at pressures above 10 MPa is quite satisfactory.

Similar to the previously discussed methane–nitrogen binary mixture, significant improvements are also achieved for the methane–ethane mixture at temperatures $T \leq 270$ K as compared to other equations of state. While the AGA8-DC92 equation is able to represent the data for 8% of ethane to within their experimental uncertainty for all measured temperatures, the equation, however, fails to accurately describe the $p\rho T$ data of mixtures containing higher fractions of ethane at temperatures of 270 K and below, as shown for the mixtures containing 16% (see Fig. 8.2) and 15% (see Fig. 8.3) of ethane. At 233 K and 15% ethane, the deviations obtained from the AGA8-DC92 equation even exceed values of 0.3% at pressures above 8 MPa. Deviations between the measurements for ethane mole fractions of 8% and higher and values calculated from the mixture model of Lemmon and Jacobsen (1999) exceed the experimental uncertainty of the data at temperatures of 270 K and lower, but, in contrast to the AGA8-DC92 equation, the deviations are within ±0.3%.

For the binary mixtures methane–nitrogen and methane–ethane, accurate $p\rho T$ data were measured in the liquid phase covering wide ranges of pressure and composition. Figure 8.4

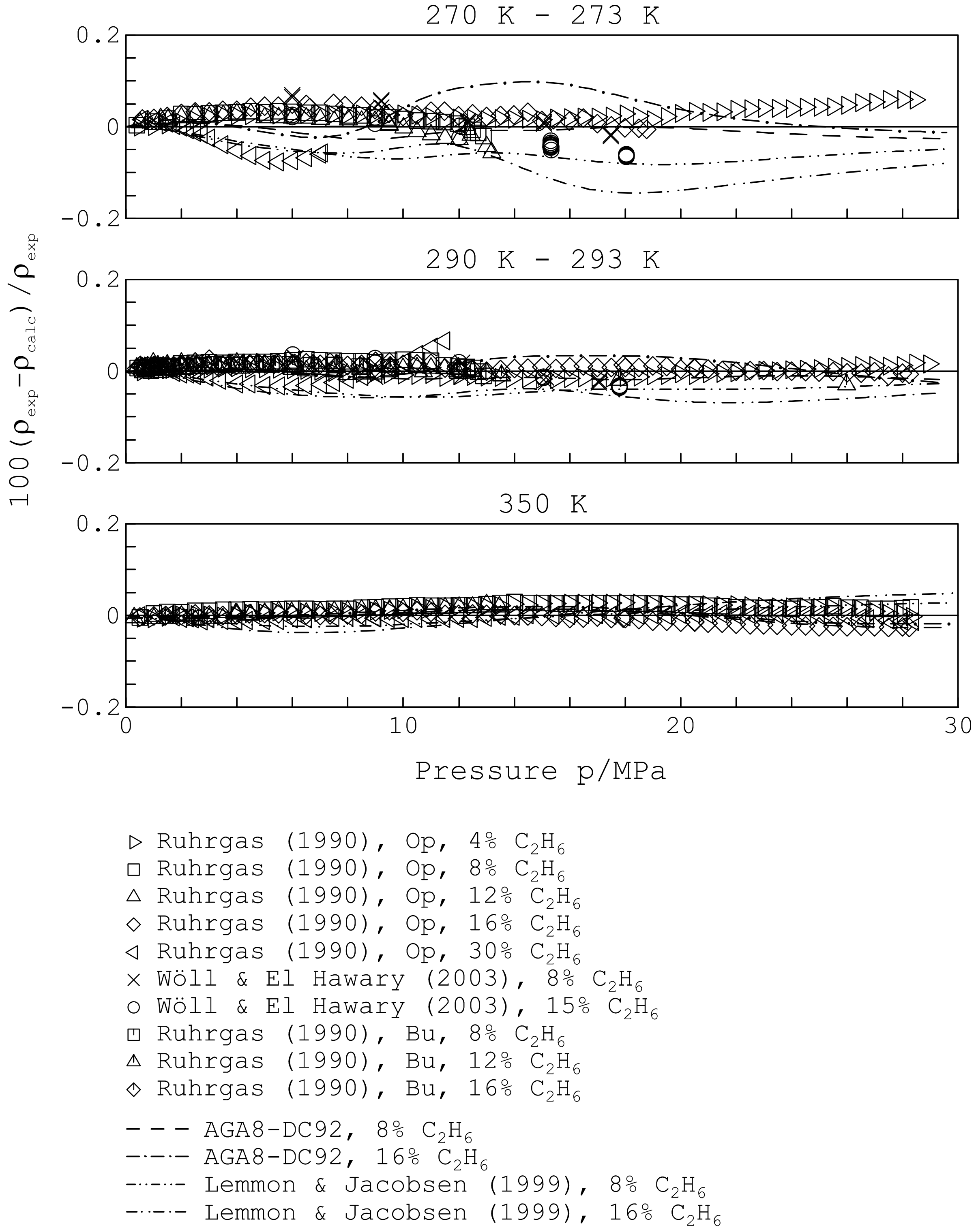

Fig. 8.2 Percentage density deviations of selected experimental $p\rho T$ data for the methane–ethane binary mixture from values calculated from the new equation of state (GERG-2004), Eqs. (7.1) – (7.10). Values calculated from the AGA8-DC92 equation of Starling and Savidge (1992) and the mixture model of Lemmon and Jacobsen (1999) are plotted for comparison. Bu: Burnett apparatus, Op: optical interferometry method.

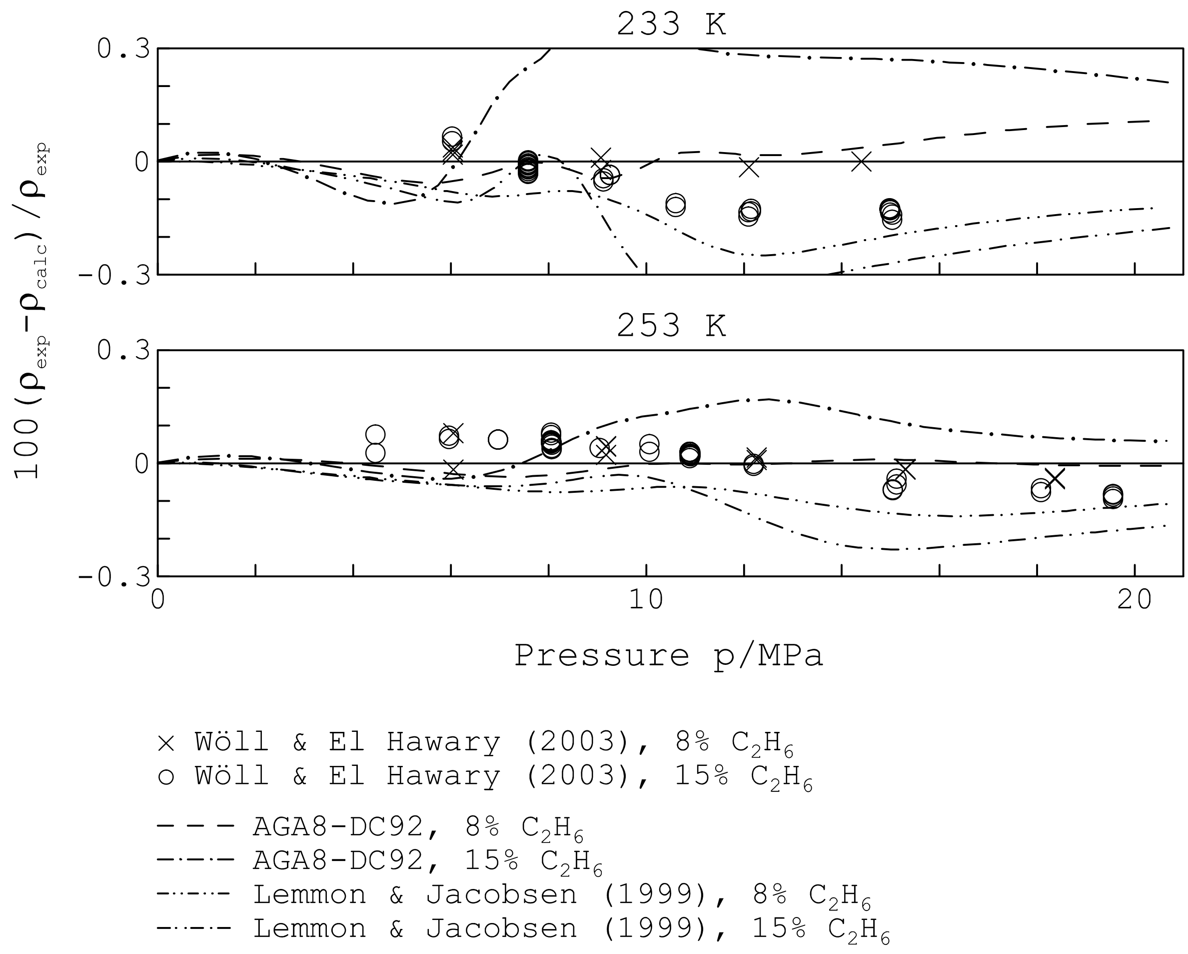

Fig. 8.3 Percentage density deviations of selected experimental $p\rho T$ data measured by Wöll and El Hawary (2003) for the methane–ethane binary mixture from values calculated from the new equation of state (GERG-2004), Eqs. (7.1) – (7.10). Values calculated from the AGA8-DC92 equation of Starling and Savidge (1992) and the mixture model of Lemmon and Jacobsen (1999) are plotted for comparison.

shows deviations of these data from values calculated with the new mixture model over temperature ranges that are important for applications with liquefied natural gas (LNG). The comparisons for the binary system methane–nitrogen are based on the data of Straty and Diller (1980) and Rodosevich and Miller (1973). While the data of Rodosevich and Miller (1973) were measured in the vicinity of the vapour-liquid phase boundary at molar concentrations of 5% and 16% of nitrogen and temperatures of 91 K to 115 K, the data of Straty and Diller (1980) cover pressures up to about 35 MPa at nitrogen mole fractions of 29%, 50%, and 68% over a wide range of temperature down to 82 K. The GERG-2004 formulation represents all of the selected data with very low deviations of clearly less than ±0.15% (generally within ±0.1%). Similar results are exemplified by the deviation plots in Fig. 8.4 for the binary system methane–ethane. The data of Rodosevich and Miller (1973) were measured over virtually the same temperature range as for the methane–nitrogen mixture and also near the phase boundary, but covering a wider range of compositions. The measurements of Haynes *et al.* (1985) cover pressures up to about 35 MPa at ethane mole

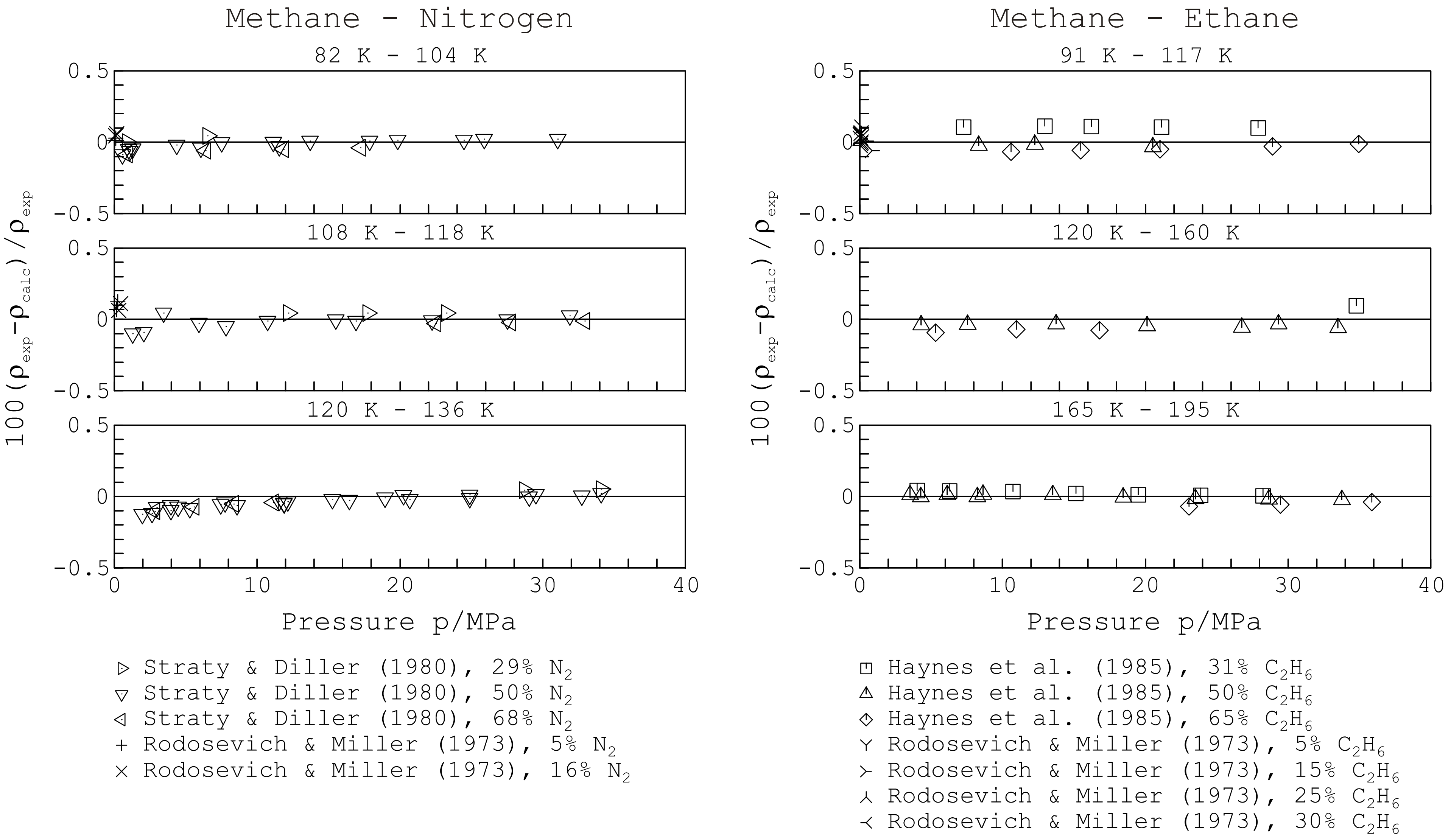

Fig. 8.4 Percentage density deviations of selected experimental $p\rho T$ data for the methane–nitrogen and methane–ethane binary mixtures from values calculated from the new equation of state (GERG-2004), Eqs. (7.1) – (7.10).

fractions of 31%, 50%, and 65% and temperatures down to 100 K. As with the methane–nitrogen binary system, all of the selected methane–ethane binary data are represented by the new equation of state to within about ±0.1%.

The GERG-2004 formulation achieves a very accurate description of the $p\rho T$ relation in the liquid phase as will be emphasised in several passages of this chapter. As mentioned in Sec. 2.1.1, the AGA8-DC92 equation of state is not valid in the liquid phase. Values calculated from cubic equations of state, which are still widely used in many technical applications, deviate from the measurements by several percents. Compared to the new equation of state, only the mixture model of Lemmon and Jacobsen (1999) yields an acceptable accuracy in the description of liquid phase densities. Values calculated from this model deviate from the measurements shown in Fig. 8.4 by up to 0.3%.

Methane–Carbon Dioxide

Even though a number of measurements from several different authors is available for the $p\rho T$ relation of the binary system methane–carbon dioxide (see Table 6.4 and Table A2.1 of the appendix), the quality and extent of the data over the range important for standard natural gas applications is scarce compared to the methane–nitrogen and methane–ethane binary mixtures (and also compared to other binary systems consisting of the natural gas main constituents). Several data sets, such as the data of Gasunie (1990), are limited to a comparatively narrow temperature and pressure range, which complicates the development of an accurate, wide-ranging equation of state. The recent and most accurate data of Glos *et al.* (2000) measured at Ruhrgas for 6% and 15% of carbon dioxide using a two-sinker densimeter significantly improved the data situation for an important but rather small range of temperatures (273 K to 290 K) and pressures (up to 10 MPa). Accurate $p\rho T$ data over wider ranges of temperature and pressure were measured by Wöll and El Hawary (2003) for carbon dioxide concentrations of 8% and 15%. These most recent data cover temperatures from 233 K to 373 K at pressures up to 18 MPa (and at densities up to 15 $\mathrm{mol \cdot dm^{-3}}$) and represent the only available accurate experimental information for the considered mixture compositions at these extended temperature and pressure conditions. These data are located near the critical region and provide valuable information on the strong curvature in this region. Further accurate gas phase densities were reported by Ruhrgas (1990). Although the data cover the temperature range from 270 K to 350 K at pressures up to 28 MPa, the data are of minor importance for standard natural gas applications because they were only measured for a comparatively high mole fraction of carbon dioxide of 31%. The data are, however, important for the extended range of application.

The GERG-2004 formulation achieves substantial improvements, especially at temperatures below 300 K, compared to the AGA8-DC92 equation and the multi-fluid mixture models of Lemmon and Jacobsen (1999) and Klimeck (2000), as shown in Fig. 8.5. All of the accurate gas phase and gas-like supercritical densities, even at comparatively low temperatures down to 233 K, are described by the new equation of state well within their experimental uncertainty, which is estimated to be less than 0.03% for the measurements of Glos *et al.* (2000), and (0.05 – 0.1)% for the data of Wöll and El Hawary (2003) (again with an increased uncertainty at pressures below 5 MPa). The uncertainty in density of the data of Gasunie (1990) is in general not better than 0.1%. For the data measured by Ruhrgas (1990), the uncertainty in density is assumed to be less than (0.07 – 0.1)% with a slightly higher uncertainty for this mixture for the measurements at elevated pressures. However, all of the previous equations of state fail to accurately describe the data as displayed in Fig. 8.5 for 8% and 15% of carbon dioxide and show deviations from the measurements below 273 K which far exceed values of 0.3%. The model of Lemmon and Jacobsen (1999) even deviates from the measurements for 15% carbon dioxide at 293 K by up to 0.3% at about 17 MPa.

In the range relevant for standard natural gas applications, experimental gas phase densities for the methane–carbon dioxide binary mixture are limited to pressures below 20 MPa. In order to be able to accurately describe the $p\rho T$ relation of natural gas mixtures containing higher fractions of carbon dioxide at pressures above 20 MPa, calculated data were additionally used in the gas phase for the development of the new binary equation for the methane–carbon dioxide mixture at temperatures from 233 K to 453 K and pressures up to 31 MPa. These data were generated from a preliminary equation developed using the available experimental measurements and values calculated from accurate natural gas data for the mixture “GU2”, which contains a comparatively high mole fraction of carbon dioxide of about 8%. Due to this comparatively high carbon dioxide concentration, the equation for the binary system methane–carbon dioxide significantly contributes to the description of this carbon dioxide rich natural gas by the new mixture model. The “correct” contribution can be determined directly from the multi-fluid mixture model by applying a (simple) corresponding states approach[78].

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[78] Assuming that all other binary equations behave accurately at the reduced properties δ and τ of the multi-component natural gas mixture, the contribution of the δ-derivative of the part of the departure function only depending on δ and τ, $\partial\alpha^{\mathrm{r}}_{ij}(\delta,\tau)/\partial\delta$, can be calculated from Eq. (7.12) for one binary subsystem *i–j* (here methane–carbon dioxide), using the experimental information for the $p\rho T$ data of the respective natural gas for the left-hand term in Eq. (7.12) according to $\alpha^{\mathrm{r}}_{\delta} = (Z_{\mathrm{exp}} - 1)/\delta_{\mathrm{exp}}$, where $Z_{\mathrm{exp}} = p_{\mathrm{exp}}/(\rho_{\mathrm{exp}} R T_{\mathrm{exp}})$ and $\delta_{\mathrm{exp}} = \rho_{\mathrm{exp}}/\rho_{\mathrm{r}}(\bar{x}_{\mathrm{exp}})$. Choosing a binary composition for which artificial data is desired, the pressures for the set of reduced mixture properties δ_{exp} and τ_{exp} obtained from the natural gas data follow from $p = \rho R T (1 + \delta_{\mathrm{exp}}\,\alpha^{\mathrm{r}}_{\delta})$, with $\alpha^{\mathrm{r}}_{\delta} = \alpha^{\mathrm{r}}_{\delta}(\delta_{\mathrm{exp}}, \tau_{\mathrm{exp}}, \bar{x})$ now calculated from Eq. (7.12) for the binary mixture. The corresponding binary mixture densities and temperatures follow from Eq. (7.4). In a similar way, the shape of a departure function, or rather its derivative with respect to δ, $\partial\alpha^{\mathrm{r}}_{ij}(\delta,\tau)/\partial\delta$, required for an accurate description of the $p\rho T$ relation of a binary mixture can be determined from accurate experimental binary data, enabling the development of a suitable functional form for α^{r}_{ij} (see also Secs. 5.3.4 and 7.11). This method also works for isochoric heat capacities providing the approximate shape of $\partial^2\alpha^{\mathrm{r}}_{ij}(\delta,\tau)/\partial\tau^2$.

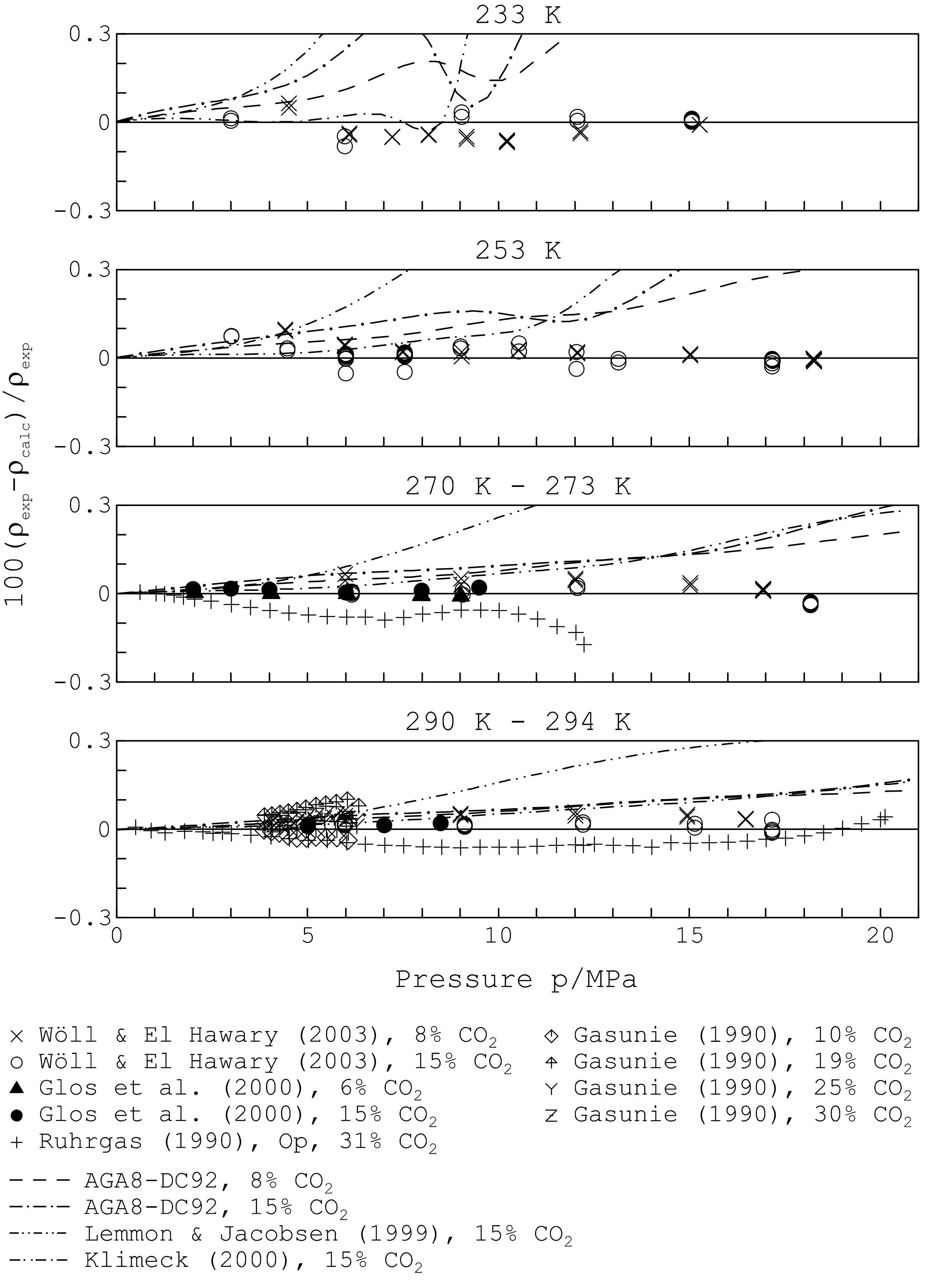

Fig. 8.5 Percentage density deviations of selected experimental $p\rho T$ data for the methane–carbon dioxide binary mixture from values calculated from the new equation of state (GERG-2004), Eqs. (7.1) – (7.10). Values calculated from the AGA8-DC92 equation of Starling and Savidge (1992) and the mixture models of Lemmon and Jacobsen (1999) and Klimeck (2000) are plotted for comparison at temperatures of 233 K, 253 K, 273 K, and 293 K. Op: optical interferometry method.

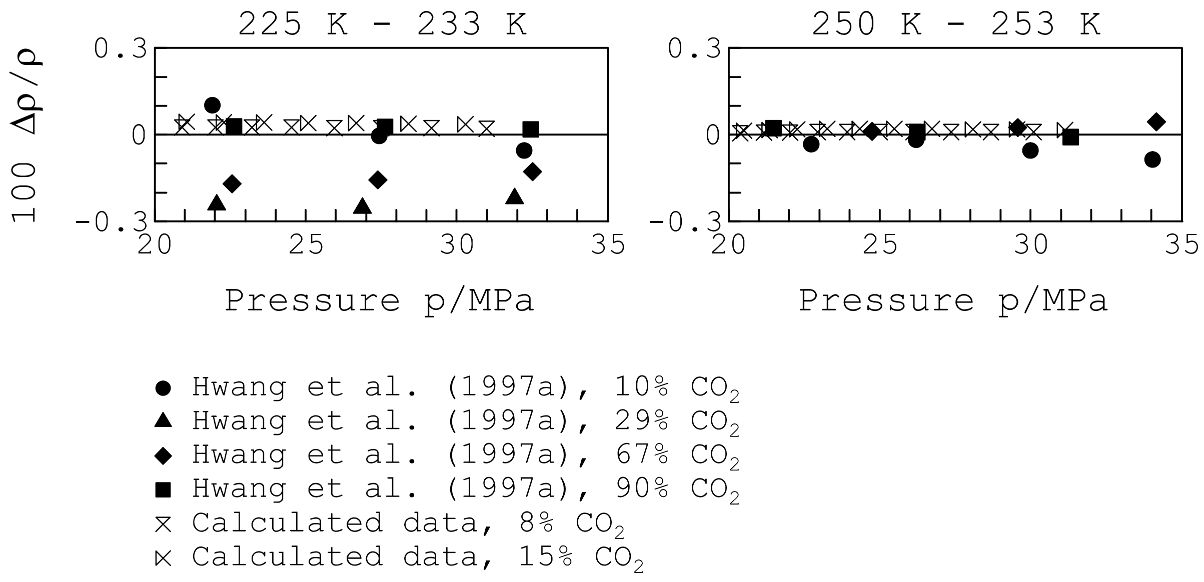

Fig. 8.6 Percentage density deviations $100\Delta\rho/\rho = 100(\rho_{\mathrm{exp}} - \rho_{\mathrm{calc}})/\rho_{\mathrm{exp}}$ of selected experimental $p\rho T$ data measured by Hwang *et al.* (1997a) for the methane–carbon dioxide binary mixture from values calculated from the new equation of state (GERG-2004), Eqs. (7.1) – (7.10). Calculated data of a preliminary equation of state are also included, see text.

Deviation plots showing the experimental measurements of Hwang *et al.* (1997a) for carbon dioxide mole fractions of 10% to 90%, and the calculated gas phase densities at molar concentrations of 8% and 15% are displayed in Fig. 8.6 for temperatures ranging from 225 K to 253 K and at pressures above 20 MPa. The experimental measurements are represented by the GERG-2004 formulation to within ±(0.1 – 0.3)%, which is in agreement with the assumed uncertainty of the data[79]. Furthermore, it is important to note that only the data for 10% of carbon dioxide represent gas phase densities at the measured temperatures, whereas the data for carbon dioxide concentrations of 29%, 67%, and 90% are liquid phase densities. Comparisons of the artificial data at pressures below 20 MPa with the available accurate gas phase densities show that the artificial data are in comparatively good agreement with the measurements. Therefore, the uncertainty in gas phase density of the new equation of state at pressures above 20 MPa is very likely to be less than (0.1 – 0.2)%, which can, however, not be proved until accurate experimental information is available at elevated pressures.

Methane–Propane and Methane–n-Butane

Deviations of selected experimental measurements for gas phase densities of the binary mixtures methane–propane and methane–n-butane from the GERG-2004 formulation are shown in Fig. 8.7. The data were measured by Ruhrgas (1990) for 7% of propane and 1.5% of

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[79] Comparisons with other measurements (known to be very accurate) show that these and other data measured using a pycnometer method are associated with an uncertainty clearly higher than 0.1%, although claimed to be less than 0.1% by the authors.

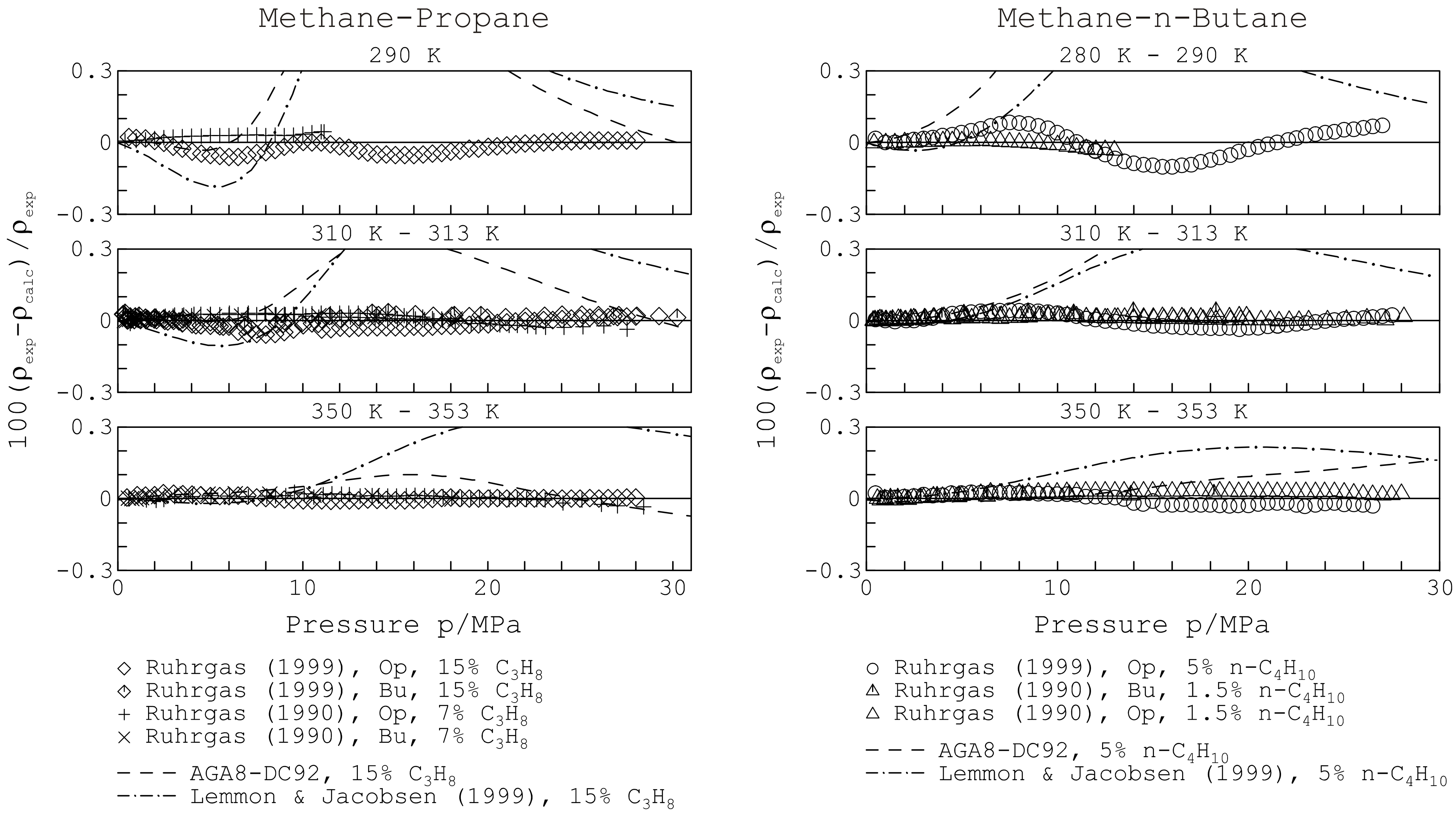

Fig. 8.7 Percentage density deviations of selected experimental $p\rho T$ data for the methane–propane and methane–n-butane binary mixtures from values calculated from the new equation of state (GERG-2004), Eqs. (7.1) – (7.10). Values calculated from the AGA8-DC92 equation of Starling and Savidge (1992) and the mixture model of Lemmon and Jacobsen (1999) are plotted for comparison. Bu: Burnett apparatus, Op: optical interferometry method.

n-butane, and by Ruhrgas (1999) for 15% of propane and 5% of n-butane using an optical interferometry method (Op) and a Burnett apparatus (Bu). The data cover temperatures from 280 K to 353 K for methane–propane and 270 K to 353 K for methane–n-butane at pressures up to 30 MPa. The new equation of state represents all of the data to within ±0.1%. Most of the measurements are described with deviations of clearly less than ±0.07%. In contrast to the GERG-2004 formulation, the AGA8-DC92 equation of state and the model of Lemmon and Jacobsen (1999) are not able to accurately describe the data. Both previous equations deviate from the measurements of the two binary mixtures at a propane mole fraction of 15% and a n-butane mole fraction of 5% by more than 0.3% even at moderate temperatures around 310 K. Considerably higher deviations between the data and values calculated from the previous equations of state are observed at lower temperatures, exceeding 1% for the methane–n-butane binary mixture in the case of the AGA8-DC92 equation of state. Even at higher temperatures around 350 K and elevated pressures, values calculated from the model of Lemmon and Jacobsen (1999) deviate from the measurements by more than 0.3% for the methane–propane mixture and more than 0.2% for the methane–n-butane mixture.

Aside from the improvements achieved in the description of the $p\rho T$ relation of the selected examples mentioned above, the description of the $p\rho T$ relation of other binary mixtures composed of the natural gas main constituents, such as nitrogen–carbon dioxide and nitrogen–ethane, is also improved compared to the previous equations of state. Moreover, data available at pressures above 30 MPa or 40 MPa are accurately described as well. Reamer *et al.* [Reamer *et al.* (1944) (CH_4–CO_2), (1945) (CO_2–C_2H_6), (1947) (CH_4–n-C_4H_{10}), (1950) (CH_4–C_3H_8), (1951) (CO_2–C_3H_8), (1952a) (N_2–C_2H_6)] and Seitz *et al.* [Seitz and Blencoe (1996) and Seitz *et al.* (1996a) (CH_4–N_2, CH_4–CO_2, N_2–CO_2)] measured data at pressures up to 69 MPa (Reamer *et al.*) and 100 MPa (Seitz *et al.*), covering wide ranges of composition at temperatures up to 511 K (Reamer *et al.*) and 673 K (Seitz *et al.*). Comparisons with measurements known to be very accurate show that data from these authors are associated with a considerably higher uncertainty than the available best measurements. Typical deviations between the data and values calculated from the GERG-2004 formulation are within ±(0.5 – 1)%, which agrees well with the assumed (from experience) uncertainty of the measurements.

8.1.2 Caloric Properties in the Homogeneous Region

Accurate data for caloric properties of binary mixtures, suitable for discussion, are primarily available for speeds of sound and enthalpy differences in the gas phase. Isochoric and isobaric heat capacities, which also cover the liquid phase, are available for only a few binary mixtures.

Methane–Nitrogen

For the binary mixture methane–nitrogen, very accurate speeds of sound were reported by Trusler (2000) and Estela-Uribe (1999), recently published together by Estela-Uribe *et al.* (2006), covering temperatures from 220 K to 400 K at pressures up to 30 MPa for nitrogen concentrations of 10% and 20%, and temperatures from 170 K to 400 K at pressures up to 16 MPa for 54% of nitrogen. The mixture containing 54% of nitrogen was studied along pseudo-isochores at molar densities between 0.2 $\mathrm{mol \cdot dm^{-3}}$ and 5 $\mathrm{mol \cdot dm^{-3}}$. The data cover large reduced temperature ranges of $1.20 \leq T/T_\mathrm{r} \leq 2.19$ for 10% nitrogen, $1.25 \leq T/T_\mathrm{r} \leq 2.28$ for 20% nitrogen, and $1.12 \leq T/T_\mathrm{r} \leq 2.62$ for 54% nitrogen[80]. The uncertainty in speed of sound is estimated to be less than (0.02 – 0.05)% for the measurements at nitrogen mole fractions of 10% and 20%, and for almost all of the data measured for 54% of nitrogen. Additional accurate speed of sound data were measured by Younglove *et al.* (1993) for nitrogen mole fractions of 5%, 15%, and 29% at temperatures from 250 K to 350 K and pressures up to 11 MPa. The uncertainty in speed of sound of these data is estimated to be higher (≤ 0.1%) than that of the measurements of Estela-Uribe *et al.* (2006).

The GERG-2004 formulation represents (almost) all of the measurements with very low deviations of less than ±0.05%, regardless of the mixture composition, as shown in the deviation plots of Fig. 8.8. The very accurate data sets of Estela-Uribe *et al.* (2006) are described by the new equation of state well within their low experimental uncertainty. The few data points (measured for 54% of nitrogen) that exceed deviations of 0.05% all lie along the pseudo-isochore at the highest molar density and are associated with an increased uncertainty as reported by the authors.

Values calculated from the AGA8-DC92 equation deviate from the measurements of Estela-Uribe *et al.* (2006) for nitrogen mole fractions of 10% and 20% at 220 K by clearly more than 0.1% at pressures around 11 MPa and above 17 MPa (with a maximum deviation of 0.4% for 20% nitrogen at about 30 MPa). Even at a considerably higher temperature of 300 K and moderate pressures, the AGA8-DC92 equation is not able to describe all of the data to within their experimental uncertainty. The model of Lemmon and Jacobsen (1999) significantly deviates from the measurements in a wide range of pressures, reaching maximum deviations of about 0.3% for 10% nitrogen around 15 MPa for 220 K, and about 0.4% for 20% nitrogen around 16 MPa for the same temperature. Even at higher temperatures of 300 K, the deviations calculated from this model exceed values of two to four times the experimental uncertainty of the data.

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[80] With regard to the targeted uncertainty in the description of speeds of sound (and other caloric properties) of multi-component natural gas mixtures at temperatures down to 250 K (see Chap. 3 and also Sec. 8.4.2), it should be noted that the measurements for 10% and 20% nitrogen at the 220 K isotherm are especially of considerable importance for the accurate description of the speed of sound of natural gases at temperatures around 250 K.

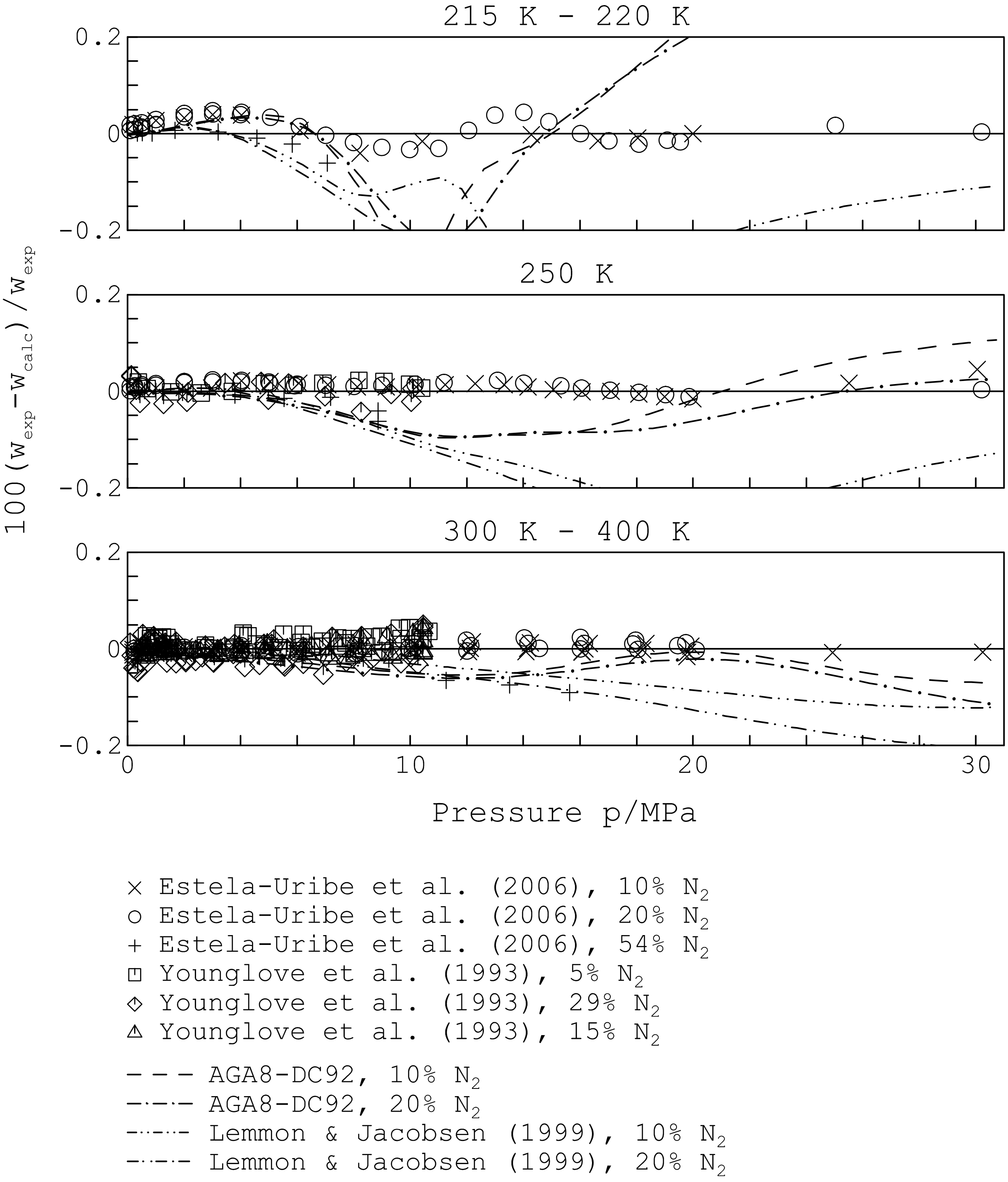

Fig. 8.8 Percentage deviations of selected experimental speed of sound data for the methane–nitrogen binary mixture from values calculated from the new equation of state (GERG-2004), Eqs. (7.1) – (7.10). Values calculated from the AGA8-DC92 equation of Starling and Savidge (1992) and the mixture model of Lemmon and Jacobsen (1999) are plotted for comparison at temperatures of 220 K, 250 K, and 300 K.

The temperature and pressure ranges covered by the speeds of sound of Estela-Uribe *et al.* (2006) for nitrogen concentrations of 10% and 20% include those covered by the very accurate $p\rho T$ data of Chamorro *et al.* (2006), measured at virtually the same mixture compositions (see Sec. 8.1.1). The data sets of these two sources are represented by the new equation of state well within their low experimental uncertainty, indicating a very high degree of thermodynamic consistency (for different thermodynamic properties).

Methane–Ethane

Experimental measurements of gas phase speeds of sound for the binary mixture methane–ethane and their percentage deviations from the GERG-2004 formulation for temperatures ranging from 250 K to 350 K are shown in Fig. 8.9. The selected data cover ethane mole fractions from 5% to 31%. The very accurate and wide ranging data set measured by Costa Gomes and Trusler (1998) for 15% ethane covers pressures up to 20 MPa. According to the authors, the uncertainty of the data at 250 K amounts to $\Delta w/w \leq 0.05\%$, whereas an uncertainty of $\Delta w/w \leq 0.03\%$ is estimated for higher temperatures. The accurate measurements of Trusler (1994) for 20% ethane cover pressures up to 13 MPa (at 375 K), and the data reported by Younglove *et al.* (1993) for ethane mole fractions of 5%, 15%, and 31% are limited to pressures up to 11 MPa. Most of the data are represented by the new equation of state with very low deviations of less than ±0.05%. The maximum deviations do not exceed 0.1%, except for one data point on the 250 K isotherm at 20 MPa. This single point, for which the new equation deviates by 0.28%, is most likely associated with an increased uncertainty since no other equation developed during the optimisation and fitting procedure was able to reproduce this particular point considerably better. Moreover, this assumption is supported by the fact that the authors mention experimental difficulties along this isotherm.

The accurate representation of the 15% ethane data along the 250 K isotherm ($T/T_\mathrm{r} = 1.19$) at pressures between 5 MPa and 10 MPa (where the speed of sound exhibits a minimum followed by a comparatively steep increase towards higher pressures) is especially of major importance for the accurate description of the speed of sound of natural gases at such comparatively low temperatures. It was observed during the development of the new equation that even a slightly less accurate description of the binary data would adversely affect the representation of the available multi-component speeds of sound (see also Sec. 8.4.2), underlining the importance of accurate and wide-ranging binary speed of sound data for the development of accurate equations of state for mixtures.

Neither the AGA8-DC92 equation nor the model of Lemmon and Jacobsen (1999) is able to describe the available speed of sound data as accurately as the new equation of state. Significant improvements compared to the previous equations are achieved by the GERG-2004 formulation not only at temperatures of $T \leq 275$ K, but also at higher temperatures as exemplified by the 350 K isotherm. Deviations between the accurate measurements of Costa Gomes and Trusler (1998) for 15% ethane and values calculated from both previous equations clearly exceed the experimental uncertainty of the data over wide ranges of temperature and pressure as shown in Fig. 8.9. At 250 K, values calculated from the AGA8-DC92 equation of

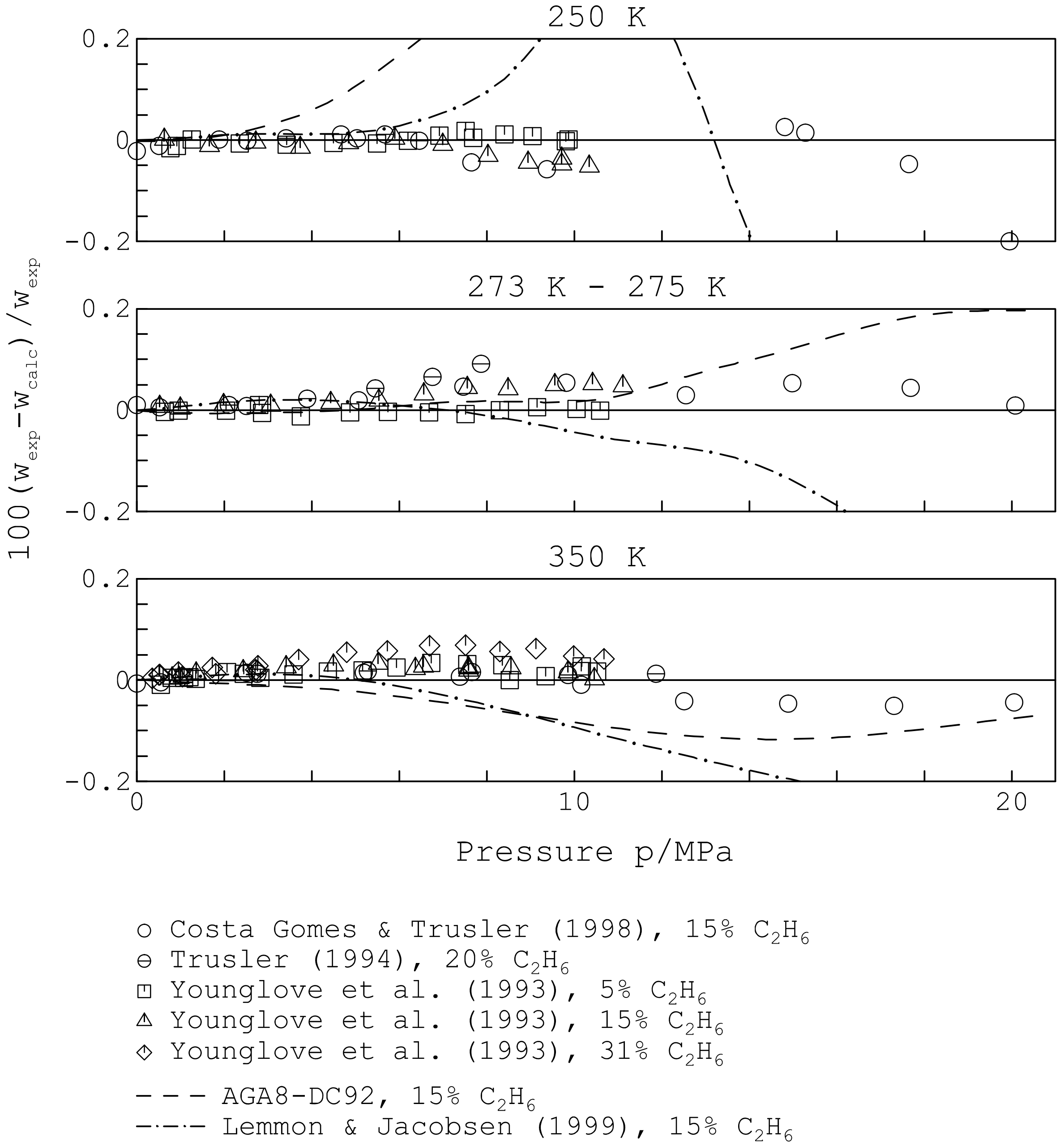

Fig. 8.9 Percentage deviations of selected experimental speed of sound data for the methane–ethane binary mixture from values calculated from the new equation of state (GERG-2004), Eqs. (7.1) – (7.10). Values calculated from the AGA8-DC92 equation of Starling and Savidge (1992) and the mixture model of Lemmon and Jacobsen (1999) are plotted for comparison at temperatures of 250 K, 275 K, and 350 K.

state deviate by more than (0.3 – 0.8)% from the data, whereas the model of Lemmon and Jacobsen (1999) shows deviations of more than (0.3 – 0.5)%. The model of Lemmon and Jacobsen (1999) deviates from the measurements by more than 0.1% even at 350 K.

The accurate and improved description of the speed of sound of binary mixtures and natural gases (see Secs. 8.1.2 and 8.4.2) is of considerable practical importance for the precise determination of mass flow-rates by means of sonic nozzles. Due to the specific mathematical relation between this caloric property and the various derivatives of the reduced Helmholtz free energy α with respect to δ and τ (see Table 7.1), the experimental information contained in accurate speeds of sound is primarily useful for the development of multi-fluid mixture models. It also advantageously contributes to the description of other caloric properties, such as enthalpy, entropy, and isobaric heat capacity, which are needed (and of much more interest) for compressor and heat exchanger design in standard and advanced technical applications for natural gases, including pipeline transport, natural gas storage, and processes with liquefied natural gas.

Figure 8.10 shows deviations between selected experimental isobaric enthalpy differences for the binary mixture methane–ethane and values calculated from the GERG-2004 formulation for temperatures ranging from 242 K to 349 K. These comparatively very accurate data were measured by Owren *et al.* (1996) for an ethane mole fraction of 15%. All of the measurements are represented by the new equation of state to within ±0.3%, which is well in agreement with the estimated uncertainty of (0.2 – 0.5)%.

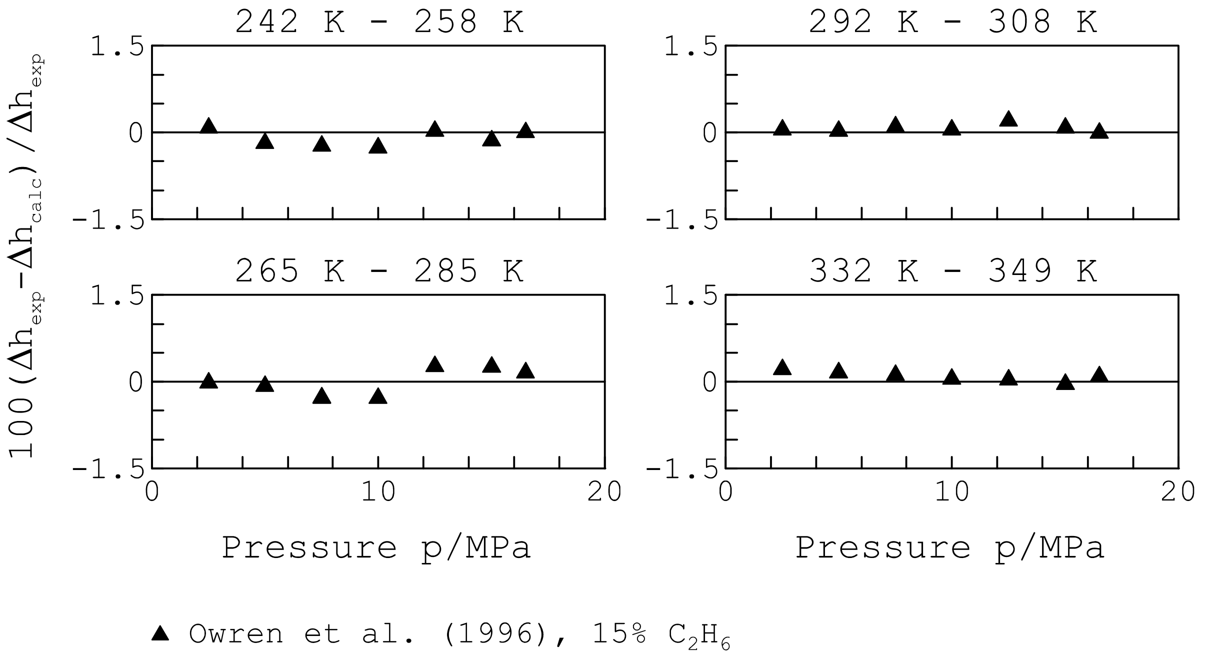

Fig. 8.10 Percentage deviations of the experimental (isobaric) enthalpy differences measured by Owren *et al.* (1996) for the methane–ethane binary mixture from values calculated from the new equation of state (GERG-2004), Eqs. (7.1) – (7.10).

Accurate and wide-ranging isochoric heat capacities of methane–ethane were measured by Mayrath and Magee (1989) in the gas and liquid regions for 31%, 50%, and 65% of ethane [the data complement the $p\rho T$ measurements carried out by Haynes *et al.* (1985) for the same mixture compositions (see also Fig. 8.4)]. The data cover temperatures from about 100 K to 328 K and were measured along several isochores ranging from $2.7\,\mathrm{mol\cdot dm^{-3}}$ to $25\,\mathrm{mol\cdot dm^{-3}}$ (corresponding to pressures up to 39 MPa). The isochoric heat capacities

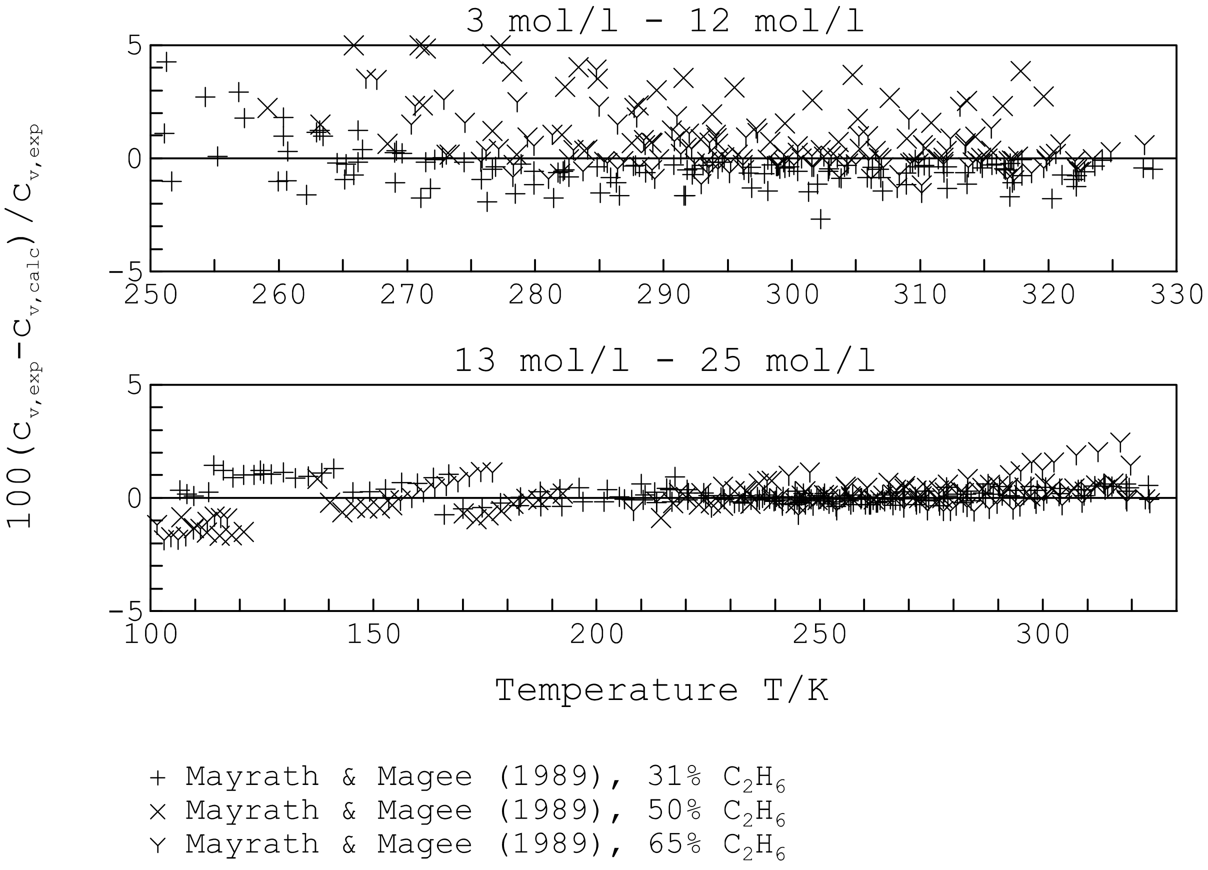

Fig. 8.11 Percentage deviations of the experimental isochoric heat capacity data measured by Mayrath and Magee (1989) for the methane–ethane binary mixture from values calculated from the new equation of state (GERG-2004), Eqs. (7.1) – (7.10).

measured for densities $\rho \geq 13\ \mathrm{mol\cdot dm^{-3}}$ are described well within the experimental uncertainty of the data, estimated to be less than (0.5 – 2)%, for all measured compositions as shown in Fig. 8.11. Most of the available data measured at lower densities (see the plot in Fig. 8.11 for $\rho \leq 12\ \mathrm{mol\cdot dm^{-3}}$) are also represented to within ±2% by the GERG-2004 formulation. The deviations rise (but are still acceptable) near critical state conditions. A comparatively large scatter in the deviations is observed for the isochoric heat capacities measured at 50% of ethane in the plot for densities $\rho \leq 12\ \mathrm{mol\cdot dm^{-3}}$. The deviations exceed 2% even at ordinary state conditions (gas phase) for the measurements along the isochores at the two lowest densities of about $6\ \mathrm{mol\cdot dm^{-3}}$ and $3.7\ \mathrm{mol\cdot dm^{-3}}$. However, none of the previous equations of state (not shown here) is able to describe these data any better than the GERG-2004 formulation, perhaps indicating an increased uncertainty for these particular measurements. The average absolute deviation for all of the 50% data amounts to about 1.17%, whereas average absolute deviations of approximately 0.54% and 0.61% are obtained for the data at 31% and 65% of ethane.

Deviations between gas phase isobaric heat capacities of Wirbser *et al.* (1996) for the methane–ethane mixture and values calculated from the new equation of state are shown in

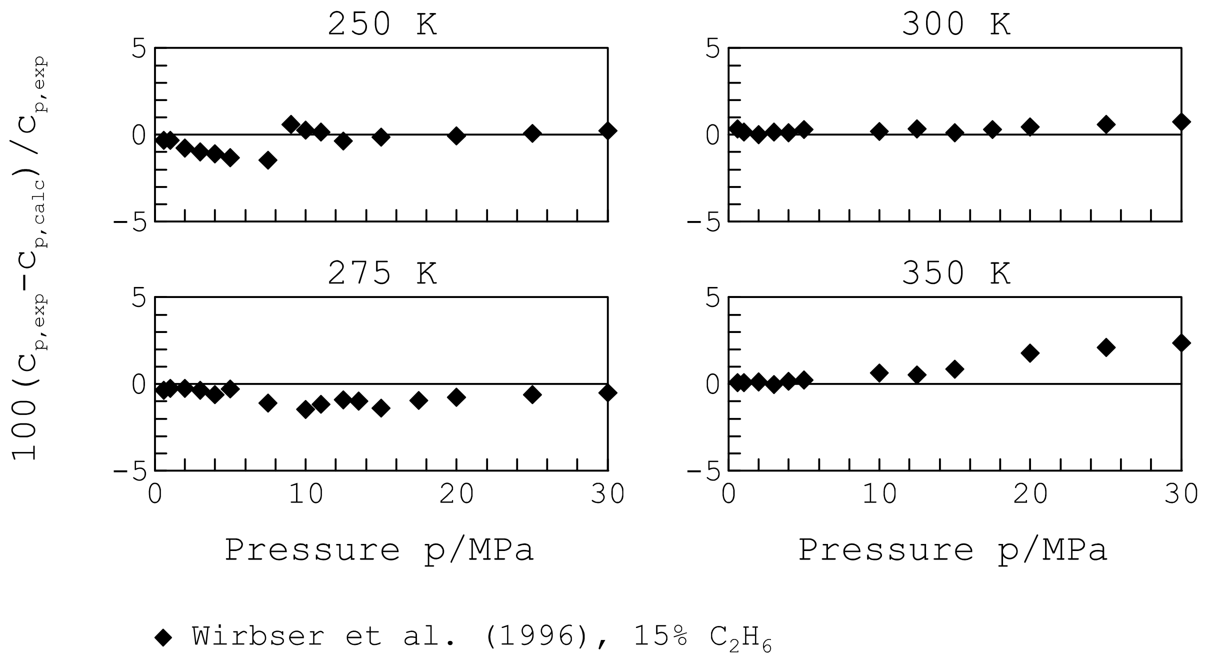

Fig. 8.12 Percentage deviations of the experimental isobaric heat capacity data measured by Wirbser *et al.* (1996) for the methane–ethane binary mixture from values calculated from the new equation of state (GERG-2004), Eqs. (7.1) – (7.10).

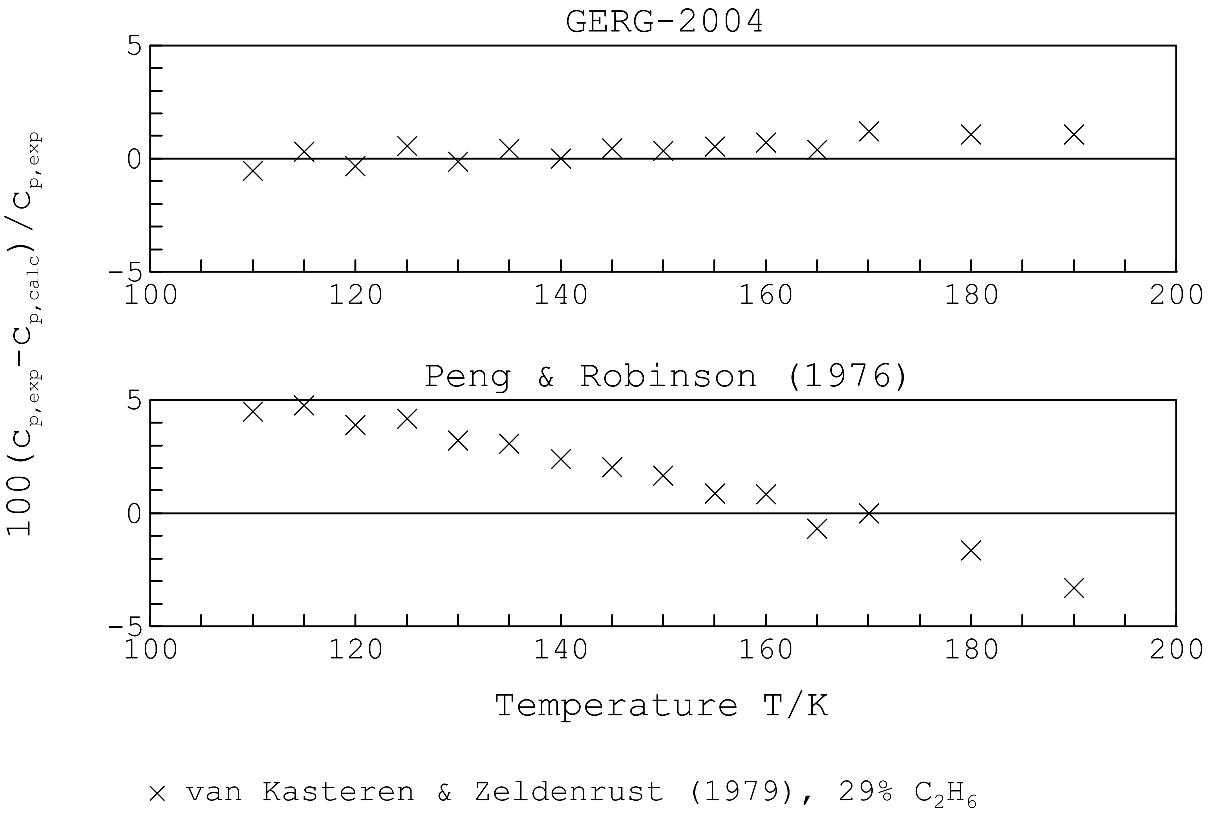

Fig. 8.13 Percentage deviations of selected experimental isobaric heat capacity data measured by van Kasteren and Zeldenrust (1979) for the methane–ethane binary mixture from values calculated from the new equation of state (GERG-2004), Eqs. (7.1) – (7.10), and the cubic equation of state of Peng and Robinson (1976).

Fig. 8.12 for temperatures ranging from 250 K to 350 K. The data were measured at 15% of ethane covering pressures up to 30 MPa and are represented by the GERG-2004 formulation to within ±(1 – 2)%. The uncertainty of these data is estimated to be not better than 2% due to considerable inconsistencies observed for all but the 300 K isotherm. This is also supported by the fact that both the AGA8-DC92 equation as well as the mixture model of Lemmon and Jacobsen (1999) yield very similar results (not shown here). Deviations between selected experimental isobaric heat capacities of methane–ethane in the liquid phase and values calculated from the GERG-2004 formulation and the cubic equation of state of Peng and Robinson (1976) are shown in Fig. 8.13. The data were measured by van Kasteren and Zeldenrust (1979) at 29% of ethane and are represented by the new equation of state well within ±1%, whereas the cubic equation of Peng and Robinson (1976) shows deviations from the measurements of up to 5%.

Methane–Carbon Dioxide and Methane–Propane

Deviations between selected speed of sound data for the binary mixtures methane–carbon dioxide and methane–propane and values calculated from the GERG-2004 formulation are presented in Fig. 8.14. Except for the measurements of Estela-Uribe (1999) for methane–carbon dioxide, and the data of Ingrain *et al.* (1993) and Trusler *et al.* (1993) for methane–propane, the available measurements are limited to pressures below 11 MPa over the complete measured temperature range. At temperatures below 350 K, none of the available accurate data sets contain measurements above this maximum pressure[81]. These limitations do not only complicate the development of accurate binary equations, but also influence the description of natural gases containing comparatively high fractions of carbon dioxide or propane at elevated pressures. Thus, for future developments, it would be very worthwhile to measure accurate speeds of sound for these (and other) binary mixtures at pressures up to at least 20 MPa over wide ranges of temperature (see also Sec. 6.1).

The most accurate and wide-ranging speeds of sound for methane–carbon dioxide were measured by Estela-Uribe (1999) at 20% of carbon dioxide, and for methane–propane by Trusler *et al.* (1993) at 15% of propane. The measurements of Estela-Uribe (1999) cover temperatures from 200 K to 450 K and pressures up to 17 MPa[82] and are all represented by the new equation of state with very low deviations of less than ±0.03%. Trusler *et al.* (1993)

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[81] Although the data of Ingrain *et al.* (1993) cover pressures up to 17 MPa for wide ranges of temperature, they are not very useful for the development of an accurate wide-ranging equation of state. As claimed by the authors, the uncertainty in speed of sound ranges from 0.1% at room temperature to 0.3% at temperatures below 233 K. A comparison with the measurements of Younglove *et al.* (1993) for the same mixture composition (10% propane), known to be more accurate, reveals that the assessment of the authors is likely to be rather optimistic.

[82] The speeds of sound at 200 K were measured for pressures up to 0.8 MPa, below the vapour-liquid phase boundary exhibiting a maximum temperature of approximately 220 K at about 5.5 MPa.

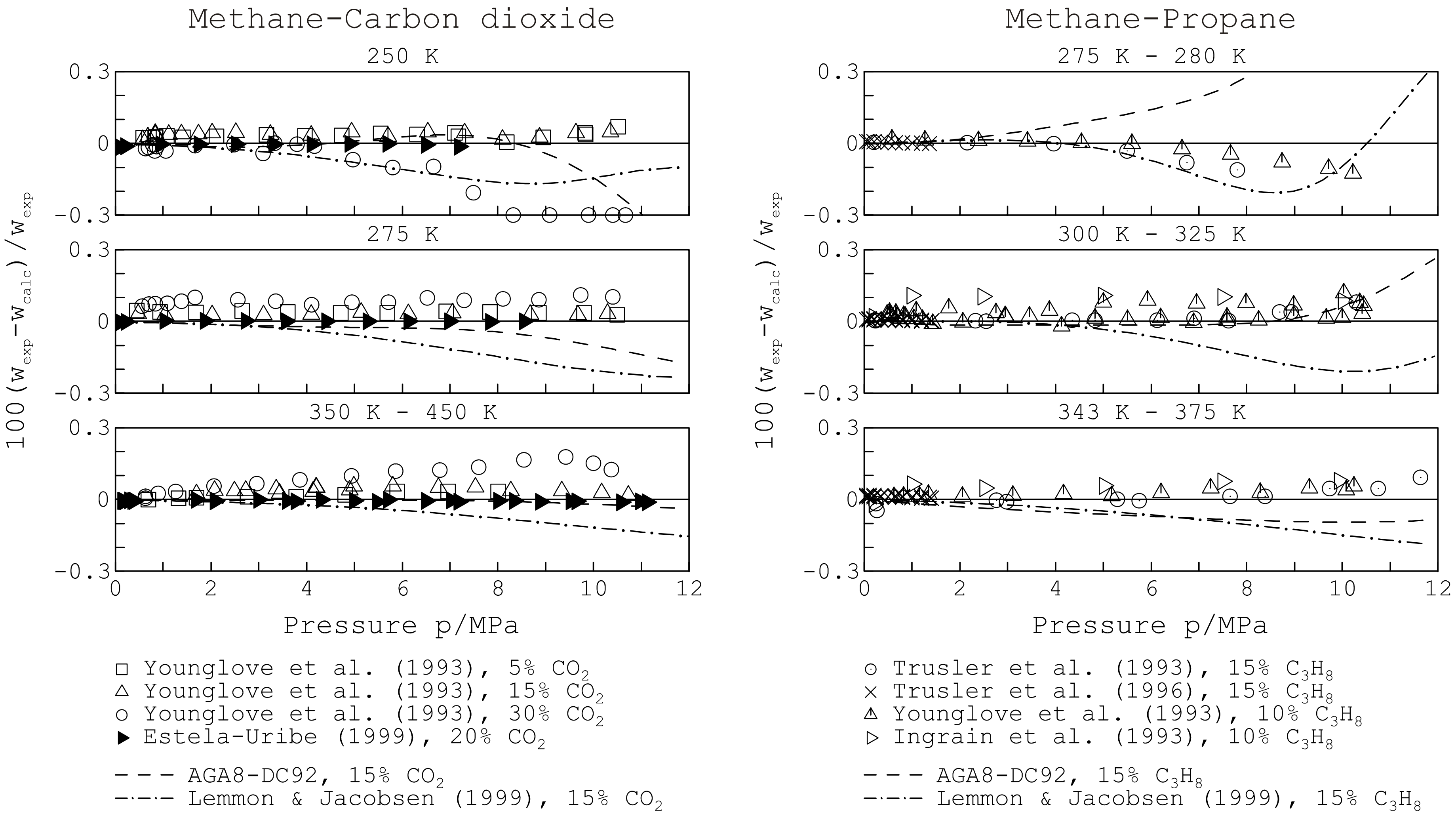

Fig. 8.14 Percentage deviations of selected experimental speed of sound data for the methane–carbon dioxide and methane–propane binary mixtures from values calculated from the new equation of state (GERG-2004), Eqs. (7.1) – (7.10). Values calculated from the AGA8-DC92 equation of Starling and Savidge (1992) and the mixture model of Lemmon and Jacobsen (1999) are plotted for comparison at temperatures of 250 K, 275 K, and 350 K for methane–carbon dioxide, and 280 K, 300 K, and 350 K for methane–propane.

measured speeds of sound for temperatures ranging from 280 K to 375 K at pressures up to 13 MPa. The data are represented by the new equation of state well within ±0.1% (the average absolute deviation of all the data amounts to 0.027%).

Further speed of sound data (with an estimated uncertainty of less than 0.1%) were measured by Younglove *et al.* (1993) for mixtures of methane–carbon dioxide and methane–propane at carbon dioxide concentrations of 5%, 15%, and 30%, and 10% of propane. Most of these data are well represented by the GERG-2004 formulation with deviations of less than ±0.1% as shown in Fig. 8.14. Considerably higher deviations appear at 250 K for the methane–carbon dioxide mixture containing 30% of carbon dioxide, corresponding to a comparatively low reduced temperature of $T/T_\mathrm{r} = 1.14$. Deviations between the data measured along this isotherm and values calculated from the new equation of state deviate by more than 0.3% at pressures above 8 MPa. However, as no other accurate speeds of sound are available for this particular composition and due to the comparatively low reduced temperature, this is not a severe problem. Moreover, when investigating the characteristics of the deviations between the data and values calculated from the new equation of state at higher temperatures (including isotherms not shown in Fig. 8.14), which reveals some inconsistency for different temperatures, it seems that these measurements might be associated with an increased uncertainty. None of the equations developed during the optimisation and fitting process was able to describe all of the measurements considerably better than the final equation.

For any mixture composition, the previous equations of state generally yield worse results for both binary systems. Values calculated from the AGA8-DC92 equation deviate from the experimental speeds of sound for methane–carbon dioxide by more than 0.2%, not only for the data for the mixture containing 15% of carbon dioxide as shown in Fig. 8.14, but also for 5% and especially for the very accurate measurements of Estela-Uribe (1999) at 20% of carbon dioxide. Values calculated from the mixture model of Lemmon and Jacobsen (1999) clearly exceed deviations of 0.1% over wide temperature and pressure ranges as exemplified for the 15% carbon dioxide data. Both previous equations are not able to describe the data for the mixture containing 30% of carbon dioxide better than the new equation of state.

Values calculated from the AGA8-DC92 equation of state deviate from the methane–propane measurements of Trusler *et al.* (1993) at 15% propane by more than 0.3% at 280 K. The AGA8-DC92 equation is not even able to describe the 10% propane data of Younglove *et al.* (1993) as accurately as the new equation of state (see Table A2.1 of the appendix). The model of Lemmon and Jacobsen (1999) exceeds 0.1% and reaches a maximum deviation of about 0.2% at 300 K. This model is not even able to accurately describe the speeds of sound at higher temperatures as shown in Fig. 8.14.

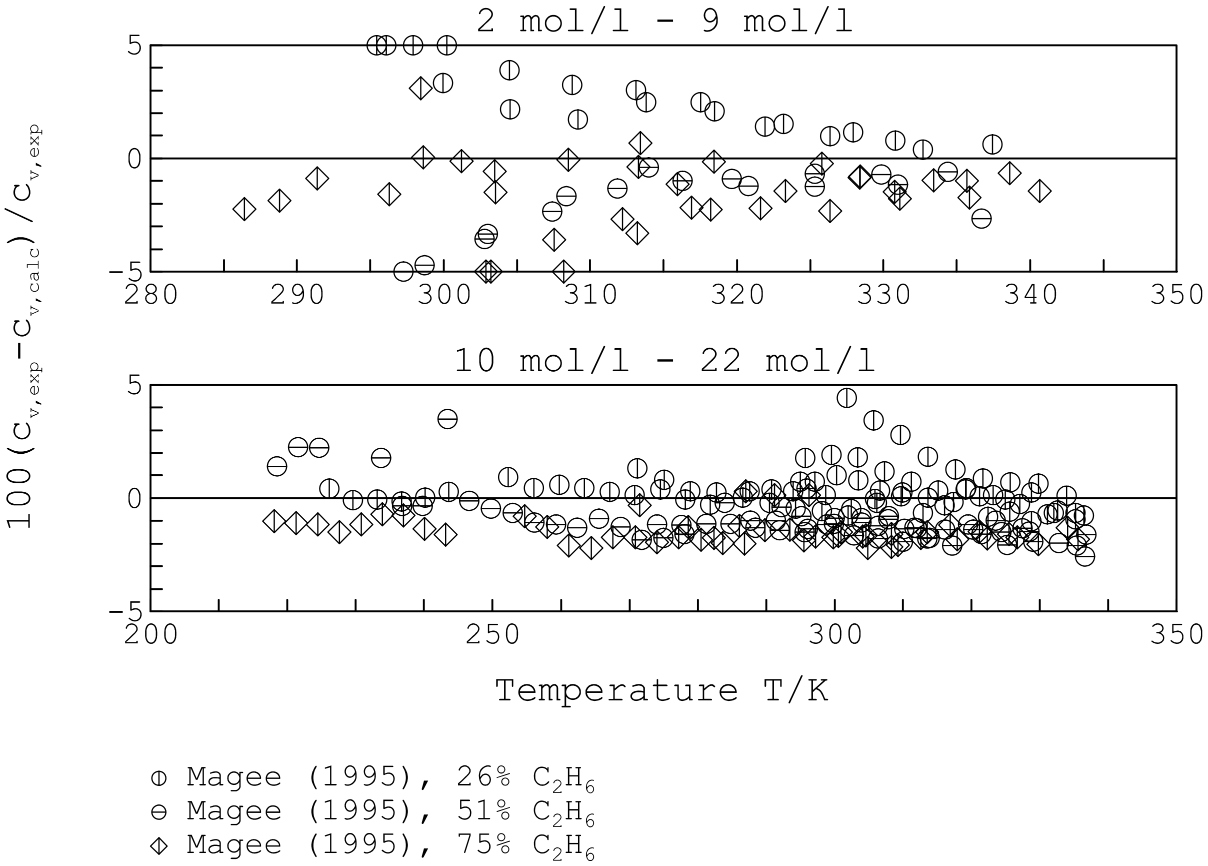

Fig. 8.15 Percentage deviations of the experimental isochoric heat capacity data measured by Magee (1995) for the carbon dioxide–ethane binary mixture from values calculated from the new equation of state (GERG-2004), Eqs. (7.1) – (7.10).

Carbon Dioxide–Ethane

Isochoric heat capacities were measured by Magee (1995) for the binary system carbon dioxide–ethane using the same experimental equipment as Mayrath and Magee (1989) for the measurements on methane–ethane (see above). The data were measured in the gas and liquid regions along several isochores ranging from about 2 $\mathrm{mol \cdot dm^{-3}}$ to 22 $\mathrm{mol \cdot dm^{-3}}$ over wide ranges of temperature for ethane mole fractions of 26%, 51%, and 75% (the pressures range up to 34 MPa). The uncertainty of the measurements is claimed by the authors to be less than 2% in the gas phase and 0.5% in the liquid phase. Most of the data are represented by the GERG-2004 formulation to within ±2% as shown in Fig. 8.15. Higher deviations are obtained when approaching near critical state conditions. The average absolute deviations of the measurements amount to about 1% for 26% ethane and around 1.5% for 51% and 75% ethane. Similar to the measurements of Mayrath and Magee (1989) for methane–ethane discussed earlier, the data measured along the isochores at the lower densities seem to be associated with an increased uncertainty. However, the achieved accuracy in the representation of these isochoric heat capacities is very satisfactory. It should also be noted that the binary mixture carbon dioxide–ethane is taken into account only by using adjusted reducing functions. The mixture model of Lemmon and Jacobsen (1999), using a generalised departure function for all of the considered binary mixtures, yields similar results (not shown here).

The examples above prove that the new equation of state achieves major and important improvements in the description of caloric properties of binary mixtures of the natural gas main constituents compared to both the AGA8-DC92 equation and the multi-fluid mixture model of Lemmon and Jacobsen (1999). Even the most accurate speed of sound data are represented by the new mixture model to within their very low experimental uncertainties over wide ranges of mixture conditions. This is also true for data of other caloric properties, particularly including those measured in the liquid phase, where the AGA8-DC92 equation is not applicable. Cubic equations of state deviate from accurate caloric data in the gas and liquid regions by several per cents (frequently considerably more than ±5%) (see also Sec. 2.1.2).

8.1.3 Vapour-Liquid Equilibrium Properties

Aside from $p\rho T$ data and data of caloric properties measured in the homogeneous gas, liquid, and supercritical regions, experimental information for the vapour-liquid equilibrium was used in the development of the different binary equations as described in Sec. 7.10. As mentioned in Chap. 6, very accurate data at equilibrium conditions are available for saturated liquid densities of several binary (and also multi-component) mixtures. Experimental *pTxy* data (i.e. simultaneous measurement of vapour pressure, saturation temperature, and equilibrium phase compositions) are in general associated with an increased uncertainty mainly resulting from errors in the measurement of the phase compositions (see Chap. 6).

Saturated Liquid Densities

Figure 8.16 shows deviations of experimental saturated liquid densities for the binary mixtures methane–nitrogen and methane–propane from values calculated from the GERG-2004 formulation, the multi-fluid mixture model of Lemmon and Jacobsen (1999), and the cubic equation of state of Peng and Robinson (1976). The data were measured by Hiza *et al.* (1977) covering wide ranges of composition, with temperatures from 95 K to 140 K. The uncertainty of the measurements is estimated to be $\Delta\rho'/\rho' \leq$ (0.1 – 0.2)%. All of the data (for both mixtures) are represented by the new equation of state with very low deviations of less than ±(0.1 – 0.15)%, which is well within the experimental uncertainty. The mixture model of Lemmon and Jacobsen (1999) achieves a comparable accuracy for the methane–nitrogen mixture, but the data for the methane–propane mixture are only represented to within ±(0.1 – 0.3)%. They show larger (but still acceptable) deviations for propane mole fractions of 14%, 25%, and 70% at the lowest measured temperatures, indicating a stronger composition

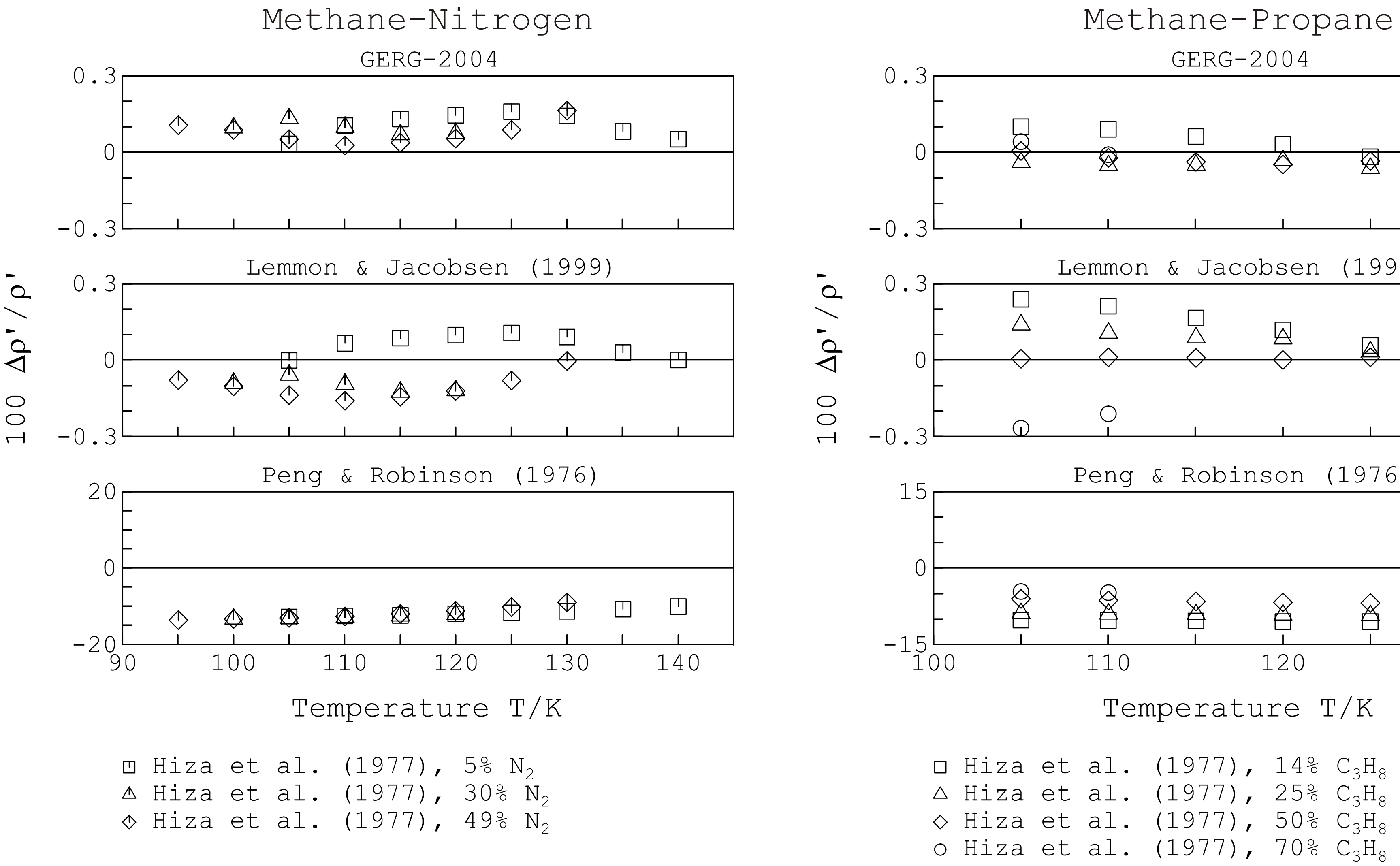

Fig. 8.16 Percentage deviations $100\Delta\rho'/\rho' = 100(\rho'_{\mathrm{exp}} - \rho'_{\mathrm{calc}})/\rho'_{\mathrm{exp}}$ of the experimental saturated liquid densities measured by Hiza *et al.* (1977) for the methane–nitrogen and methane–propane binary mixtures from values calculated from the new equation of state (GERG-2004), Eqs. (7.1) – (7.10), the mixture model of Lemmon and Jacobsen (1999), and the cubic equation of state of Peng and Robinson (1976).

dependence compared to the GERG-2004 formulation. Deviations of more than 10% for the methane–nitrogen data are obtained from the cubic equation of Peng and Robinson (1976), nearly independent of the mixture composition. For the methane–propane data, the cubic equation deviates from the measurements by approximately 5% to 10%, depending on the propane concentration. Thus, the deviations between values calculated from the cubic equation of Peng and Robinson (1976) and the data are 50 to 100 times larger than those obtained from the GERG-2004 formulation. The poor representation of saturated liquid densities (and also compressed liquid densities) by cubic equations of state can be observed for many binary and multi-component mixtures (see also Sec. 8.4.4).

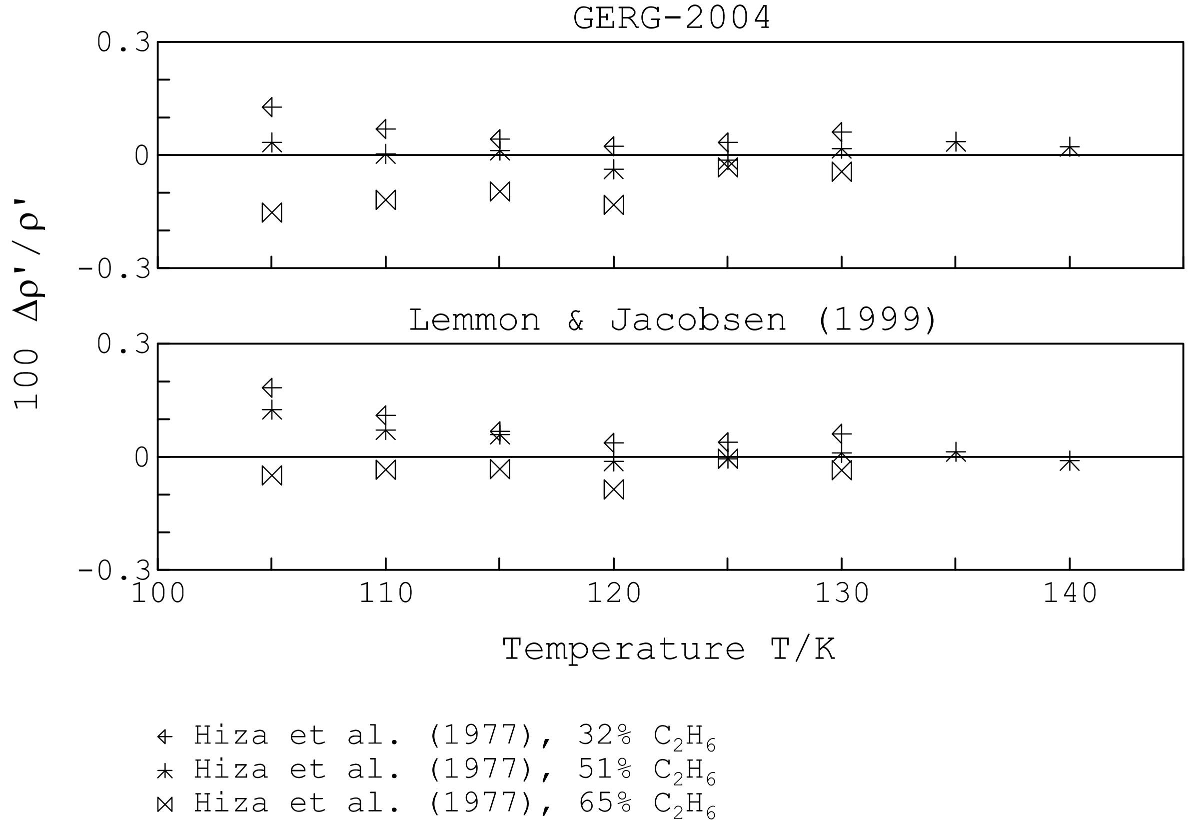

Fig. 8.17 Percentage deviations $100\Delta\rho'/\rho' = 100(\rho'_{\mathrm{exp}} - \rho'_{\mathrm{calc}})/\rho'_{\mathrm{exp}}$ of the experimental saturated liquid densities measured by Hiza *et al.* (1977) for the methane–ethane binary mixture from values calculated from the new equation of state (GERG-2004), Eqs. (7.1) – (7.10), and the mixture model of Lemmon and Jacobsen (1999).

Deviations between saturated liquid densities for methane–ethane and values calculated from the GERG-2004 formulation and the mixture model of Lemmon and Jacobsen (1999) for temperatures ranging from 105 K to 140 K and ethane mole fractions of 32%, 51%, and 65% are shown in Fig. 8.17. Values calculated from the new equation of state agree with the measurements of Hiza *et al.* (1977) to within ±(0.1 – 0.15)%. The model of Lemmon and Jacobsen (1999) shows a very similar representation, which is within ±(0.1 – 0.2)%, supporting the description of saturated liquid densities by the new mixture model.

The GERG-2004 formulation achieves a similar high accuracy in the description of saturated liquid densities as well for other binary mixtures, e.g. nitrogen–ethane and nitrogen–propane; for further details see Table A2.1 of the appendix.

The *pTxy* Relation

Figure 8.18 shows the representation of selected experimental vapour pressures for the binary mixture methane–nitrogen by the new equation of state at subcritical temperatures (91 K to 100 K) and in the critical region of the mixture (150 K to 155 K). The displayed percentage deviations were calculated at a given temperature T and given composition $\bar{x} = \bar{x}'$ of the liquid phase (bubble point pressure calculation). The available binary data for this mixture cover the complete composition range for temperatures from between 78 K and 190 K (which is close to the critical temperature of pure methane) (see also Table 6.4). The GERG-2004 formulation represents the most reliable measurements, assumed to be those of Parrish and Hiza (1973), Stryjek *et al.* (1974a), and McClure *et al.* (1976), to within ±(1 – 2)%, which agrees well with the experimental uncertainty of the data. Note that the uncertainty in vapour pressure is in general estimated to be $\Delta p_\mathrm{s}/p_\mathrm{s} \leq (1-3)\%$ (see also Chap. 6). From the plots shown in Fig. 8.18 it is obvious that data measured by different authors deviate among one another by (partly) more than 2% or 3% at virtually the same mixture conditions in both the subcritical and critical regions of the mixture. Similar (or even worse) experimental situations are observed for most binary systems (see also the discussions below). Although the data situation for VLE properties of methane–nitrogen is (compared to other binary mixtures) very satisfactory, the poor consistency between data sets of different authors, and also within a single data set, complicates the development of equations of state for mixtures. These difficulties are compensated for to a certain extent when (much more) accurate experimental information is available for properties in the homogeneous gas, liquid, and supercritical regions, or for saturated liquid densities (see above). Nevertheless, due to the flexible structure of mixture models based on a multi-fluid approximations, the representation of binary *pTxy* data by such an equation of state strongly depends on the data sets chosen by the correlator used in the development of the equation. The use of "wrong" VLE measurements can adversely affect the description of data in the homogeneous region and vice versa.

In the critical region of the mixture (at temperatures above the critical temperature of nitrogen), the cubic equation of state of Peng and Robinson (1976) yields quite similar results compared to the GERG-2004 formulation as shown for the 150 K isotherm in Fig. 8.18. At lower temperatures, values calculated from the cubic equation deviate significantly from the measurements by more than 2%, thus exceeding the uncertainty of the data. Even higher deviations of more than 5% are obtained for the mixture model of Lemmon and Jacobsen (1999).

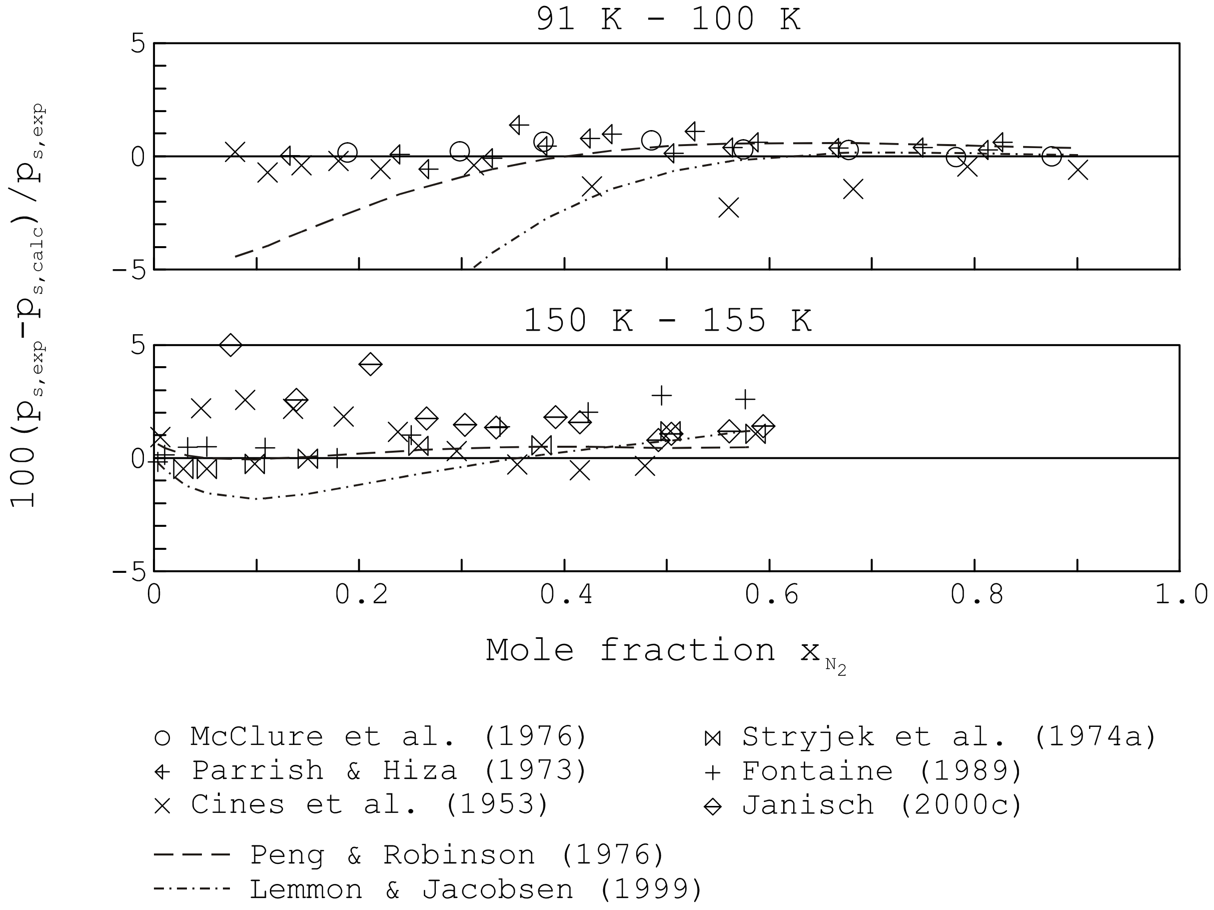

Fig. 8.18 Percentage deviations of selected experimental vapour pressures for the methane–nitrogen binary mixture from values calculated from the new equation of state (GERG-2004), Eqs. (7.1) – (7.10). Values calculated from the cubic equation of state of Peng and Robinson (1976) and the mixture model of Lemmon and Jacobsen (1999) are plotted for comparison at temperatures of 100 K and 150 K.

As mentioned in Sec. 5.5.4 (see also Secs. 5.5.3 and 7.10), the vapour pressure at a given temperature and liquid phase composition is not the only VLE property of a *pTxy* data set that was used in the development (nonlinear fitting) of the binary equations of the new mixture model. Further (and experienced to also be important), experimental information can additionally be utilised by nonlinearly fitting the measured vapour phase composition. Deviations between experimentally determined vapour phase compositions and values calculated from the GERG-2004 formulation for given temperatures and liquid phase compositions are shown in Fig. 8.19 for the same mixture and data sets as in Fig. 8.18. Those data assumed to be the most reliable for this mixture (see above) are represented by the new equation of state with deviations of less than ±(0.5 – 1) mole-%, which is well in agreement with the experimental uncertainty of such measurements (as estimated from experience). Frequently, the scatter in a single data set significantly exceeds values of 1 mole-%, and deviations between data sets of different authors can even exceed values of 2 mole-% (or more) as shown in Fig. 8.19 for the data of Cines *et al.* (1953) and Janisch (2000c). Only the

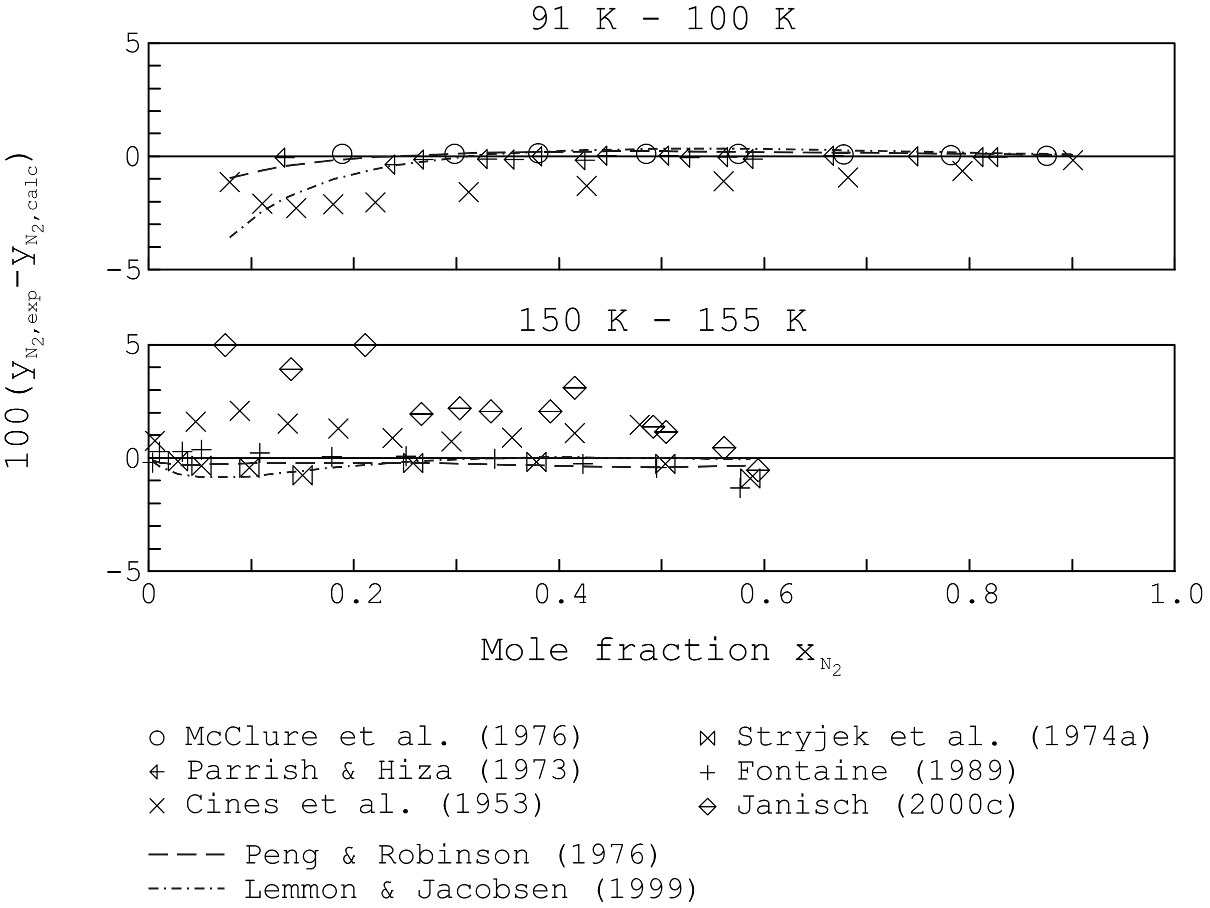

Fig. 8.19 Deviations of selected experimental nitrogen mole fractions in the saturated vapour phase for the methane–nitrogen binary mixture from values calculated from the new equation of state (GERG-2004), Eqs. (7.1) – (7.10). Values calculated from the cubic equation of state of Peng and Robinson (1976) and the mixture model of Lemmon and Jacobsen (1999) are plotted for comparison at temperatures of 100 K and 150 K.

best, i.e. most accurate and consistent, *pTxy* measurements are accurate to within (1 – 2)% in vapour pressure and (0.5 – 1) mole-% in vapour phase composition. Other authors are able to accurately measure the vapour pressure, but show inconsistencies in the measured vapour phase composition and vice versa.

Compared to the GERG-2004 formulation, the behaviour of the cubic equation of Peng and Robinson (1976) is quite similar concerning the description of the measured vapour phase compositions for the temperatures shown in Fig. 8.19, whereas the mixture model of Lemmon and Jacobsen (1999) deviates by more than 1 mole-% from the most reliable data at 100 K.

Percentage deviations between selected experimental vapour pressures of the binary mixture methane–ethane and values calculated from the GERG-2004 formulation are shown in Fig. 8.20 for temperatures in the critical region of the mixture. The deviation plots complement the comparisons previously made in Figs. 7.7 and 7.16, showing a pressure-temperature and a pressure-composition diagram for methane–ethane including accurate

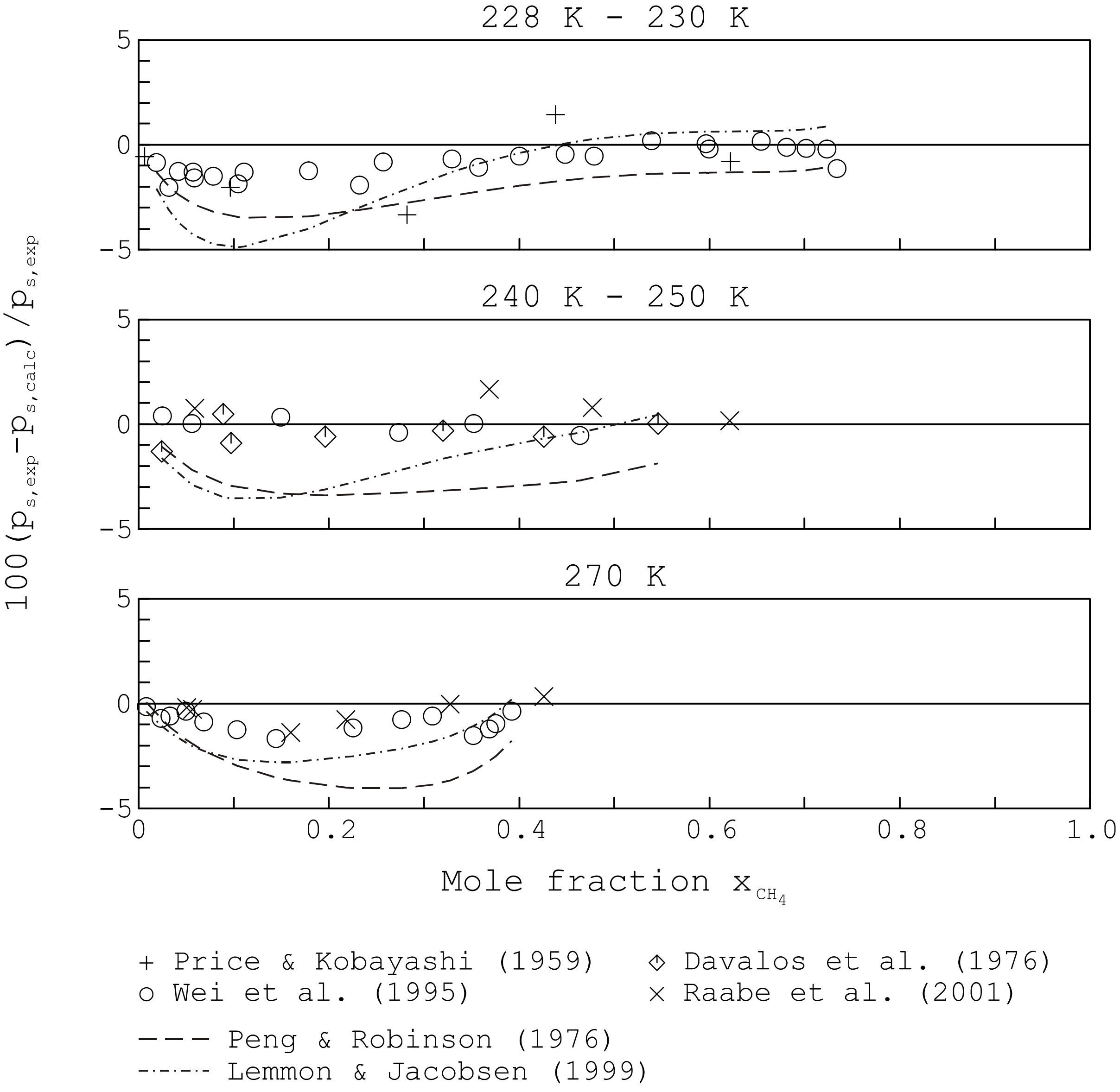

Fig. 8.20 Percentage deviations of selected experimental vapour pressures for the methane–ethane binary mixture from values calculated from the new equation of state (GERG-2004), Eqs. (7.1) – (7.10). Values calculated from the cubic equation of state of Peng and Robinson (1976) and the mixture model of Lemmon and Jacobsen (1999) are plotted for comparison at temperatures of 230 K, 250 K, and 270 K.

experimental VLE measurements. Such total comparisons between VLE data and values calculated from equations of state are very useful for investigating the capabilities of equations of state in the description of the VLE behaviour of mixtures, especially when dealing with very poor data which only allow for a qualitative comparison. Similar to the binary mixture methane–nitrogen, the VLE data situation for methane–ethane, the second-most important binary mixture for natural gas applications, is quite satisfactory. As mentioned in Sec. 7.7.3 and shown in Fig. 8.20, the new equation of state is able to represent the most accurate measurements with deviations of less than ±2% over wide ranges of temperature and composition for both the subcritical and critical regions of the mixture. The cubic equation of state of Peng and Robinson (1976) partly deviates from the measurements in the mixture critical region by more than 2% as displayed in Fig. 8.20. The same is valid for the mixture model of Lemmon and Jacobsen (1999) due to fitting other data with significant differences to the data shown here.

Aside from data measured at mixture subcritical and critical temperatures, a number of accurate measurements were carried out by Wichterle and Kobayashi (1972a) for methane concentrations ranging from about 90% to almost pure methane, focusing on the transition from subcritical to critical around temperatures of 190 K. These data are well represented by the GERG-2004 formulation to within ±1%.

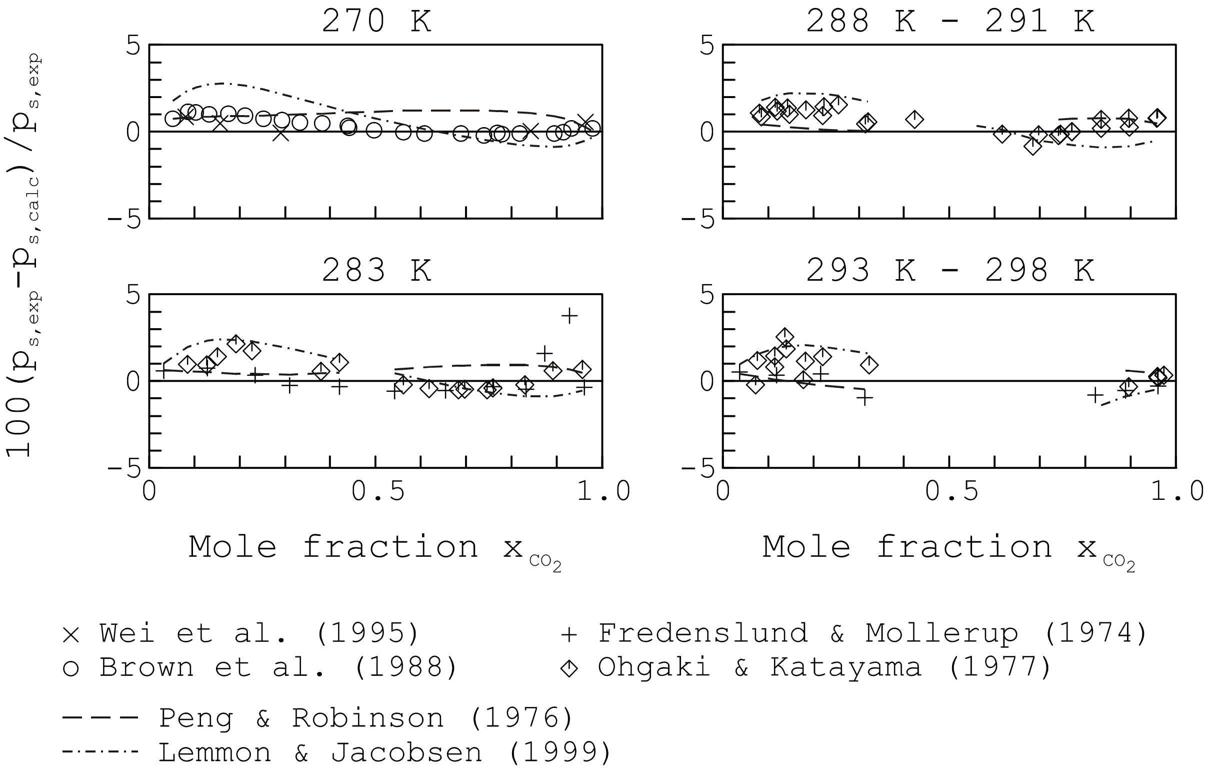

Fig. 8.21 Percentage deviations of selected experimental vapour pressures for the carbon dioxide–ethane binary mixture from values calculated from the new equation of state (GERG-2004), Eqs. (7.1) – (7.10). Values calculated from the cubic equation of state of Peng and Robinson (1976) and the mixture model of Lemmon and Jacobsen (1999) are plotted for comparison.

As a full mixture model, the GERG-2004 formulation is not only able to accurately describe common VLE behaviour as shown for the examples discussed above, but also for mixtures exhibiting unusual phase behaviour, e.g. an azeotrope, as displayed for the binary mixture carbon dioxide–ethane in Figs. 8.21 and 8.22. Figure 8.21 shows percentage deviations between vapour pressure data of four different authors and values calculated from the new equation of state in the high temperature region where the disappearance of the azeotrope is

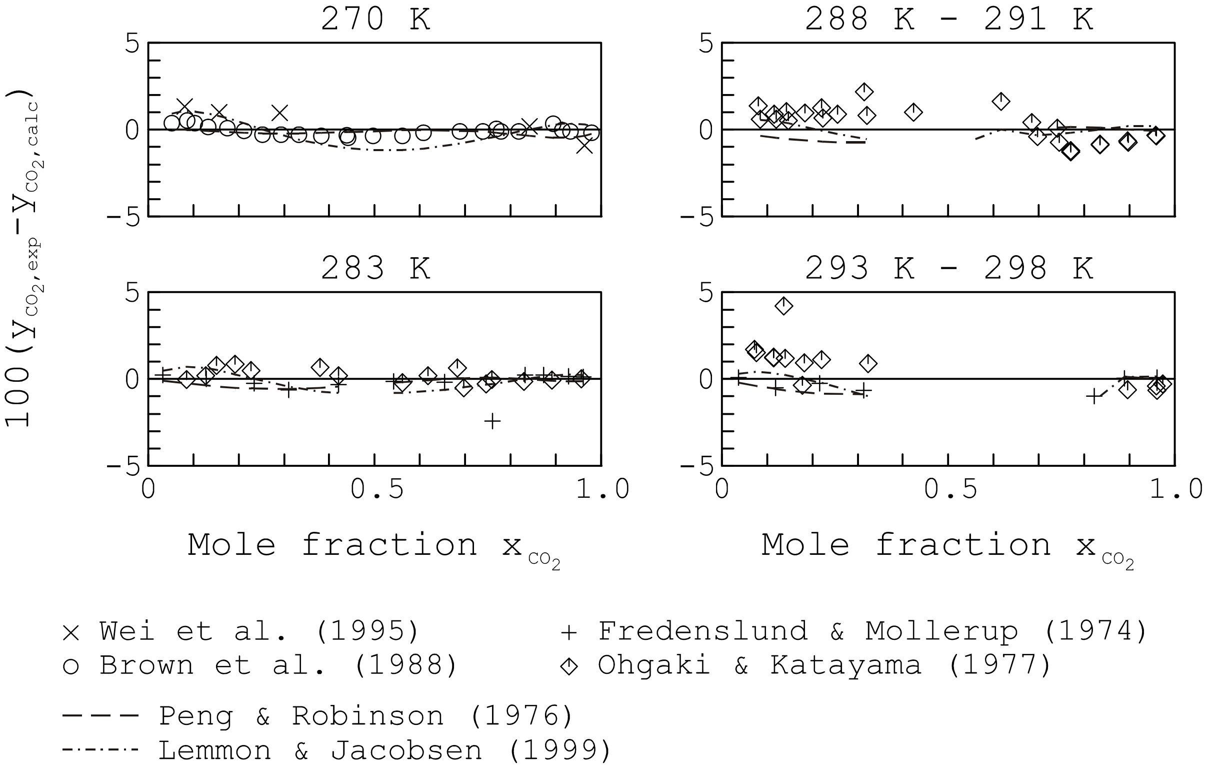

Fig. 8.22 Deviations of selected experimental carbon dioxide mole fractions in the saturated vapour phase for the carbon dioxide–ethane binary mixture from values calculated from the new equation of state (GERG-2004), Eqs. (7.1) – (7.10). Values calculated from the cubic equation of state of Peng and Robinson (1976) and the mixture model of Lemmon and Jacobsen (1999) are plotted for comparison.

observed. For the temperature range displayed in the deviation plots, the azeotropic points appear in a narrow range of carbon dioxide mole fractions approximately between 69% and 70%. The most reliable measurements of these authors are represented by the GERG-2004 formulation to within ±(1 – 2)% (a few data points are obviously associated with increased uncertainties as can be deduced from the considerably large scatter in the respective deviations). The new mixture model also accurately describes the simultaneously measured vapour phase compositions as shown in Fig. 8.22. Typical deviations between experimental vapour phase compositions and values calculated from the new equation of state are within ±(0.5 – 1) mole-% for the data of Brown *et al.* (1988) and Fredenslund and Mollerup (1974), and within ±(1 – 2) mole-% for the measurements of Ohgaki and Katayama (1977). The latter seem to be associated with a higher uncertainty than those measured by Brown *et al.* (1988) and Fredenslund and Mollerup (1974), due to the larger scatter in the data as is obvious from the comparisons displayed in Figs. 8.21 and 8.22. Although the cubic equation of state of Peng and Robinson (1976) shows on average, compared to the GERG-2004 formulation, a similar representation of the selected measurements, the model of Lemmon and Jacobsen (1999) exhibits somewhat higher deviations from those data assumed to be the most accurate.

8.2 The Representation of Thermal and Caloric Properties of Selected Binary Mixtures of Hydrocarbons from Ethane to n-Octane

Most of the binary mixtures consisting of the hydrocarbons ethane, propane, n-butane, isobutane, n-pentane, isopentane, n-hexane, n-heptane, and n-octane, comprising a total of 36 binary systems, are characterised by using only adjusted reducing functions. For the six binary mixtures composed of ethane, propane, n-butane, and isobutane, a generalised departure function is additionally used (see also Table 7.16). Several of the binary hydrocarbon systems are taken into account without any fitting but by using different combining rules as described in Secs. 5.2 and 7.10. This mainly concerns those binary hydrocarbon mixtures containing either isobutane or isopentane as one component (see also Fig. 7.14).

8.2.1 The $p\rho T$ Relation in the Homogeneous Region

Except for a few data sets covering mixture conditions in the homogeneous gas phase, the majority of $p\rho T$ data available for binary hydrocarbon mixtures was measured in the liquid phase ranging from atmospheric to moderate or elevated pressures and covering wide ranges of composition. A considerable amount of measurements is available for saturated liquid and saturated vapour densities, often being of questionable accuracy as will be shown in Sec. 8.2.3. The following examples focus on the representation of experimental (homogeneous) liquid phase densities by the new equation of state; for the description of the $p\rho T$ relation in the liquid phase of ternary hydrocarbon mixtures see Sec. 8.4.3.

Ethane–Propane, Propane–n-Butane, and n-Butane–Isobutane

Figure 8.23 shows percentage deviations of selected experimental liquid densities for various compositions of the binary mixture ethane–propane from values calculated from the GERG-2004 formulation and the mixture model of Lemmon and Jacobsen (1999). The data measured by Parrish (1984) are represented by the new equation of state to within about ±(0.1 – 0.2)%, which is well within the targeted uncertainty defined for liquid phase densities. Larger deviations, ranging from 0.1% to slightly above 0.5%, are obtained from the model of Lemmon and Jacobsen (1999).

Experimental liquid densities for the binary mixtures propane–n-butane and n-butane–isobutane and their percentage deviations from the GERG-2004 formulation and other multi-fluid mixture models are shown in Figs. 8.24 and 8.25. The selected data cover wide ranges of temperature and composition and are in general represented by the new equation of state with low deviations of less than ±(0.1 – 0.15)%, including the recently published measurements of

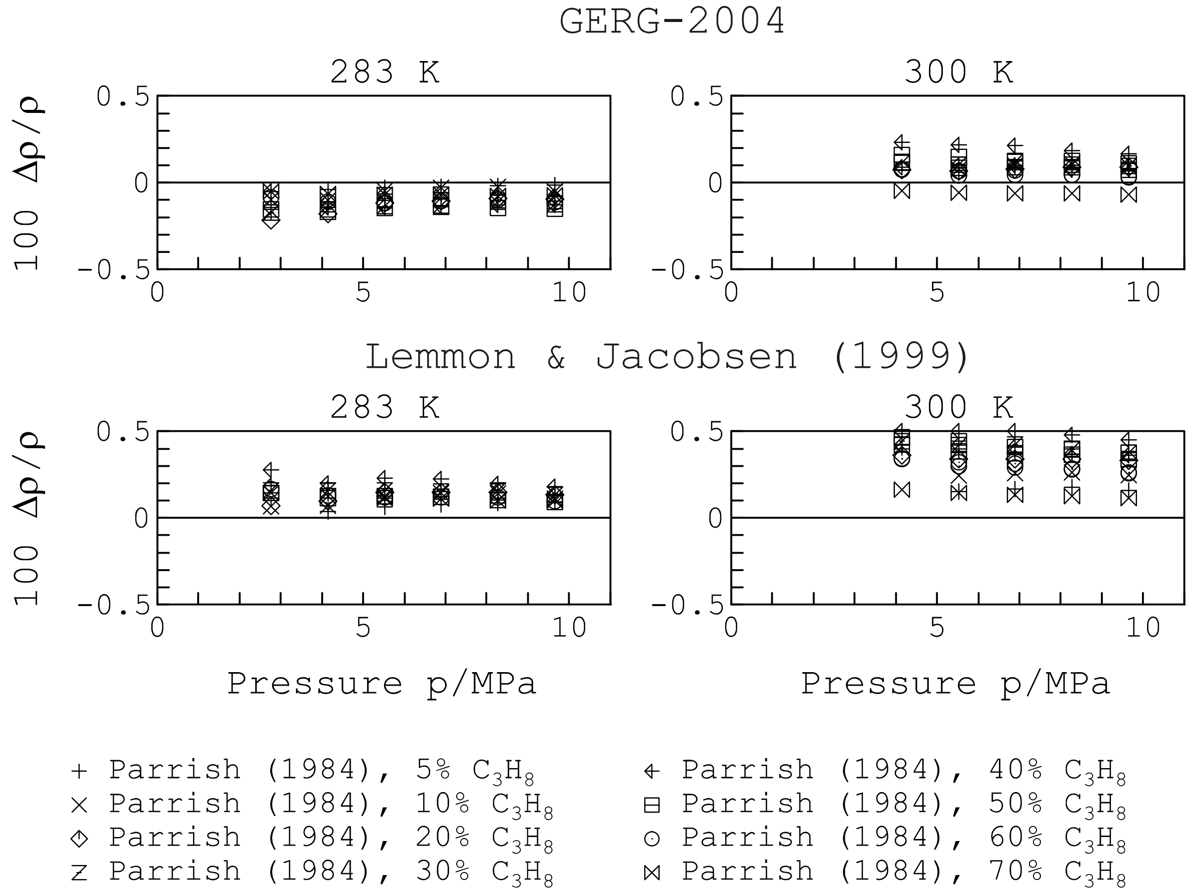

Fig. 8.23 Percentage density deviations $100\Delta\rho/\rho = 100(\rho_{\text{exp}} - \rho_{\text{calc}})/\rho_{\text{exp}}$ of selected experimental $p\rho T$ data measured by Parrish (1984) for the ethane–propane binary mixture from values calculated from the new equation of state (GERG-2004), Eqs. (7.1) – (7.10), and the mixture model of Lemmon and Jacobsen (1999).

Kayukawa *et al.* (2005a), which were not available at the time the equation was developed. The data of Parrish (1986) seem to be more accurate than the measurements on ethane–propane of Parrish (1984). A similar accurate description by the new equation of state is also achieved for compressed liquid densities available for the binary mixture propane–isobutane (not shown here). Typical deviations observed for this system are within ±(0.1 – 0.2)% over wide ranges of temperature and composition, and at pressures up to 35 MPa (see also Table A2.1 of the appendix). Note that the data of Kayukawa *et al.* (2005a), available for the three binary mixtures propane–n-butane, propane–isobutane, and n-butane–isobutane, were measured starting from pressures close to the saturation conditions. Additionally, saturated liquid densities were measured by the authors at the same temperatures and compositions as in the homogeneous region. These data are accurately represented by the GERG-2004 formulation as well (typical deviations are within ±0.2%).

Compared to the GERG-2004 formulation, the multi-fluid mixture model of Lemmon and Jacobsen (1999) yields quite similar results for the n-butane–isobutane mixture (not shown here), but shows deviations ranging from 0.1% to right below 0.3% for propane–n-butane,

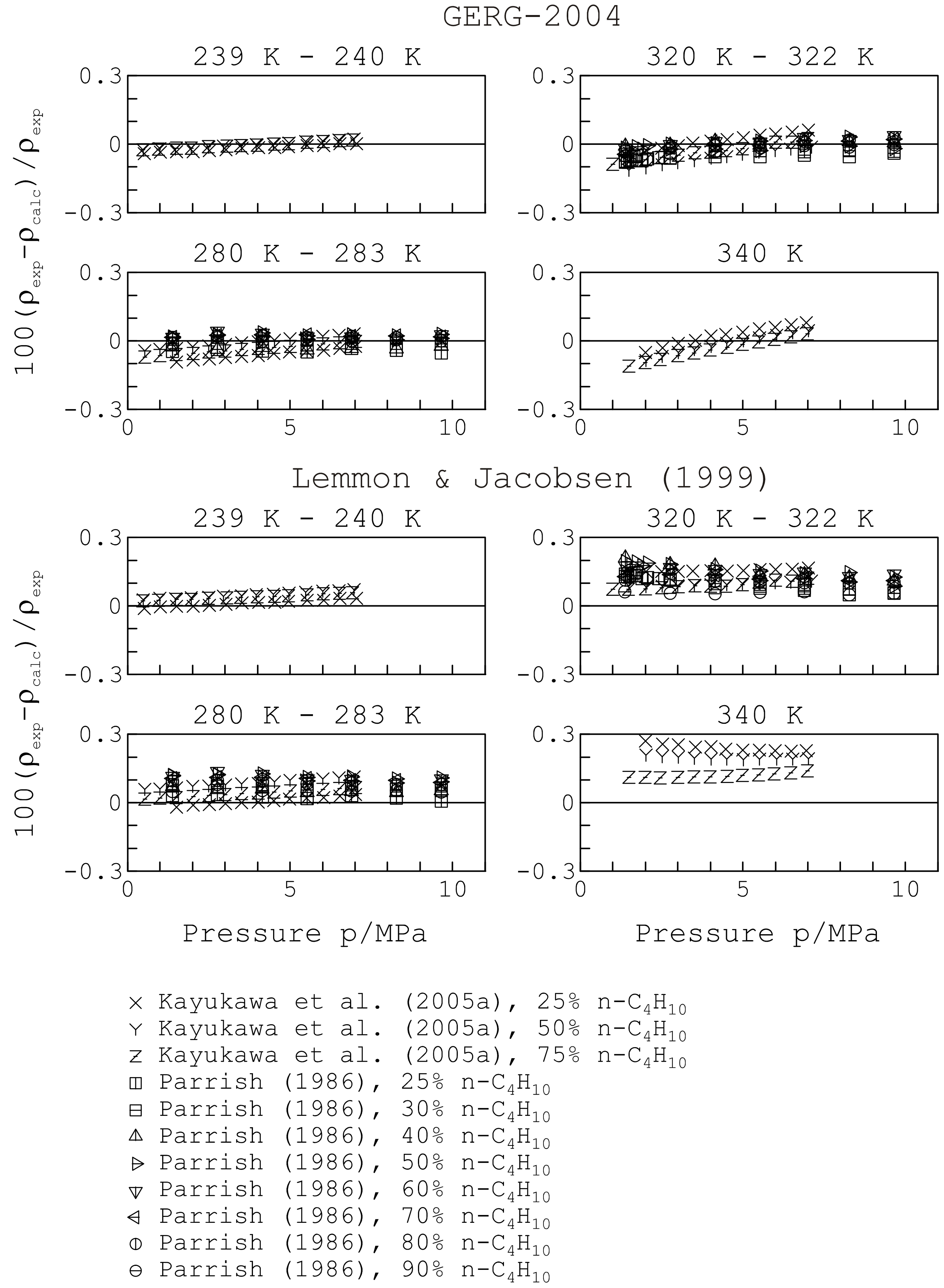

Fig. 8.24 Percentage density deviations of selected experimental $p\rho T$ data for the propane–n-butane binary mixture from values calculated from the new equation of state (GERG-2004), Eqs. (7.1) – (7.10), and the mixture model of Lemmon and Jacobsen (1999).

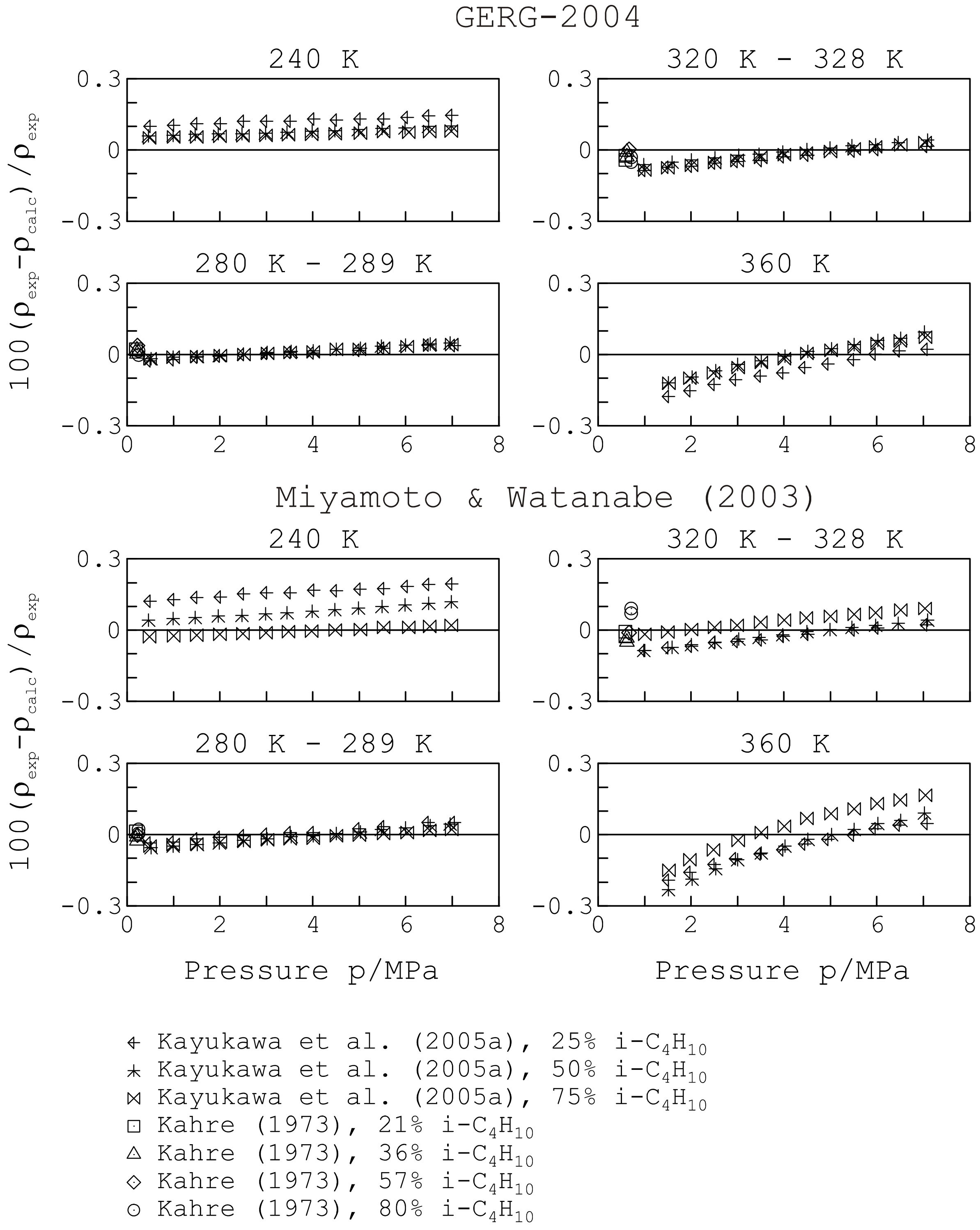

Fig. 8.25 Percentage density deviations of selected experimental $p\rho T$ data for the n-butane–isobutane binary mixture from values calculated from the new equation of state (GERG-2004), Eqs. (7.1) – (7.10), and the mixture model of Miyamoto and Watanabe (2003).

whereas the new equation represents the measurements to within ±0.1% as shown in Fig. 8.24. The recent multi-fluid mixture model of Miyamoto and Watanabe (2003) yields quite similar results for propane–n-butane (not shown here), but shows larger deviations than the GERG-2004 formulation for the n-butane–isobutane mixture as displayed in Fig. 8.25.

The apparent higher uncertainties of the other mixture models are caused by fitting different data sets. The models do not have higher uncertainties, but they show a different description.

n-Pentane–n-Hexane and n-Hexane–n-Heptane

Measurements are generally scarce for liquid phase densities of binary mixtures consisting of the "heavier" hydrocarbons n-pentane, n-hexane, n-heptane, and n-octane. Although covering the entire composition range, several of the available data are of low value for the development of wide-ranging mixture models, since they were only measured at atmospheric pressure and ambient temperatures of 293 K or 298 K [e.g. Chevalier *et al.* (1990)], or in a comparatively narrow temperature range from 283 K to 313 K [Goates *et al.* (1981)]. Data measured at atmospheric pressure but over a wider range of temperature from 273 K to 363 K using a vibrating tube densimeter were very recently reported by Ramos-Estrada *et al.* (2006) for the binary mixtures n-pentane–n-hexane, n-pentane–n-heptane, and n-hexane–n-heptane. Figure 8.26 exemplifies the representation of the n-hexane–n-heptane data by the GERG-2004 formulation, which is able to describe all measurements with low deviations of less than ±(0.1 – 0.2)%. The data measured by Ramos-Estrada *et al.* (2006) for n-pentane–n-hexane are well represented to within ±(0.1 – 0.3)%, and most of those measured for n-pentane–n-heptane are within ±(0.1 – 0.5)% (both not shown here).

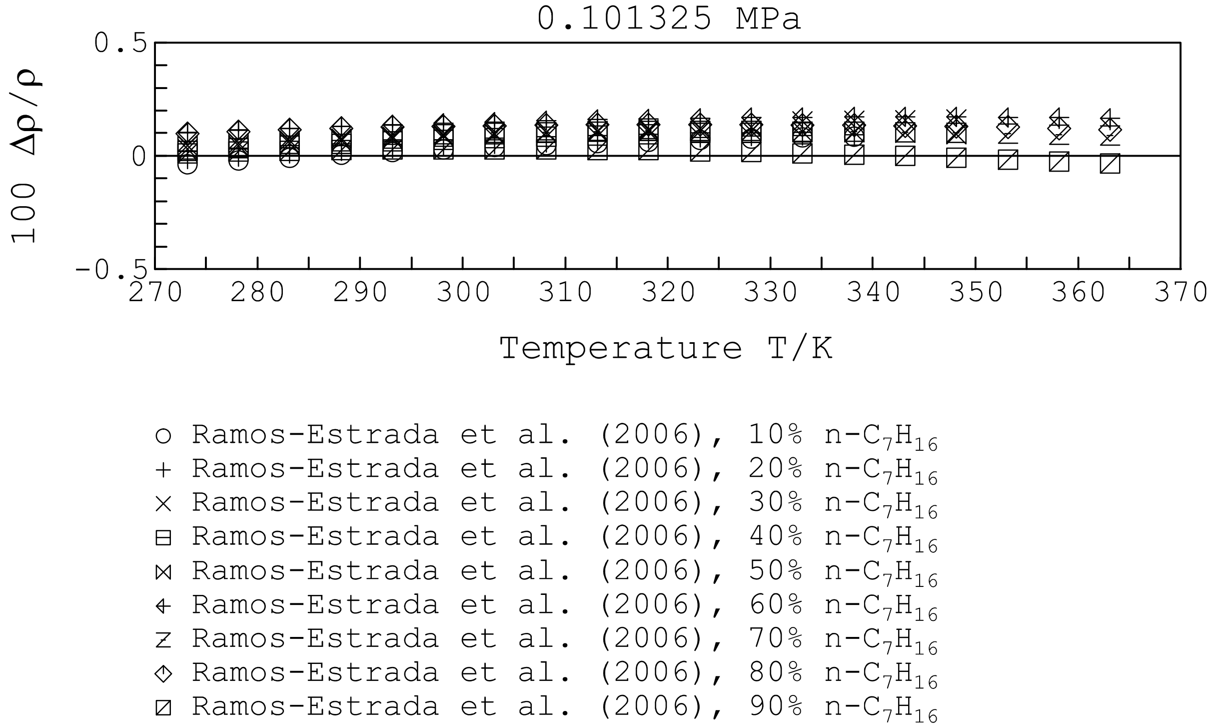

Fig. 8.26 Percentage density deviations $100\Delta\rho/\rho = 100(\rho_{\text{exp}} - \rho_{\text{calc}})/\rho_{\text{exp}}$ of the experimental $p\rho T$ data measured by Ramos-Estrada *et al.* (2006) for the n-hexane–n-heptane binary mixture from values calculated from the new equation of state (GERG-2004), Eqs. (7.1) – (7.10).

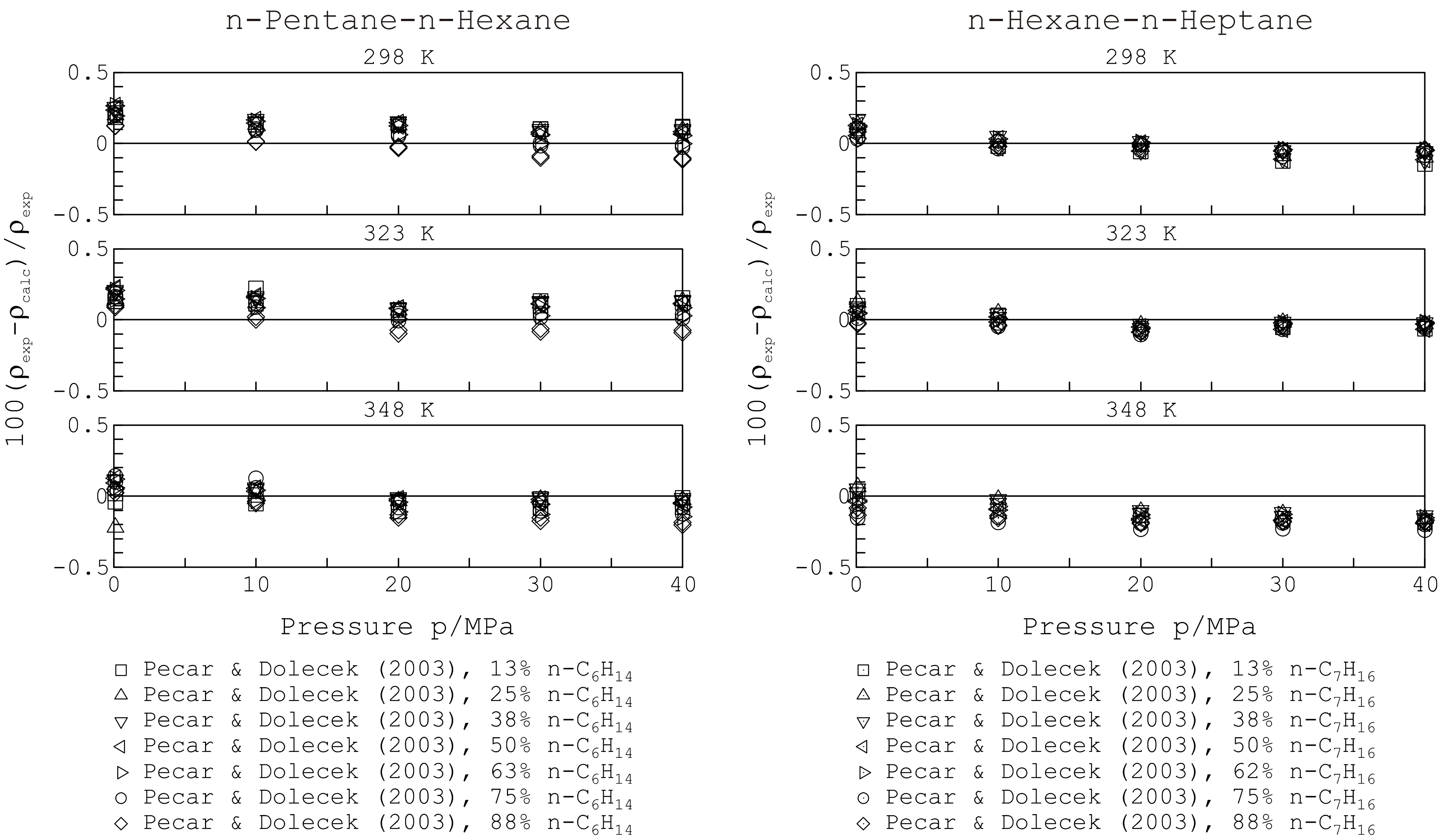

Fig. 8.27 Percentage density deviations of selected experimental $p\rho T$ data measured by Pecar and Dolecek (2003) for the n-pentane–n-hexane and n-hexane–n-heptane binary mixtures from values calculated from the new equation of state (GERG-2004), Eqs. (7.1) – (7.10).

Data measured over wide ranges of mixture conditions (temperature, pressure, and composition) were recently reported by Pecar and Dolecek (2003) for binary (and ternary) mixtures consisting of n-pentane, n-hexane, and n-heptane. The data were measured with a vibrating tube densimeter at 298 K, 323 K, and 348 K, and in the pressure range from 0.1 MPa to 40 MPa covering a wide range of distinct compositions. The uncertainty in density of these measurements is estimated by the authors to be less than 1%. Selected data for the binary mixtures n-pentane–n-hexane and n-hexane–n-heptane and their percentage deviations from the GERG-2004 formulation are shown in Fig. 8.27. Although the measurements were not available at the time the new equation of state was developed, they are all represented by the GERG-2004 formulation to within low deviations of ±(0.1 – 0.3)%. The data measured for the binary mixture n-pentane–n-heptane are all represented to within ±(0.1 – 0.5)% (not shown here). The average absolute deviations amount to 0.098% for the data for n-pentane–n-hexane, 0.309% for n-pentane–n-heptane, and 0.078% for n-hexane–n-heptane (see also Table A2.1 of the appendix).

A similar accurate description of liquid phase densities by the new equation of state is also achieved for the binary hydrocarbon mixtures n-hexane–n-octane and n-heptane–n-octane, for which, however, only density data measured at atmospheric pressure are available (see also Table A2.1 of the appendix).

8.2.2 Caloric Properties in the Homogeneous Region

Measurements of caloric properties of binary mixtures composed of other than the natural gas main constituents are scarce. Moreover, the few caloric data available for binary mixtures consisting of secondary natural gas components (including binary hydrocarbon mixtures) are limited in the covered mixture conditions (see also Table 6.4).

Accurate isochoric heat capacities were measured by Duarte-Garza and Magee (1999) in the liquid phase of the binary hydrocarbon mixture propane–isobutane for 30% and 70% of isobutane. The uncertainty in isobaric heat capacity is claimed by the authors to be 0.7%. As shown in Fig. 8.28, the GERG-2004 formulation represents the measurements well within deviations of ±(1 – 1.5)%, which is satisfactory and in good agreement with the accurate description achieved for the heat capacity measurements of Mayrath and Magee (1989) for methane–ethane and of Magee (1995) for carbon dioxide–ethane using the same experimental equipment (see also Figs. 8.11 and 8.15).

8.2.3 Vapour-Liquid Equilibrium Properties

Whereas the data situation for VLE properties of important binary mixtures of natural gas main constituents is quite satisfactory (see Sec. 8.1.3), many of the available VLE data for

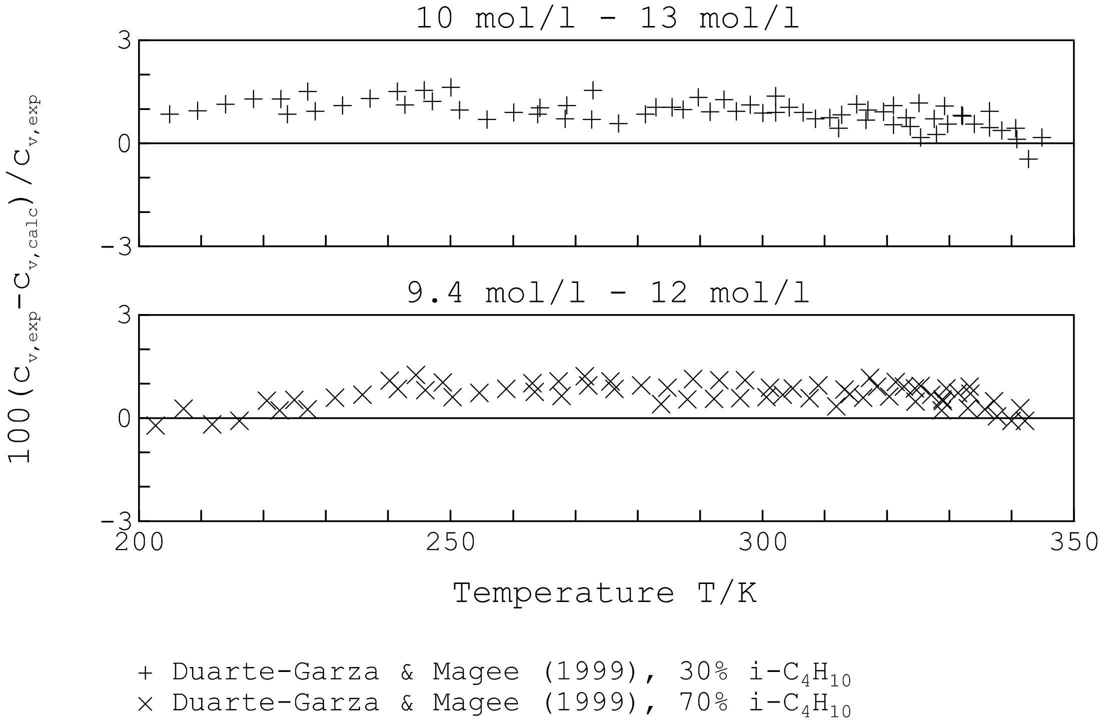

Fig. 8.28 Percentage deviations of the experimental isochoric heat capacity data measured by Duarte-Garza and Magee (1999) for the propane–isobutane binary mixture from values calculated from the new equation of state (GERG-2004), Eqs. (7.1) – (7.10).

binary hydrocarbon mixtures are of comparatively poor quality. As mentioned before, experimental saturated liquid and saturated vapour densities are often associated with an increased uncertainty exceeding values of 1%. A comparatively large scatter in the measurements available for the *pTxy* relation is frequently observed, and data sets measured by different sources at virtually the same mixture conditions deviate from each other by several percents, complicating the development of accurate binary equations. For several binary systems only a few VLE data are available.

Ethane–n-Butane and Ethane–Isobutane

Selected experimental *pTxy* measurements for ethane–n-butane and their deviations from the GERG-2004 formulation are shown in Fig. 8.29. The most accurate and consistent data seem to be those of Benedict *et al.* (1942). The new equation of state represents the measured vapour pressures of these authors to within ±(0.5 – 1)% at subcritical temperatures as well as in the critical region of the mixture. In addition, the simultaneously measured vapour phase compositions are well described to within ±(0.5 – 1) mole-%. The data of Lhoták and Wichterle (1981) cover a wider range of composition but show a large scatter in the deviations for both the vapour pressures and vapour phase compositions. The data of Mehra and Thodos (1965) and Dingrani and Thodos (1978) are also obviously of poor quality regarding the measured vapour pressures, but show a better consistency in the simultaneously

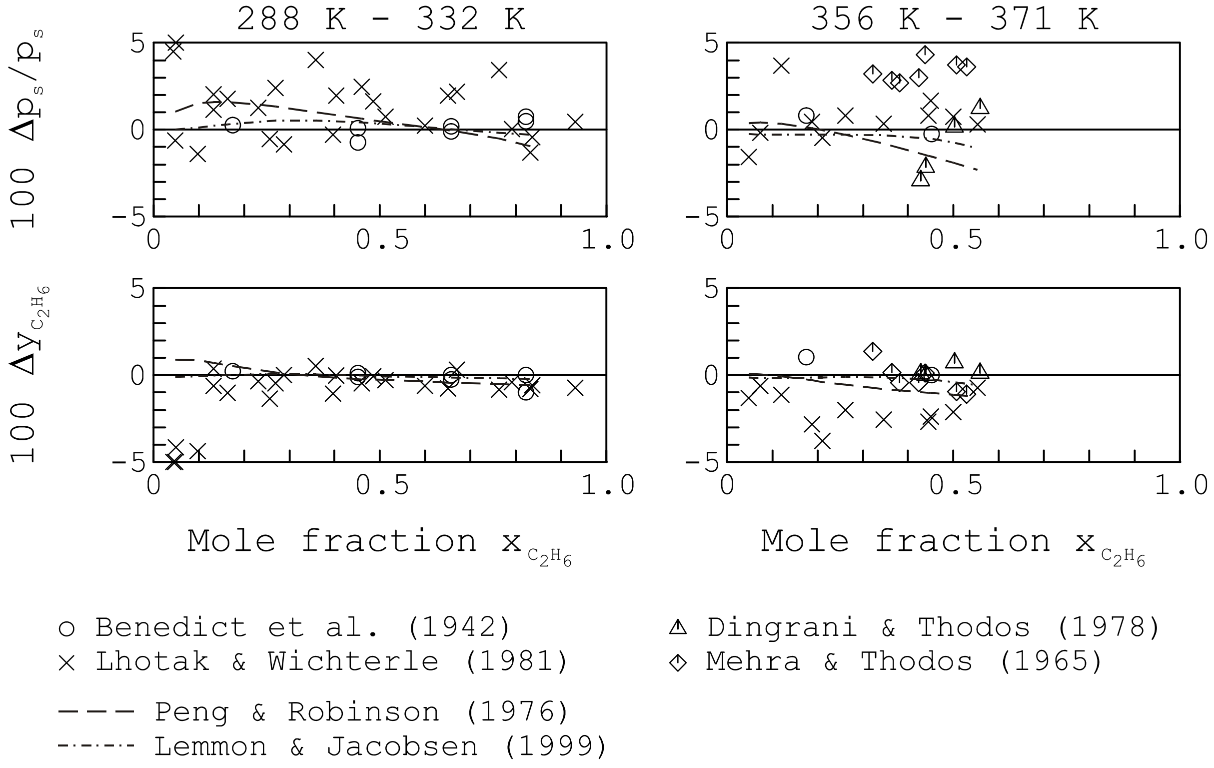

Fig. 8.29 Representation of selected experimental vapour pressures and ethane mole fractions in the saturated vapour phase for the ethane–n-butane binary mixture by the new equation of state (GERG-2004), Eqs. (7.1) – (7.10): $100\,\Delta p_{\mathrm{s}}/p_{\mathrm{s}} = 100\,(p_{\mathrm{s,exp}} - p_{\mathrm{s,calc}})/p_{\mathrm{s,exp}}$, $100\,\Delta y_{\mathrm{C_2H_6}} = 100\,(y_{\mathrm{C_2H_6,exp}} - y_{\mathrm{C_2H_6,calc}})$. Values calculated from the cubic equation of state of Peng and Robinson (1976) and the mixture model of Lemmon and Jacobsen (1999) are plotted for comparison at temperatures of 323 K and 363 K.

measured vapour phase compositions, represented by the new equation of state to within ±(0.5 – 1.5) mole-%. Compared to the GERG-2004 formulation, the multi-fluid mixture model of Lemmon and Jacobsen (1999) exhibits a very similar description of the phase behaviour of this mixture at temperatures of 323 K and 363 K, whereas the cubic equation of state of Peng and Robinson (1976) yields slightly different and worse results.

Comparisons between different VLE data measured by Besserer and Robinson (1973c) for the binary mixture ethane–isobutane and values calculated from the GERG-2004 formulation are shown in Figs. 8.30 and 8.31. The *pTxy* relation of this mixture was measured in the temperature range from 311 K to 394 K. In addition, the saturated liquid and saturated vapour densities were experimentally determined, thus providing a complete set of simultaneously measured VLE properties. The data are, however, of poor quality as is oftentimes seen for VLE data in the comparatively large scatter of the deviations for the different equilibrium properties. Most of the experimental vapour pressures are represented by the new equation of state to within ±2%. Most of the measured vapour phase compositions are described to within ±(1 – 2) mole-%. Typical percentage deviations for saturated liquid densities are within ±(1 – 2)%. Those for saturated vapour densities are approximately twice as high.

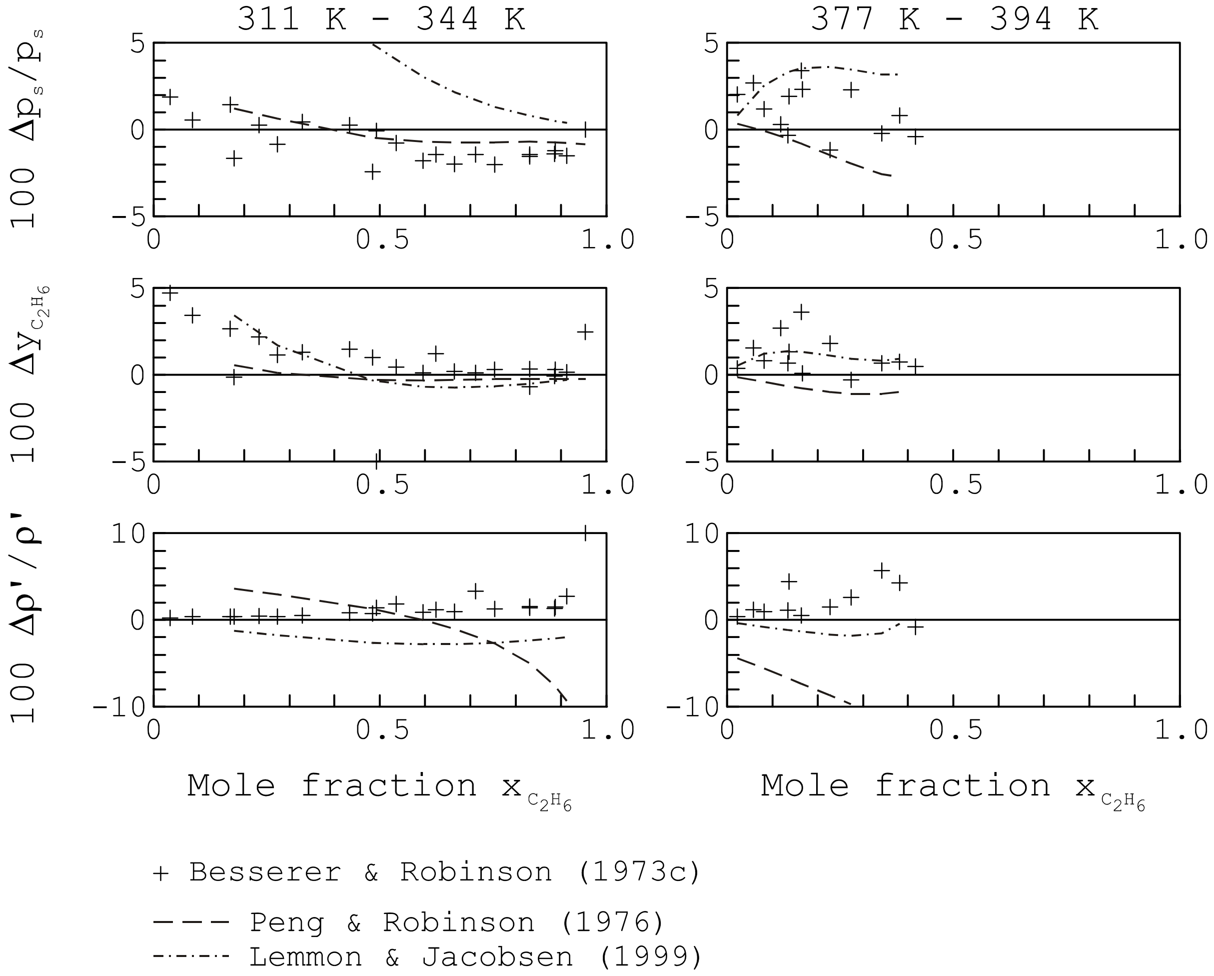

Fig. 8.30 Representation of the experimental vapour pressures, ethane mole fractions in the saturated vapour phase, and saturated liquid densities measured by Besserer and Robinson (1973c) for the ethane–isobutane binary mixture by the new equation of state (GERG-2004), Eqs. (7.1) – (7.10): $100\,\Delta p_s/p_s = 100\,(p_{s,\mathrm{exp}} - p_{s,\mathrm{calc}})/p_{s,\mathrm{exp}}$, $100\,\Delta y_{C_2H_6} = 100\,(y_{C_2H_6,\mathrm{exp}} - y_{C_2H_6,\mathrm{calc}})$, $100\,\Delta\rho'/\rho' = 100\,(\rho'_{\mathrm{exp}} - \rho'_{\mathrm{calc}})/\rho'_{\mathrm{exp}}$. Values calculated from the cubic equation of state of Peng and Robinson (1976) and the mixture model of Lemmon and Jacobsen (1999) are plotted for comparison.

Whereas the new equation of state is able to describe the data for different measured equilibrium properties with reasonable accuracy (taking into account the increased uncertainty of the measurements), both the cubic equation of state of Peng and Robinson (1976) and the multi-fluid mixture model of Lemmon and Jacobsen (1999) show all in all a less accurate description of the different properties. Values calculated from the cubic equation at 311 K and 377 K deviate from the measured saturated liquid densities by clearly more than 5% or 10%. The model of Lemmon and Jacobsen (1999) shows considerably larger deviations for the measured vapour pressures, clearly exceeding values of 5% at 311 K for ethane mole fractions below 50%.

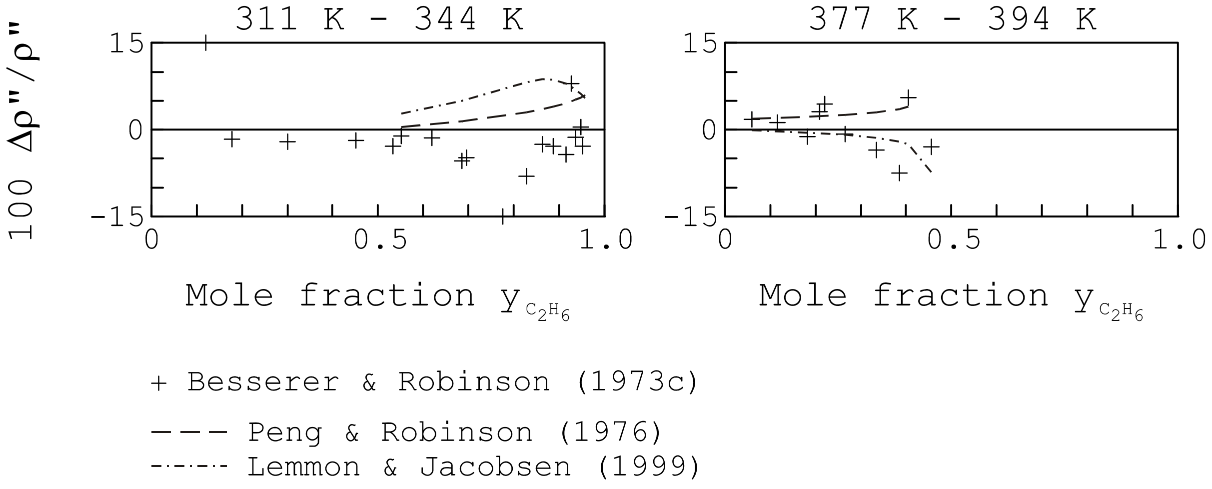

Fig. 8.31 Percentage deviations of the experimental saturated vapour densities measured by Besserer and Robinson (1973c) for the ethane–isobutane binary mixture from values calculated from the new equation of state (GERG-2004), Eqs. (7.1) – (7.10). Values calculated from the cubic equation of state of Peng and Robinson (1976) and the mixture model of Lemmon and Jacobsen (1999) are plotted for comparison.

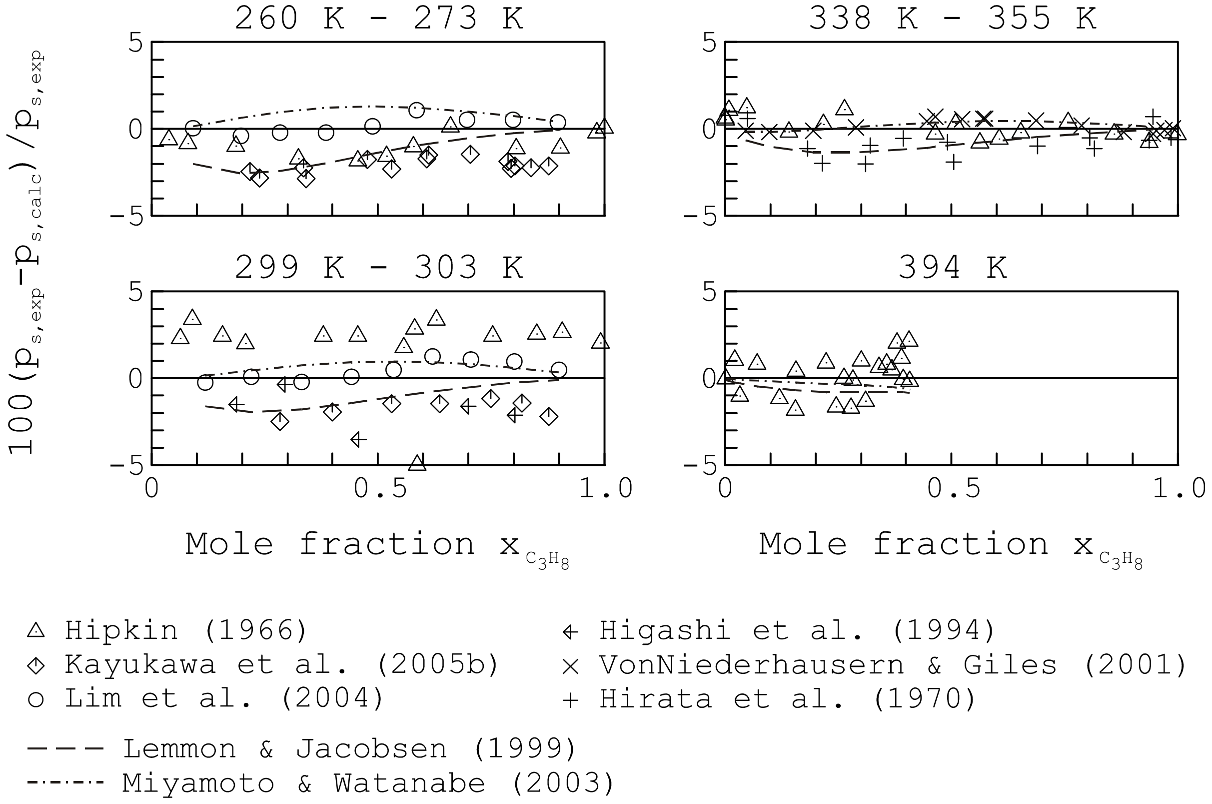

Fig. 8.32 Percentage deviations of selected experimental vapour pressures for the propane–isobutane binary mixture from values calculated from the new equation of state (GERG-2004), Eqs. (7.1) – (7.10). Values calculated from the mixture models of Lemmon and Jacobsen (1999) and Miyamoto and Watanabe (2003) are plotted for comparison at temperatures of 273 K, 303 K, 355 K, and 394 K.

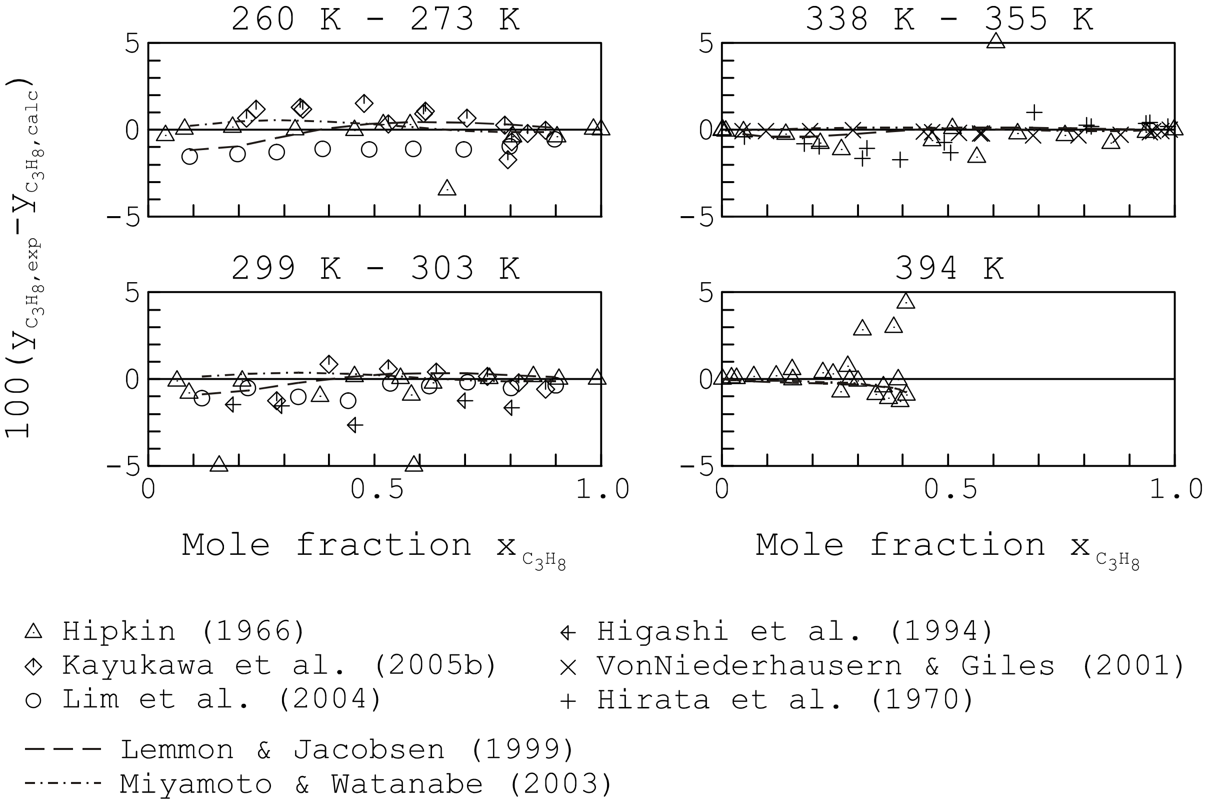

Fig. 8.33 Deviations of selected experimental propane mole fractions in the saturated vapour phase for the propane–isobutane binary mixture from values calculated from the new equation of state (GERG-2004), Eqs. (7.1) – (7.10). Values calculated from the mixture models of Lemmon and Jacobsen (1999) and Miyamoto and Watanabe (2003) are plotted for comparison at temperatures of 273 K, 303 K, 355 K, and 394 K.

Binary Mixtures of Propane, n-Butane, and Isobutane

Percentage deviations of selected experimental vapour pressures and vapour phase compositions for propane–isobutane from values calculated from the GERG-2004 formulation are shown in Figs. 8.32 and 8.33. A wide ranging data set was reported by Hipkin (1966) covering the entire composition range at temperatures from 267 K to 394 K. The most accurate data set seems to be the one measured by VonNiederhausern and Giles (2001) covering temperatures from 322 K to 355 K, and showing very good consistency in both the experimental vapour pressures and the vapour phase compositions. The data are represented by the new equation of state with low deviations of less than ±(0.5 – 1)% for vapour pressures and less than ±(0.2 – 0.4) mole-% for vapour phase compositions. The vapour pressure data reported by Hipkin (1966), Hirata *et al.* (1970), Higashi *et al.* (1994), Lim *et al.* (2004), and Kayukawa *et al.* (2005b) seem to be associated with an increased uncertainty and are represented by the GERG-2004 formulation to within ±(1 – 3)% (except for a few points). The vapour pressures measured by these authors systematically deviate from each other by about 2% (or more) at nearly the same mixture conditions in the temperature range from

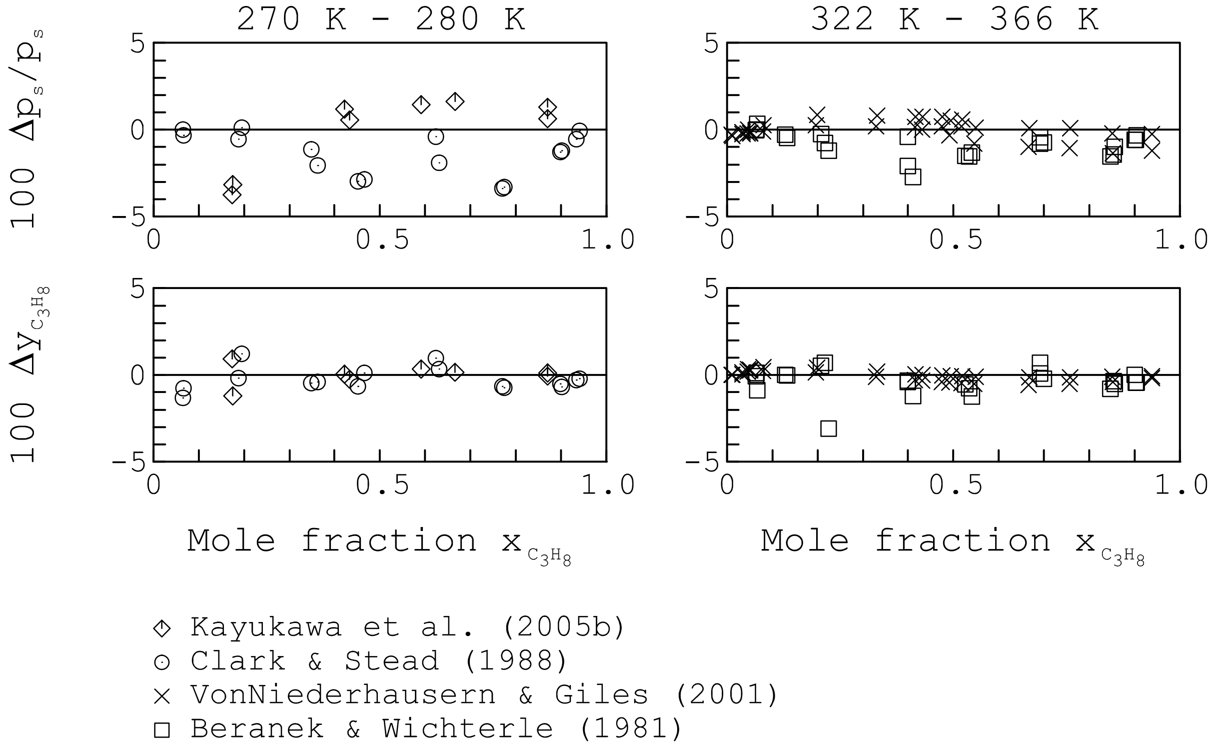

Fig. 8.34 Representation of selected experimental vapour pressures and propane mole fractions in the saturated vapour phase for the propane–n-butane binary mixture by the new equation of state (GERG-2004), Eqs. (7.1) – (7.10): $100\,\Delta p_s/p_s = 100\,(p_{s,\mathrm{exp}} - p_{s,\mathrm{calc}})/p_{s,\mathrm{exp}}$, $100\,\Delta y_{C_3H_8} = 100\,(y_{C_3H_8,\mathrm{exp}} - y_{C_3H_8,\mathrm{calc}})$.

299 K to 303 K. The experimental uncertainty in vapour phase composition of these authors seems to be in general not better than (1 – 2) mole-%. The representation of these measurements by the GERG-2004 formulation agrees well with this estimated uncertainty.

Compared to the accurate description achieved by the GERG-2004 formulation for the *pTxy* relation of propane–isobutane, the recent multi-fluid mixture model of Miyamoto and Watanabe (2003) yields a similar representation of the *pTxy* relation, whereas the model of Lemmon and Jacobsen (1999) shows a somewhat different representation of the selected vapour pressure data at subcritical temperatures as displayed in Fig. 8.32 due to fitting different data sets.

For the binary mixtures propane–n-butane and n-butane–isobutane, a similar accurate description of the *pTxy* relation is achieved by the GERG-2004 formulation as for propane–isobutane, as shown in Figs. 8.34 and 8.35. Several of the selected data sets are obviously associated with an increased (but typical) uncertainty, thus limiting the achievable accuracy of any equation of state. The previous multi-fluid mixture models of Miyamoto and Watanabe (2003) and Lemmon and Jacobsen (1999) yield quite similar results (not shown here) for these two binary mixtures compared to the representation of the data by the new equation of state.

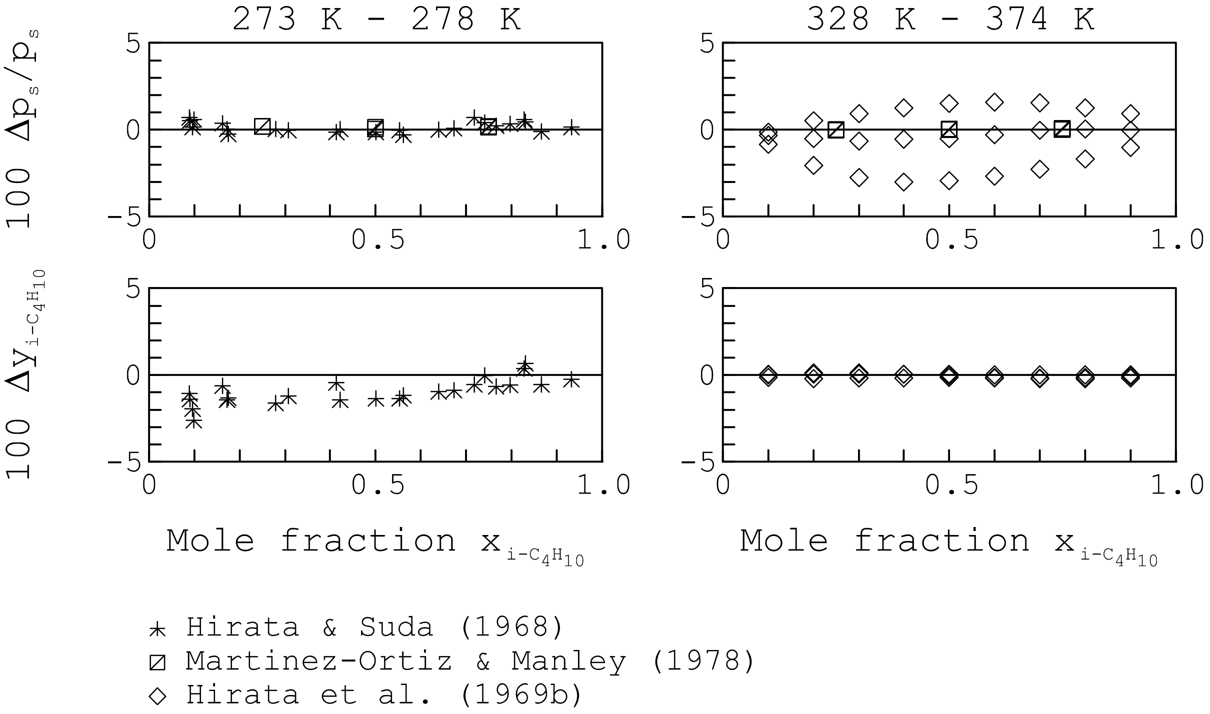

Fig. 8.35 Representation of selected experimental vapour pressures and isobutane mole fractions in the saturated vapour phase for the n-butane–isobutane binary mixture by the new equation of state (GERG-2004), Eqs. (7.1) – (7.10): $100\,\Delta p_{\mathrm{s}}/p_{\mathrm{s}} = 100\,(p_{\mathrm{s,exp}} - p_{\mathrm{s,calc}})/p_{\mathrm{s,exp}}$, $100\,\Delta y_{\mathrm{i\text{-}C_4H_{10}}} = 100\,(y_{\mathrm{i\text{-}C_4H_{10},exp}} - y_{\mathrm{i\text{-}C_4H_{10},calc}})$.

Other Binary Hydrocarbon Mixtures

The representation of selected experimental *pTxy* data for the binary mixtures propane–n-pentane, propane–n-heptane, and n-pentane–n-heptane by the GERG-2004 formulation is shown in Figs. 8.36 – 8.38. The comparisons exemplify the description of the *pTxy* relation by the new equation of state for binary hydrocarbon mixtures containing (or consisting of) the “heavier” hydrocarbons n-pentane, n-hexane, n-heptane, and n-octane. For instance, similar results as for the selected examples are also obtained for n-butane–n-hexane, n-butane–n-heptane, n-butane–n-octane, n-pentane–n-octane, etc.

Measurements are in general scarce and are often of comparatively poor quality for these binary hydrocarbon mixtures, such as the data of Sage and Lacey (1940) for propane–n-pentane (see Fig. 8.36) and of Kay (1971) for propane–n-heptane (see Fig. 8.37). The selected experimental vapour pressures for these binary mixtures are represented by the new equation of state to within ±3% for propane–n-pentane and ±5% for propane–n-heptane. Deviations between experimental vapour phase compositions and values calculated from the GERG-2004 formulation are generally less than ±(2 – 3) mole-%. For propane–n-heptane, higher deviations between measured and calculated vapour phase compositions are observed at propane concentrations below 25%. Taking into account the obviously increased

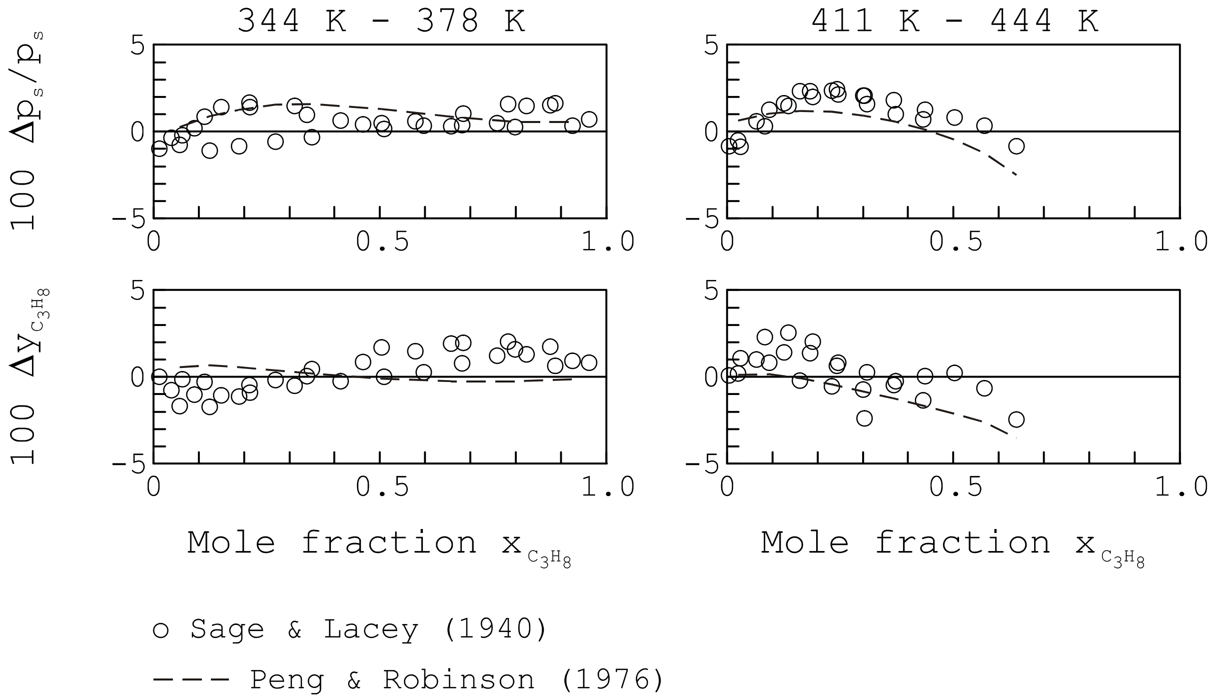

Fig. 8.36 Representation of selected experimental vapour pressures and propane mole fractions in the saturated vapour phase measured by Sage and Lacey (1940) for the propane–n-pentane binary mixture by the new equation of state (GERG-2004), Eqs. (7.1) – (7.10): $100\,\Delta p_{\mathrm{s}}/p_{\mathrm{s}} = 100\,(p_{\mathrm{s,exp}} - p_{\mathrm{s,calc}})/p_{\mathrm{s,exp}}$, $100\,\Delta y_{\mathrm{C_3H_8}} = 100\,(y_{\mathrm{C_3H_8,exp}} - y_{\mathrm{C_3H_8,calc}})$. Values calculated from the cubic equation of state of Peng and Robinson (1976) are plotted for comparison.

uncertainty in the measurements, the description of the *pTxy* relation of such binary hydrocarbon mixtures by the new equation of state is quite satisfactory, which is also supported by the fact that the cubic equation of state of Peng and Robinson (1976) yields on average comparable results.

The measurements of Cummings *et al.* (1933) for n-pentane–n-heptane (see Fig. 8.38) are represented by the GERG-2004 formulation with deviations of less than ±(1 – 2)% for vapour pressures and of less than ±(1 – 2) mole-% for vapour phase compositions. The cubic equation of Peng and Robinson (1976) shows a very similar description of these measurements.

All in all, the comparisons above have shown that the new equation of state describes liquid phase densities of binary hydrocarbon mixtures over wide ranges of temperature, pressure, and composition very accurately. Typical deviations are clearly within ±(0.1 – 0.5)%. In general, experimental vapour pressures are represented to within ±(1 – 3)% and vapour phase compositions are within ±(1 – 2) mole-%. Larger deviations (e.g. up to ±5% or more for vapour pressures and up to ±3 mole-% or more for vapour phase compositions) are occasionally observed for certain binary mixtures. In general, the low quality of the available data limits the achievable accuracy of the new mixture model (and any other equation).

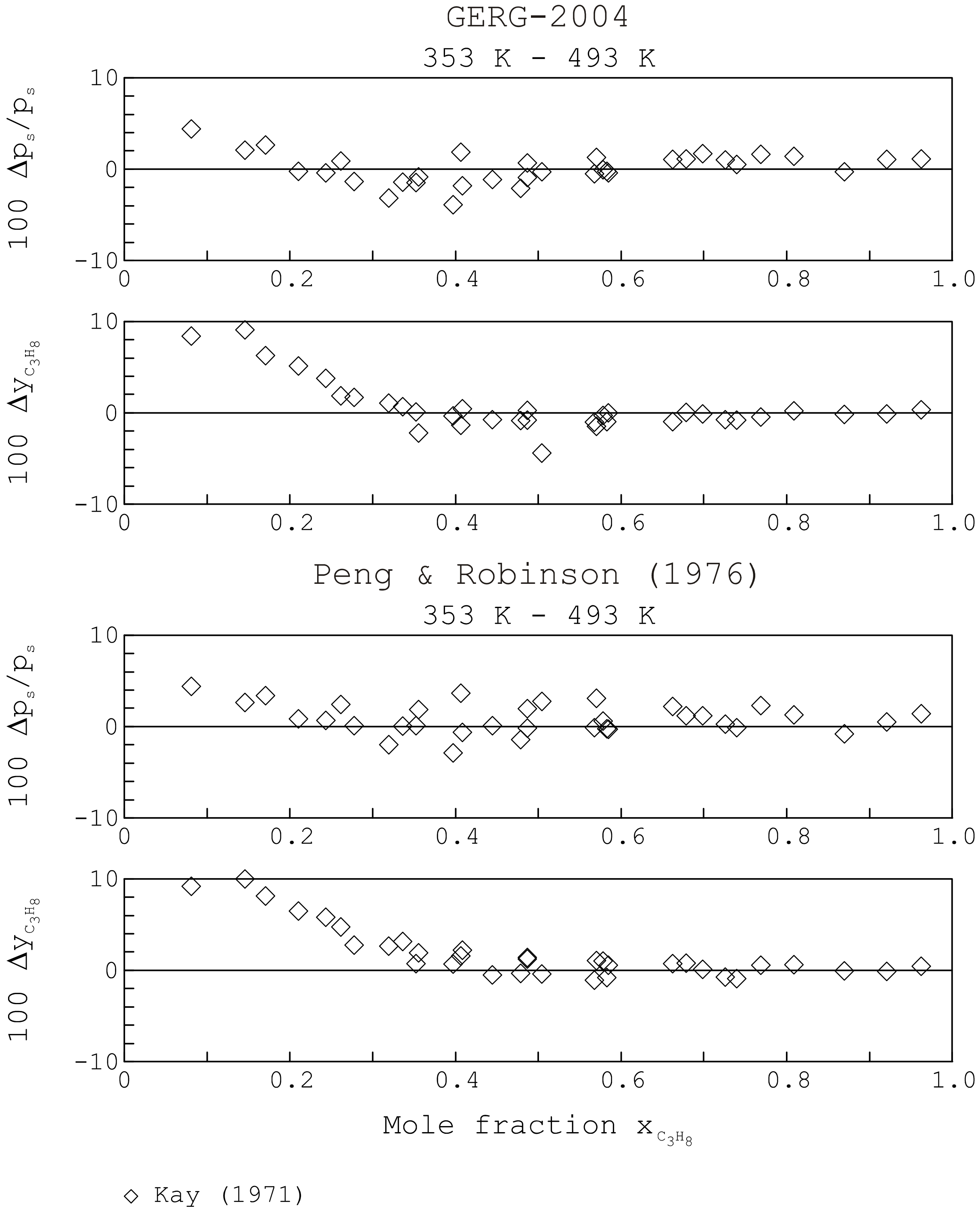

Fig. 8.37 Representation of selected experimental vapour pressures and propane mole fractions in the saturated vapour phase measured by Kay (1971) for the propane–n-heptane binary mixture by the new equation of state (GERG-2004), Eqs. (7.1) – (7.10), and the cubic equation of state of Peng and Robinson (1976): $100\,\Delta p_{\mathrm{s}}/p_{\mathrm{s}} = 100\,(p_{\mathrm{s,exp}} - p_{\mathrm{s,calc}})/p_{\mathrm{s,exp}}$, $100\,\Delta y_{\mathrm{C_3H_8}} = 100\,(y_{\mathrm{C_3H_8,exp}} - y_{\mathrm{C_3H_8,calc}})$.

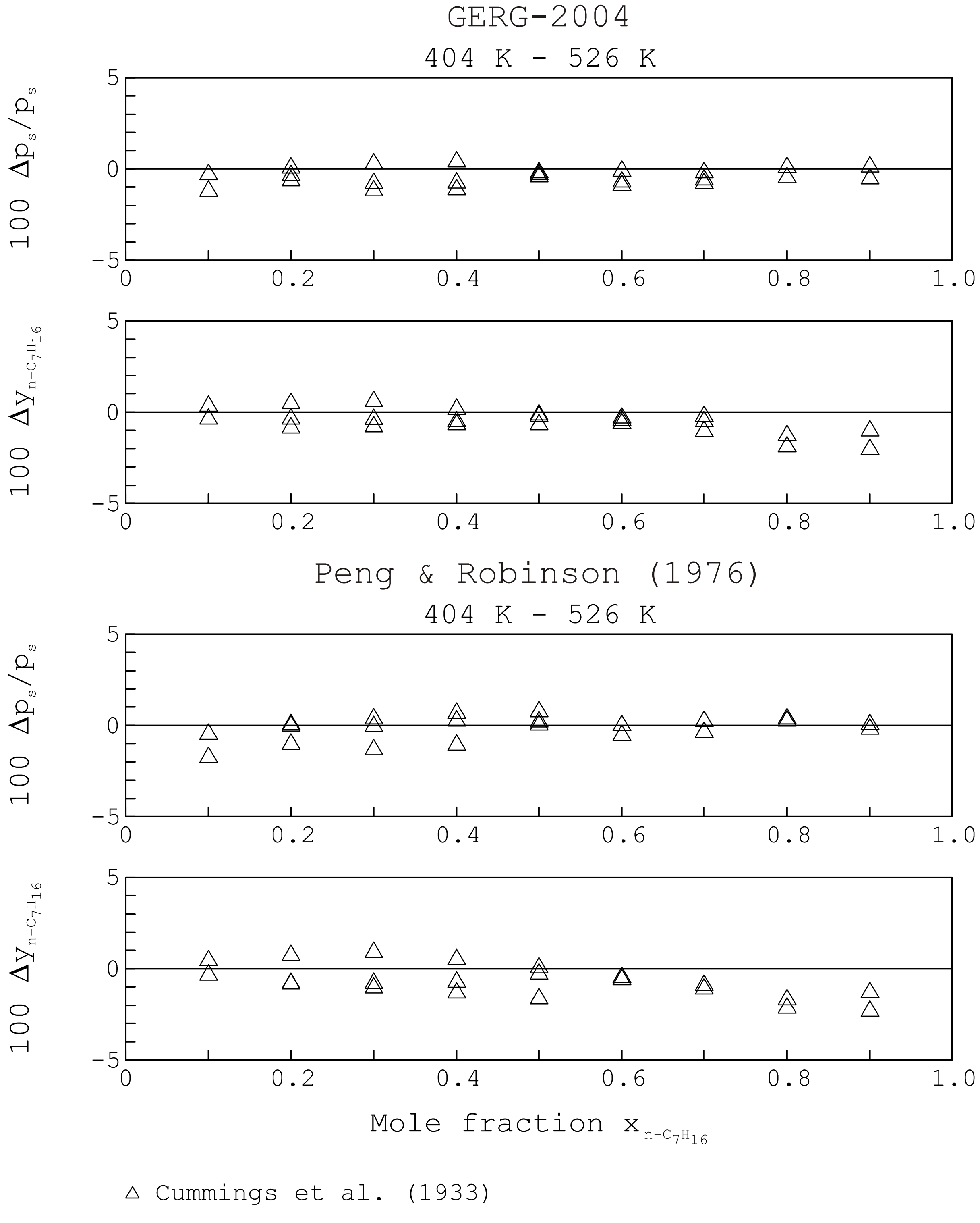

Fig. 8.38 Representation of the experimental vapour pressures and n-heptane mole fractions in the saturated vapour phase measured by Cummings *et al.* (1933) for the n-pentane–n-heptane binary mixture by the new equation of state (GERG-2004), Eqs. (7.1) – (7.10), and the cubic equation of state of Peng and Robinson (1976): $100\,\Delta p_{\mathrm{s}}/p_{\mathrm{s}} = 100\,(p_{\mathrm{s,exp}} - p_{\mathrm{s,calc}})/p_{\mathrm{s,exp}}$, $100\,\Delta y_{\text{n-C}_7\text{H}_{16}} = 100\,(y_{\text{n-C}_7\text{H}_{16}\text{,exp}} - y_{\text{n-C}_7\text{H}_{16}\text{,calc}})$.

8.3 The Representation of Thermal Properties of Other Selected Binary Mixtures

The comparisons compiled in the subsections below exemplify the accuracy achieved by the new mixture model for thermal properties of binary mixtures that do not fit into one of the previously discussed groups of binary mixtures. The following subsections focus on the representation of data for binary mixtures containing one (or two) of the secondary natural gas components hydrogen, oxygen, carbon monoxide, water, helium, or argon.

8.3.1 The $p\rho T$ Relation in the Homogeneous Region

Very accurate experimental gas phase densities are reported in the databank GERG TM7 [Jaeschke *et al.* (1997)] for binary mixtures of the main natural gas components (methane, nitrogen, carbon dioxide, and ethane) with hydrogen, and for methane–carbon monoxide, nitrogen–carbon monoxide, and nitrogen–helium. These data cover temperatures ranging from 270 K to 350 K at pressures up to 30 MPa, and different ranges of composition (wide for CH_4–H_2, N_2–H_2, and N_2–He, and limited for CH_4–CO, N_2–CO, CO_2–H_2, and C_2H_6–H_2). Most of these accurate data are represented by the GERG-2004 formulation to within ±(0.07 – 0.1)% as shown below for methane–hydrogen, which agrees well with the experimental uncertainties of the measurements. Higher maximum deviations are observed for only few data sets.

Density data from other sources (also including measurements in the liquid phase) are often associated with a considerably larger uncertainty, occasionally showing inconsistencies of more than ±1% between data sets of different authors or even within a single series of measurements.

Methane–Hydrogen

The accurate description of the $p\rho T$ relation of hydrogen–hydrocarbon, nitrogen–hydrogen, and carbon dioxide–hydrogen binary mixtures is of considerable importance for the accurate description of natural gas–hydrogen mixtures containing a high mole fraction of hydrogen (e.g. 10% or 20%) (see also Sec. 8.4.1).

A wide ranging data set is available for methane–hydrogen, which is the most important binary mixture concerning the influence on the description of natural gas–hydrogen mixtures. As shown in Fig. 8.39, the GERG-2004 formulation represents (almost) all of the selected experimental gas phase densities measured by Ruhrgas (1990) for methane–hydrogen to within low deviations of ±(0.07 – 0.1)% over wide ranges of temperature and pressure, and for all hydrogen mole fractions from 15% to 75%. In contrast to this very accurate

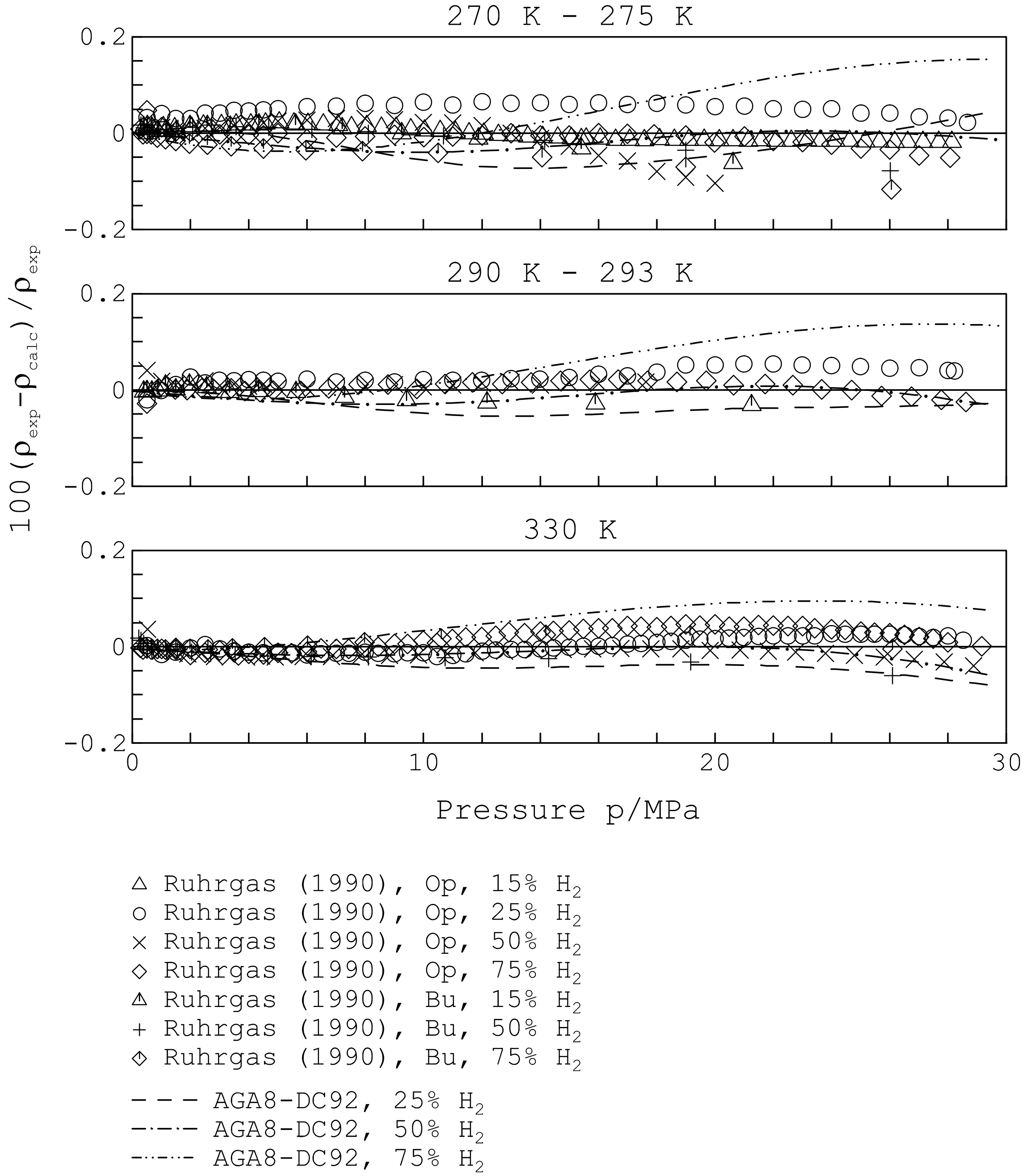

Fig. 8.39 Percentage density deviations of selected experimental $p\rho T$ data measured by Ruhrgas (1990) for the methane–hydrogen binary mixture from values calculated from the new equation of state (GERG-2004), Eqs. (7.1) – (7.10). Values calculated from the AGA8-DC92 equation of Starling and Savidge (1992) are plotted for comparison. Bu: Burnett apparatus, Op: optical interferometry method.

description, values calculated from the AGA8-DC92 equation of state deviate from the measurements by more than 0.1% at 270 K for the 25% and 75% hydrogen data, and at 290 K for the 75% hydrogen data. Taking a closer look at the deviation plots, even for the data measured on the 330 K isotherm, a considerably poorer composition dependence of the deviations can generally be observed for the AGA8-DC92 equation.

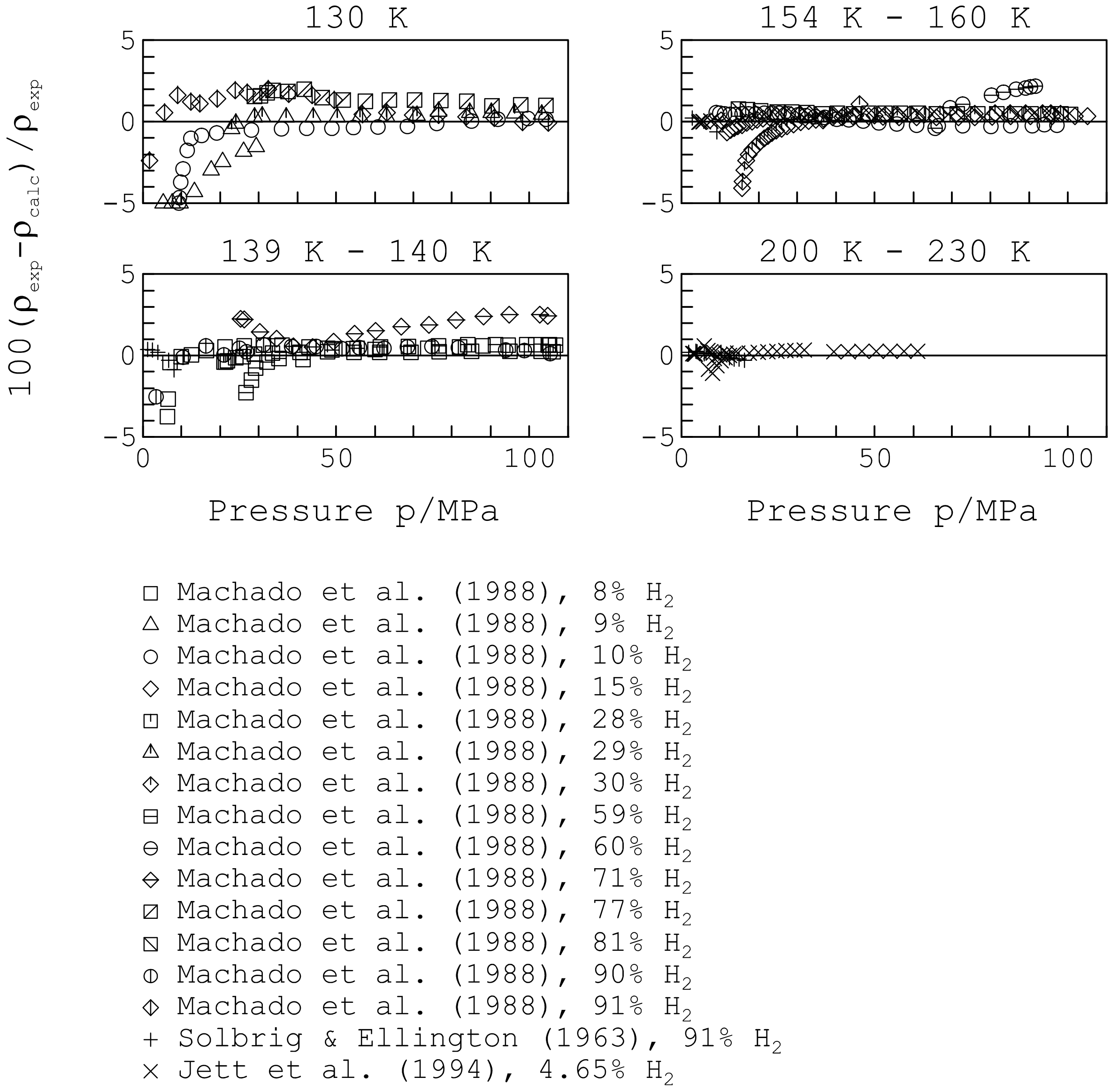

Fig. 8.40 Percentage density deviations of selected experimental *pρT* data covering the homogeneous gas, liquid, and supercritical regions for the methane–hydrogen binary mixture from values calculated from the new equation of state (GERG-2004), Eqs. (7.1) – (7.10).

Percentage deviations between experimental densities (covering the homogeneous gas, liquid, and supercritical regions) for methane–hydrogen at temperatures ranging from 130 K to 230 K and values calculated from the GERG-2004 formulation are shown in Fig. 8.40. The data of Machado *et al.* (1988) represent the only measurements available at temperatures from 130 K to 159 K covering a wide range of liquid and supercritical mixture state conditions. The data were measured for hydrogen mole fractions from about 8% to 91% and pressures up to around 100 MPa. Most of these measurements are represented by the new equation of state to within ±(0.5 – 2)%, which is quite satisfactory taking into account the comparatively low quality of the measurements compared to those present for gas phase densities at higher

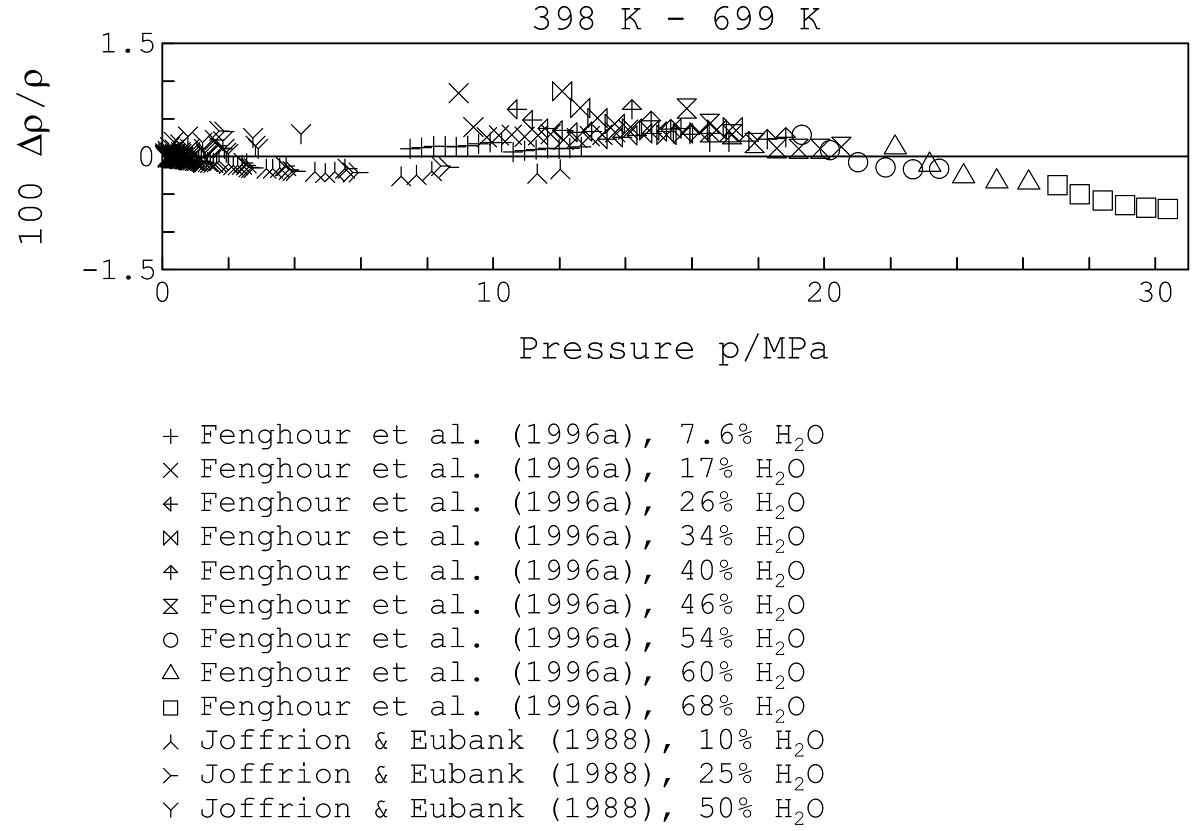

Fig. 8.41 Percentage density deviations $100\Delta\rho/\rho = 100(\rho_{\text{exp}} - \rho_{\text{calc}})/\rho_{\text{exp}}$ of selected experimental $p\rho T$ data for the methane–water binary mixture from values calculated from the new equation of state (GERG-2004), Eqs. (7.1) – (7.10).

temperatures (see Fig. 8.39). Higher deviations are observed in the vicinity of the mixture phase boundary[83]. Typical deviations obtained for the measurements of Solbrig and Ellington (1963) for 91% of hydrogen (covering temperatures from 139 K to 422 K at pressures up to 23 MPa), and of Jett *et al.* (1994) for approximately 5% of hydrogen (covering temperatures from 154 K to 273 K at pressures up to 68 MPa), are within ±(0.2 – 0.4)%.

Binary Mixtures Containing Water

The accurate knowledge of the $p\rho T$ relation of gaseous mixtures containing water is of considerable importance in many technical applications. The presence of water is frequently encountered in natural gases, causing problems in the production, transmission, and distribution of natural gas, even though often only present in small amounts. Water is responsible for the undesired formation of ice and gas hydrates that can lead to a blockage of

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[83] According to the authors, the measurements were carried out starting at pressures of about 100 MPa, and were extended down to pressures just above the region of phase separation, or to lower pressures at high hydrogen concentrations. Therefore, all densities are assumed to be homogeneous.

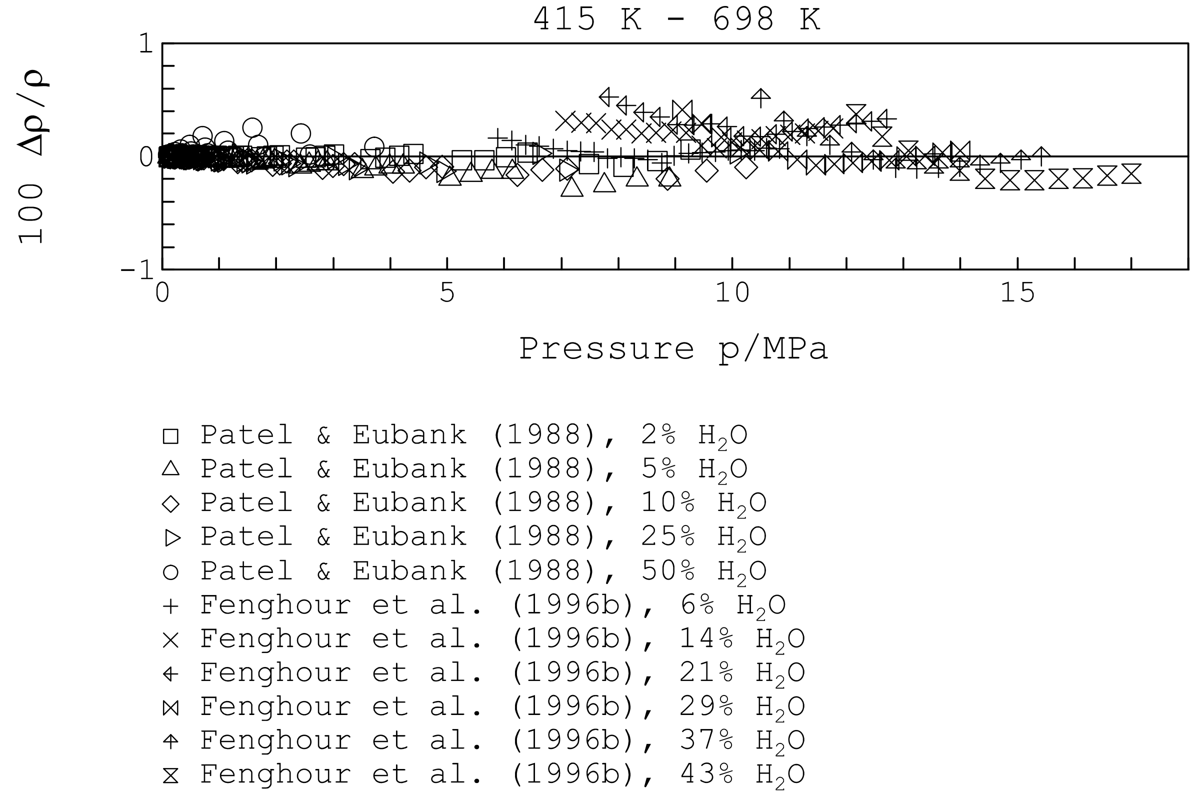

Fig. 8.42 Percentage density deviations $100\Delta\rho/\rho = 100(\rho_{\text{exp}} - \rho_{\text{calc}})/\rho_{\text{exp}}$ of selected experimental $p\rho T$ data for the carbon dioxide–water binary mixture from values calculated from the new equation of state (GERG-2004), Eqs. (7.1) – (7.10).

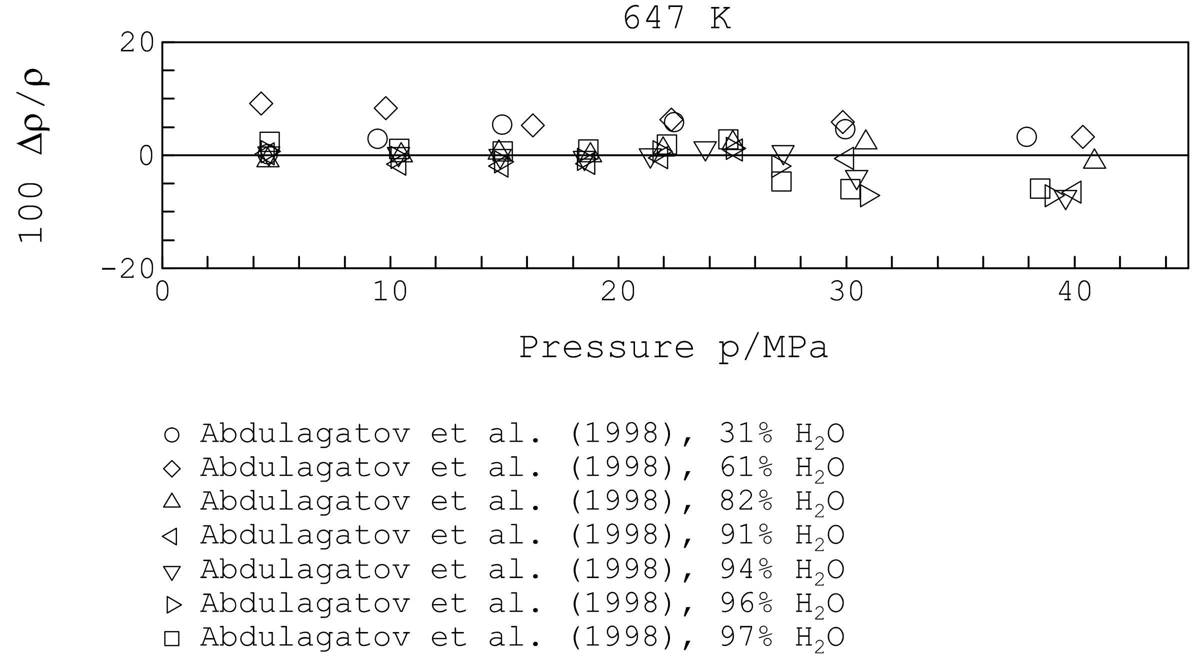

Fig. 8.43 Percentage density deviations $100\Delta\rho/\rho = 100(\rho_{\text{exp}} - \rho_{\text{calc}})/\rho_{\text{exp}}$ of selected experimental $p\rho T$ data measured by Abdulagatov *et al.* (1998) for the n-pentane–water binary mixture from values calculated from the new equation of state (GERG-2004), Eqs. (7.1) – (7.10).

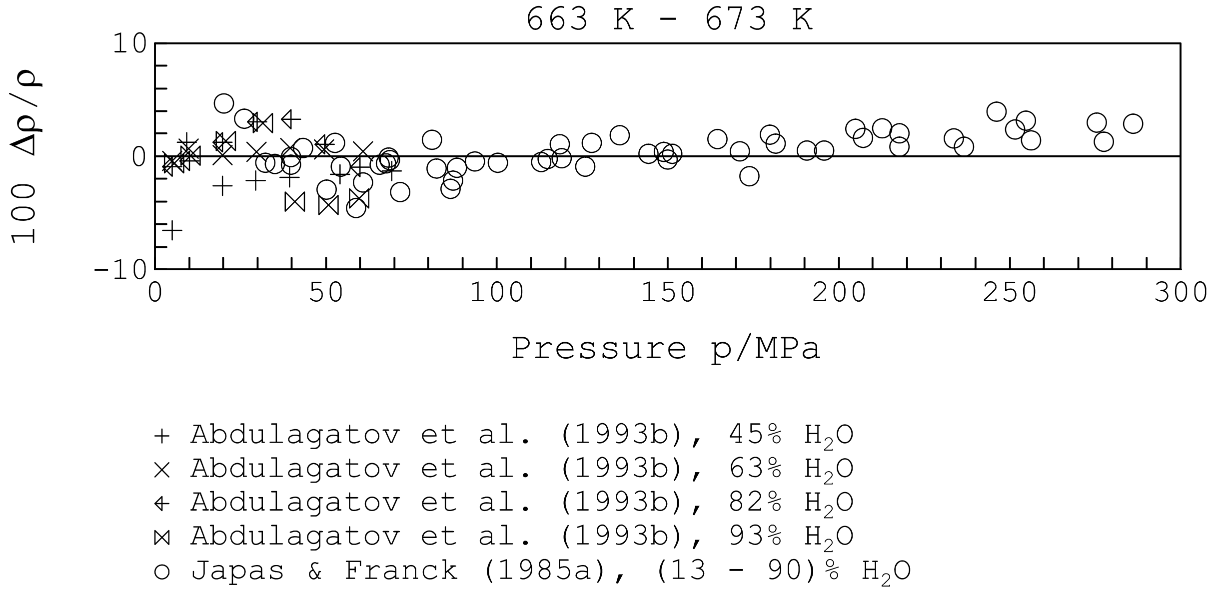

Fig. 8.44 Percentage density deviations $100\Delta\rho/\rho = 100(\rho_{\text{exp}} - \rho_{\text{calc}})/\rho_{\text{exp}}$ of selected experimental $p\rho T$ data for the nitrogen–water binary mixture from values calculated from the new equation of state (GERG-2004), Eqs. (7.1) – (7.10).

transport pipelines. There is also the risk of corrosion of pipes when weak acids are formed from sour gas constituents dissolved in water. Aside from nitrogen, oxygen, and carbon dioxide, water is one of the main constituents of typical combustion gases. Moreover, research is on-going aiming at the development of a technology that enables cost-effective and efficient medium to long-term storage of electrical energy based on compressed humid air. Accurate $p\rho T$ data (and data of other thermodynamic properties) for binary mixtures of natural gas main constituents and water, or secondary hydrocarbons and water are, however, generally scarce. This is also valid for binary mixtures of dry air components and water.

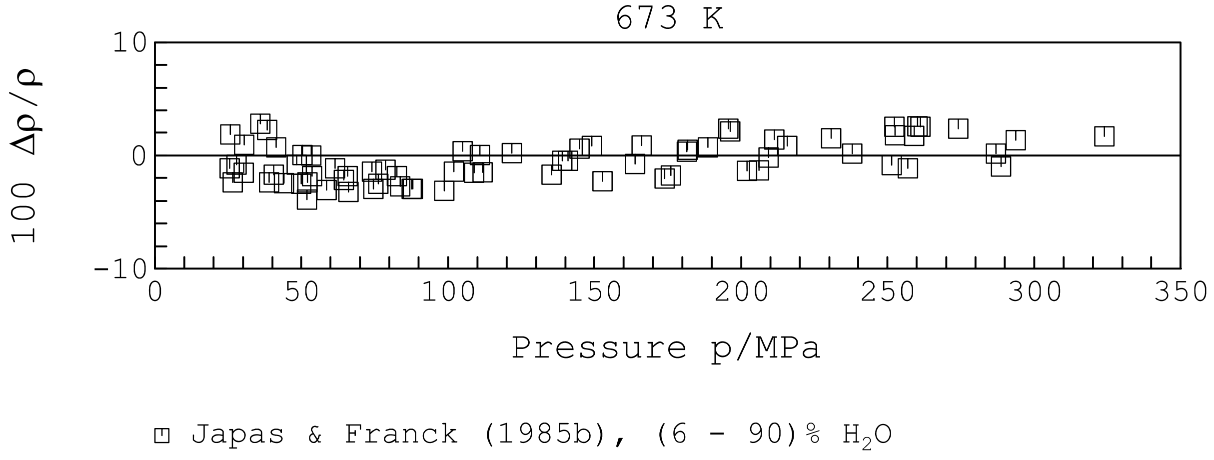

Fig. 8.45 Percentage density deviations $100\Delta\rho/\rho = 100(\rho_{\text{exp}} - \rho_{\text{calc}})/\rho_{\text{exp}}$ of selected experimental $p\rho T$ data measured by Japas and Franck (1985b) for the oxygen–water binary mixture from values calculated from the new equation of state (GERG-2004), Eqs. (7.1) – (7.10).

Figures 8.41 – 8.45 show percentage density deviations between selected measurements for methane–water, carbon dioxide–water, n-pentane–water, nitrogen–water, and oxygen–water, and values calculated from the GERG-2004 formulation. Sufficiently accurate data, measured using isochoric apparatuses, were reported by Joffrion and Eubank (1988) and Fenghour *et al.* (1996a) for methane–water (see Fig. 8.41), and by Patel and Eubank (1988) and Fenghour *et al.* (1996b) for carbon dioxide–water (see Fig. 8.42). The measurements cover wide composition ranges at temperatures from close to the saturation boundary up to about 700 K, and pressures up to 30 MPa (see Table A2.1 of the appendix for further details). Most of these data are represented by the new equation of state to within low deviations of ±(0.2 – 0.5)% as shown in Figs. 8.41 and 8.42.

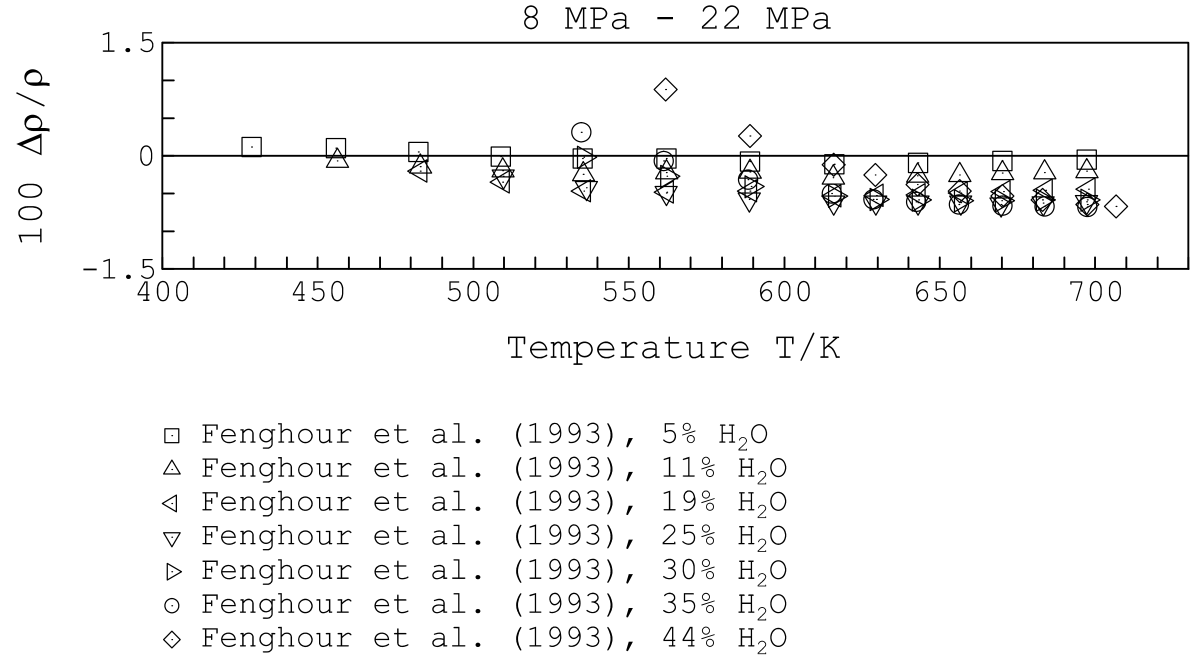

Fig. 8.46 Percentage density deviations $100\Delta\rho/\rho = 100(\rho_{\mathrm{exp}} - \rho_{\mathrm{calc}})/\rho_{\mathrm{exp}}$ of selected experimental $p\rho T$ data measured by Fenghour *et al.* (1993) for the nitrogen–water binary mixture from values calculated from the new equation of state (GERG-2004), Eqs. (7.1) – (7.10).

Considerably larger deviations are observed for the (less accurate) measurements of Abdulagatov *et al.* (1998) for n-pentane–water, for those of Japas and Franck (1985a) and Abdulagatov *et al.* (1993b) for nitrogen–water, and for the data of Japas and Franck (1985b) for oxygen–water as displayed in Figs. 8.43 – 8.45. The measurements of Japas and Franck (1985a, 1985b) cover the entire composition range at pressures up to about 300 MPa and are represented by the new equation of state to within ±(2 – 5)%. At lower temperatures and also along the vapour-liquid phase boundary of the respective mixtures (not shown here), the data are described almost to within the same range of percentage deviations. For nitrogen–water, a comparatively accurate data set is available measured by Fenghour *et al.* (1993) that complements the measurements of Japas and Franck (1985a) and Abdulagatov *et al.* (1993b) discussed above. Deviations between selected measurements of this source and values calculated from the GERG-2004 formulation are displayed in Fig. 8.46. The data extend from temperatures near the phase boundary up to about 700 K and are well represented by the new equation of state with deviations of less than ±(0.5 – 0.7)% (except for one single point slightly above this range).

8.3.2 Vapour-Liquid Equilibrium Properties

Many of the available data for thermal properties at vapour-liquid equilibrium states for binary mixtures containing one (or two) of the secondary natural gas components hydrogen, oxygen, carbon monoxide, water, helium, and argon are of comparatively poor quality. Likewise for binary hydrocarbon mixtures, experimental saturated liquid and saturated vapour densities are often associated with an increased uncertainty. The development of accurate binary equations is complicated due to the comparatively large scatter in the measurements available for the *pTxy* relation and inconsistencies between data sets measured by different authors at virtually the same mixture conditions. Only a few VLE data are available for several binary systems.

Methane–n-Octane

Figure 8.47 shows percentage deviations between selected experimental saturated liquid densities for methane–n-octane and values calculated from the GERG-2004 formulation. The data were measured by Kohn and Bradish (1964) and cover n-octane mole fractions from 53% to 97% and temperatures from 223 K to 423 K. Whereas the new equation of state is able to represent all of the measurements within deviations of ±(0.5 – 0.8)%, values calculated from the cubic equation of state of Peng and Robinson (1976) significantly deviate from the measurements. As shown in Fig. 8.47, the deviations obtained from the cubic equation range from about 2% up to approximately 6%.

n-Heptane–Hydrogen

Experimental VLE data for binary mixtures containing hydrogen are scarce and often of poor quality. Such mixtures are characterised by a strongly increasing critical pressure when temperature decreases. As an example, Fig. 8.48 shows deviations of the experimental vapour pressures and vapour phase compositions of Peter and Reinhartz (1960) for n-heptane–hydrogen from values calculated from the GERG-2004 formulation. The measurements cover pressures up to about 78 MPa at 424 K and up to 39 MPa at 499 K. The new equation of state represents the data with comparatively large deviations of up to about ±20%. Deviations between the corresponding vapour phase compositions and values calculated from the GERG-

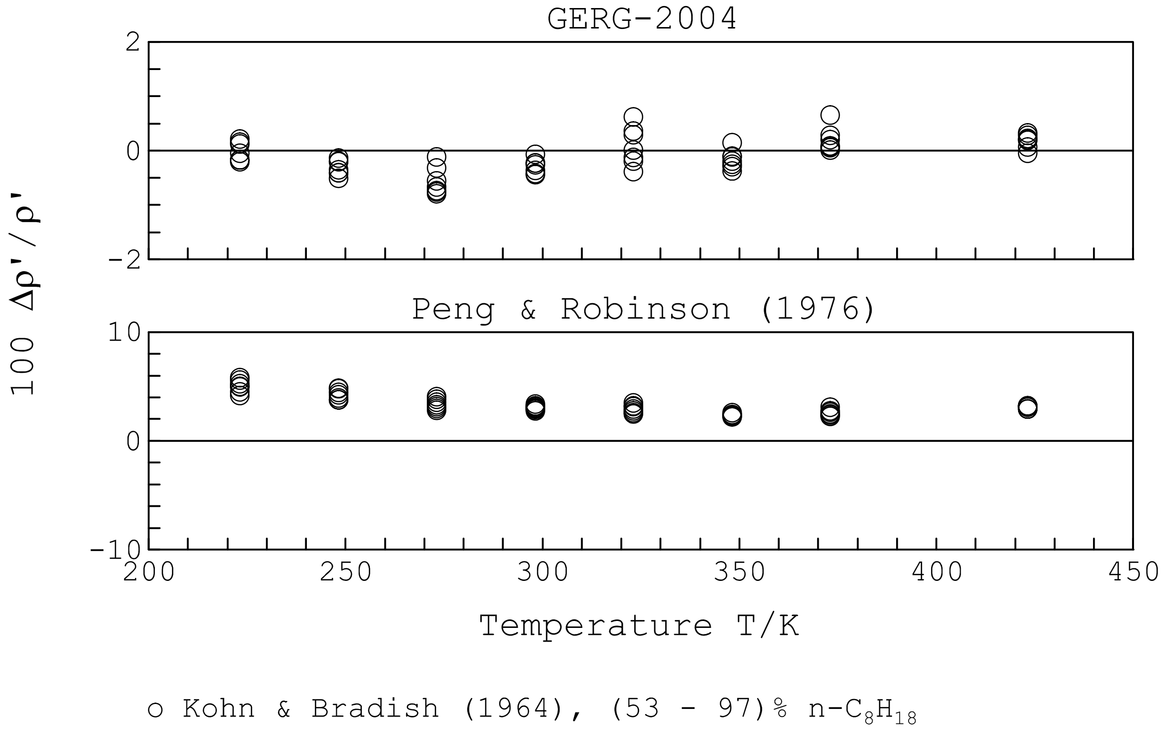

Fig. 8.47 Percentage deviations $100\Delta\rho'/\rho' = 100(\rho'_{\text{exp}} - \rho'_{\text{calc}})/\rho'_{\text{exp}}$ of the experimental saturated liquid densities measured by Kohn and Bradish (1964) for the methane–n-octane binary mixture from values calculated from the new equation of state (GERG-2004), Eqs. (7.1) – (7.10), and the cubic equation of state of Peng and Robinson (1976).

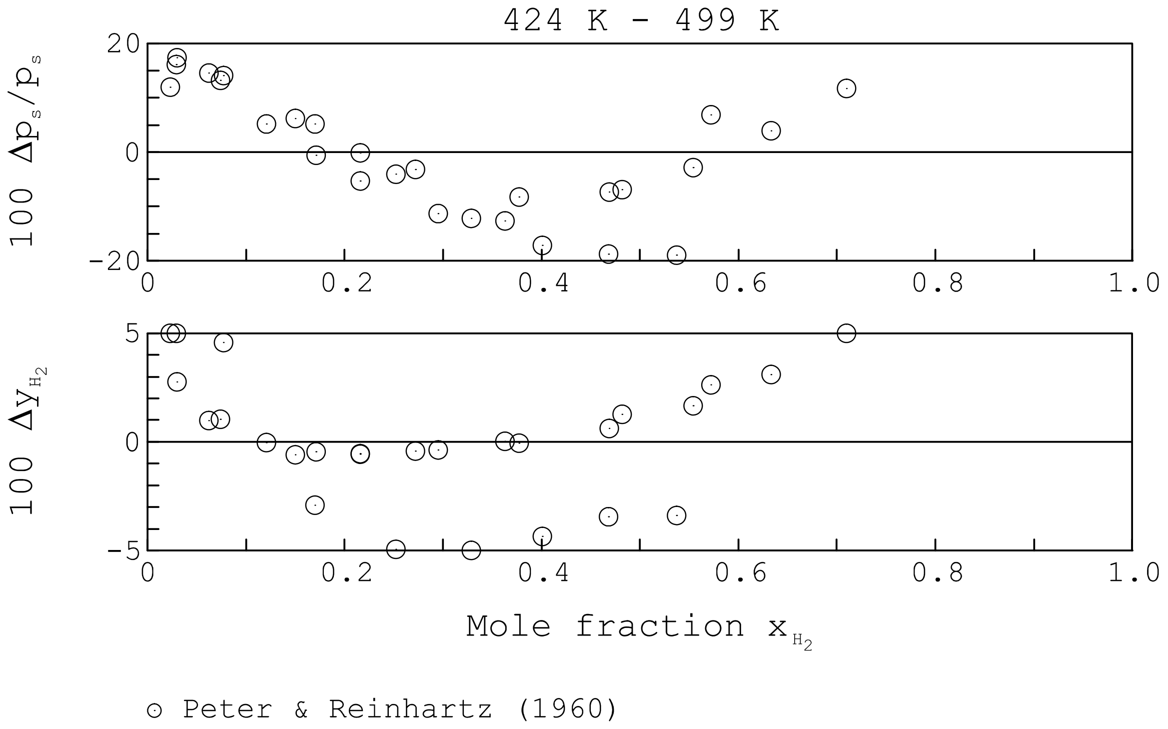

Fig. 8.48 Representation of the experimental vapour pressures and hydrogen mole fractions in the saturated vapour phase measured by Peter and Reinhartz (1960) for the n-heptane–hydrogen binary mixture by the new equation of state (GERG-2004), Eqs. (7.1) – (7.10): $100\Delta p_s/p_s = 100(p_{s,\text{exp}} - p_{s,\text{calc}})/p_{s,\text{exp}}$, $100\Delta y_{H_2} = 100(y_{H_2,\text{exp}} - y_{H_2,\text{calc}})$.

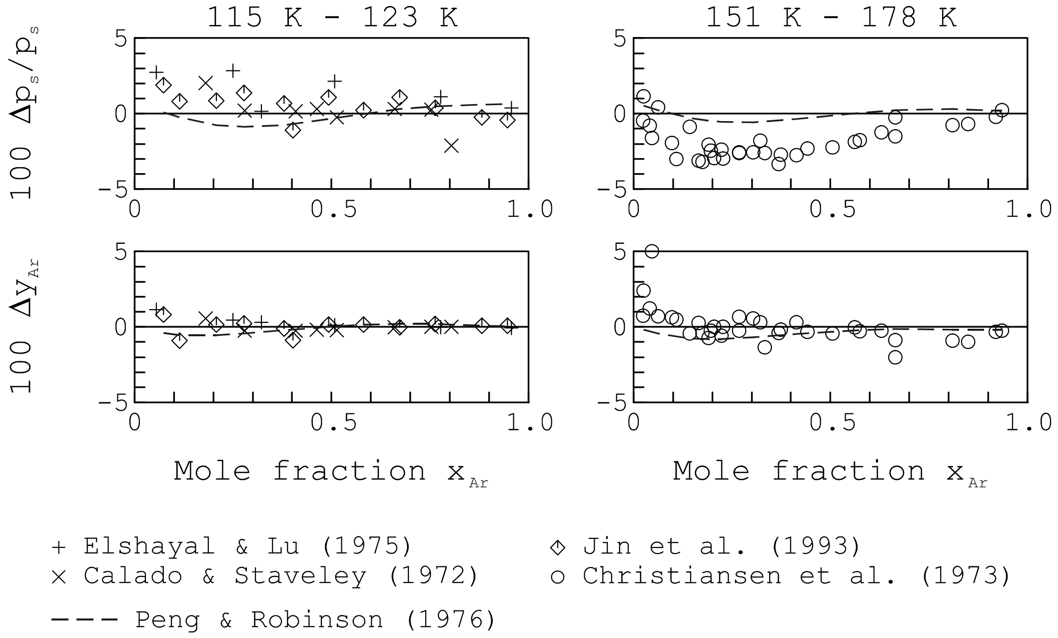

Fig. 8.49 Representation of selected experimental vapour pressures and argon mole fractions in the saturated vapour phase for the methane–argon binary mixture by the new equation of state (GERG-2004), Eqs. (7.1) – (7.10): $100\,\Delta p_{\mathrm{s}}/p_{\mathrm{s}} = 100\,(p_{\mathrm{s,exp}} - p_{\mathrm{s,calc}})/p_{\mathrm{s,exp}}$, $100\,\Delta y_{\mathrm{Ar}} = 100\,(y_{\mathrm{Ar,exp}} - y_{\mathrm{Ar,calc}})$. Values calculated from the cubic equation of state of Peng and Robinson (1976) are plotted for comparison at temperatures of 123 K and 151 K.

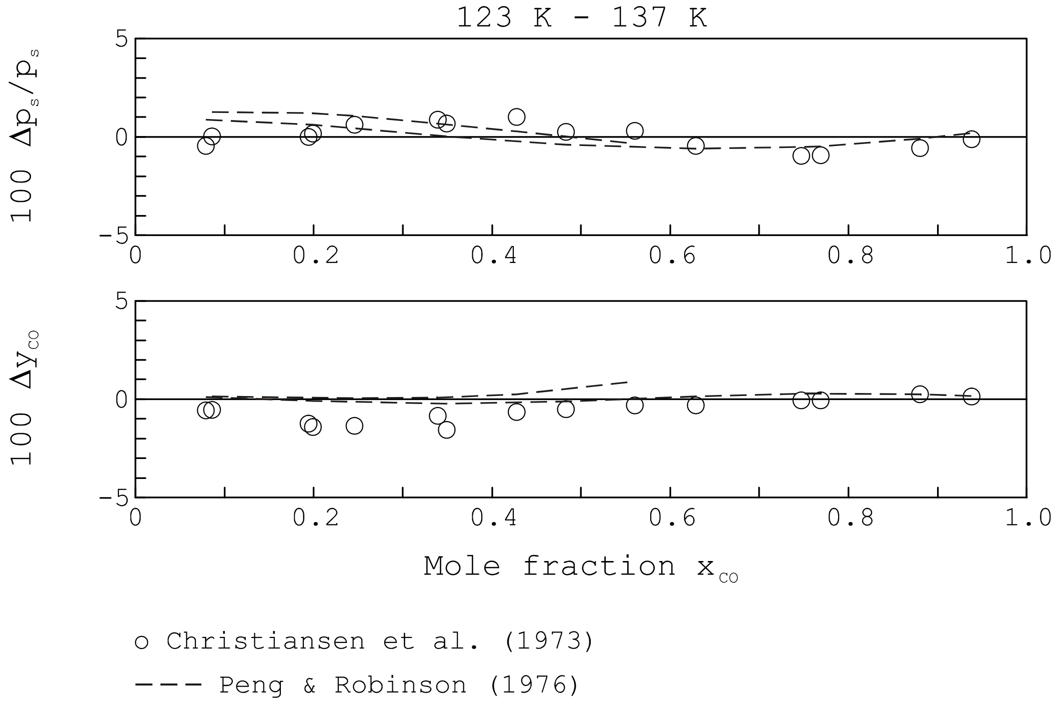

Fig. 8.50 Representation of the experimental vapour pressures and carbon monoxide mole fractions in the saturated vapour phase measured by Christiansen *et al.* (1973) for the carbon monoxide–argon binary mixture by the new equation of state (GERG-2004), Eqs. (7.1) – (7.10): $100\,\Delta p_{\mathrm{s}}/p_{\mathrm{s}} = 100\,(p_{\mathrm{s,exp}} - p_{\mathrm{s,calc}})/p_{\mathrm{s,exp}}$, $100\,\Delta y_{\mathrm{CO}} = 100\,(y_{\mathrm{CO,exp}} - y_{\mathrm{CO,calc}})$. Values calculated from the cubic equation of state of Peng and Robinson (1976) are plotted for comparison at temperatures of 123 K and 137 K.

2004 formulation range from below ±1 mole-% to more than ±5 mole-%. The poor data situation for this binary mixture (and others) limits the achievable accuracy of any mixture equation. Considerably larger deviations are obtained from the cubic equation of state of Peng and Robinson (1976) (not shown here) using the binary interaction parameters taken from the literature [Knapp *et al.* (1982)].

Methane–Argon and Carbon Monoxide–Argon

Figure 8.49 displays the description of the *pTxy* relation for the binary mixture methane–argon obtained from the GERG-2004 formulation. The selected experimental vapour pressures are represented by the new equation of state to within ±(1 – 3)% for subcritical temperatures as well as in the mixture critical region. As frequently observed, the data show a comparatively large scatter among themselves and between different authors. Typical deviations between the corresponding vapour phase compositions and values calculated from the GERG-2004 formulation are within ±(0.5 – 1) mole-%. All in all, the description achieved by the new equation of state is quite satisfactory and supported by the cubic equation of state of Peng and Robinson (1976) yielding quite similar results. The same is true for the description of the *pTxy* relation of carbon monoxide–argon as shown in Fig. 8.50. Here, both the GERG-2004 formulation and the cubic equation of Peng and Robinson (1976) represent the selected experimental vapour pressures with deviations of less than about ±1%. The corresponding vapour phase compositions are represented by both equations to within ±(0.5 – 1.5) mole-%.

Binary Mixtures of the Air Components Nitrogen, Oxygen, and Argon

Wide-ranging and comparatively accurate *pTxy* data sets are available for binary mixtures of the air components nitrogen, oxygen, and argon. Figures 8.51 – 8.53 show deviations between a number of selected *pTxy* data (vapour pressures and vapour phase compositions) for nitrogen–oxygen, nitrogen–argon, and oxygen–argon, and values calculated from the GERG-2004 formulation. The sum of all measurements covers wide ranges of temperature and the entire composition range at subcritical conditions as well as in the mixture critical region. Most of the selected experimental vapour pressures are well represented by the new equation of state to within ±(1 – 3)%. The most accurate vapour pressure data are represented with low deviations of less than ±(0.5 – 1)%. The measured vapour phase compositions of the three binary mixtures are also very accurately described by the new equation. Typical deviations between the most consistent data and values calculated from the GERG-2004 formulation are less than ±(0.5 – 1) mole-%. All in all, the achieved description of the *pTxy* relation of the three binary mixtures nitrogen–oxygen, nitrogen–argon, and oxygen–argon is very satisfactory.

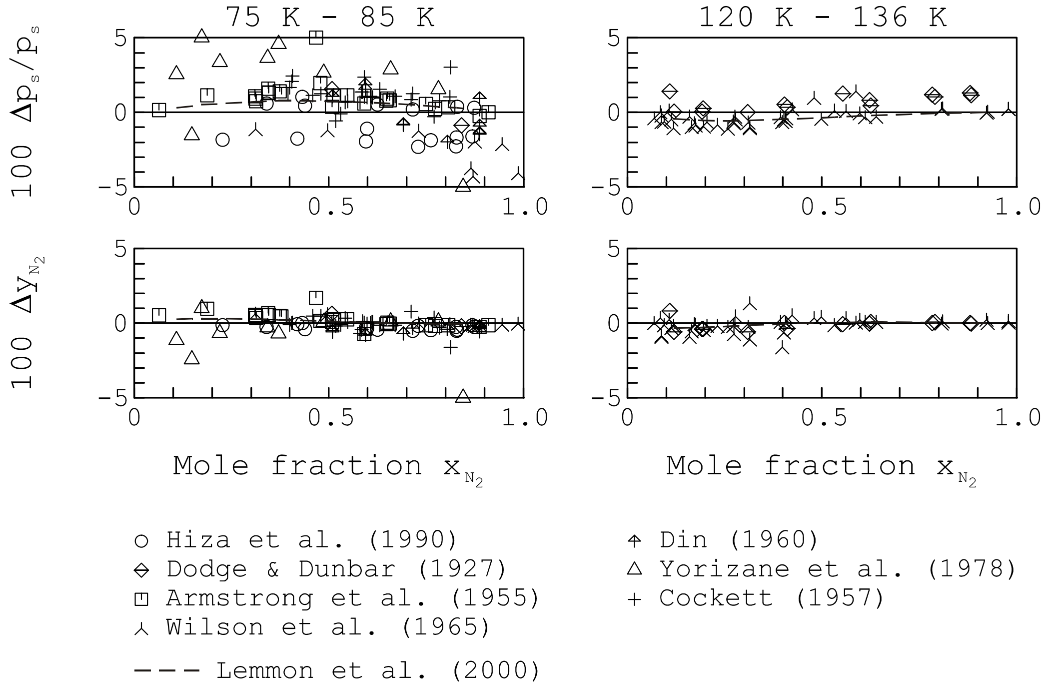

Fig. 8.51 Representation of selected experimental vapour pressures and nitrogen mole fractions in the saturated vapour phase for the nitrogen–oxygen binary mixture by the new equation of state (GERG-2004), Eqs. (7.1) – (7.10): $100\,\Delta p_s/p_s = 100(p_{s,\mathrm{exp}} - p_{s,\mathrm{calc}})/p_{s,\mathrm{exp}}$, $100\,\Delta y_{N_2} = 100(y_{N_2,\mathrm{exp}} - y_{N_2,\mathrm{calc}})$. Values calculated from the mixture model of Lemmon *et al.* (2000) are plotted for comparison at temperatures of 80 K and 120 K.

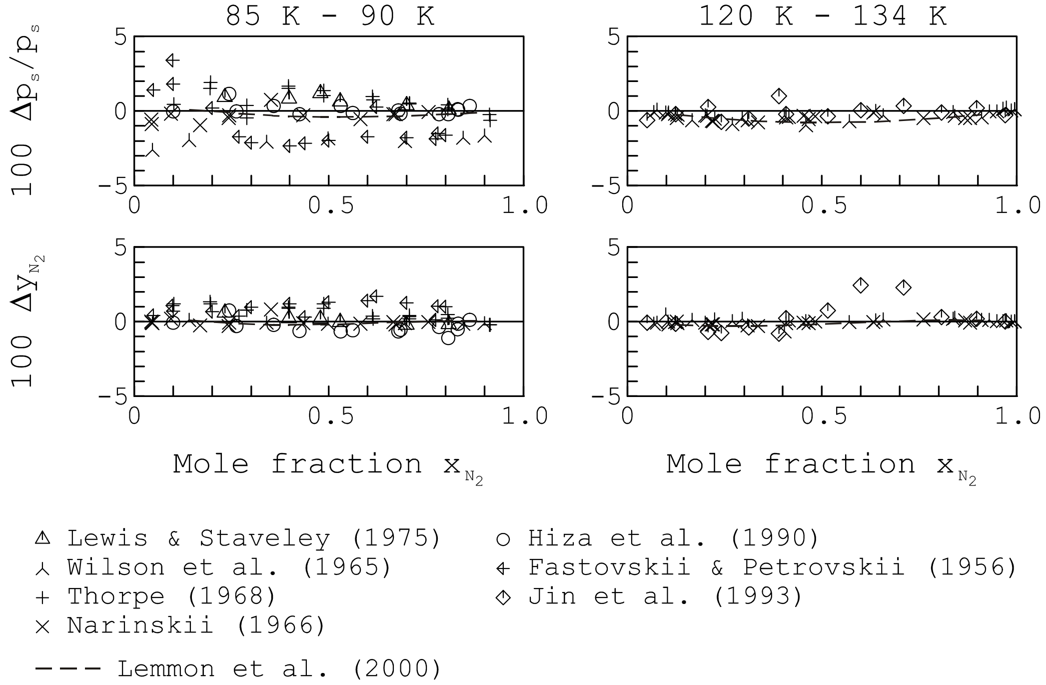

Fig. 8.52 Representation of selected experimental vapour pressures and nitrogen mole fractions in the saturated vapour phase for the nitrogen–argon binary mixture by the new equation of state (GERG-2004), Eqs. (7.1) – (7.10): $100\,\Delta p_s/p_s = 100(p_{s,\mathrm{exp}} - p_{s,\mathrm{calc}})/p_{s,\mathrm{exp}}$, $100\,\Delta y_{N_2} = 100(y_{N_2,\mathrm{exp}} - y_{N_2,\mathrm{calc}})$. Values calculated from the mixture model of Lemmon *et al.* (2000) are plotted for comparison.

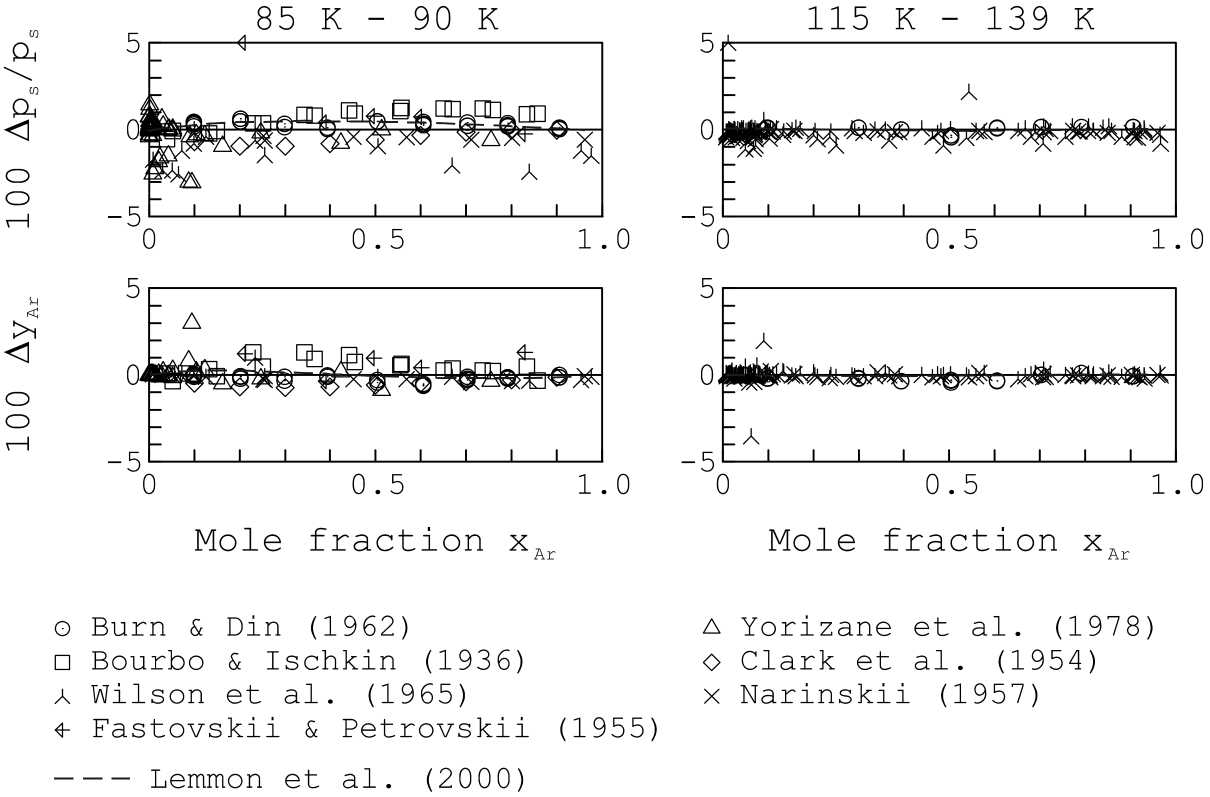

Fig. 8.53 Representation of selected experimental vapour pressures and argon mole fractions in the saturated vapour phase for the oxygen–argon binary mixture by the new equation of state (GERG-2004), Eqs. (7.1) – (7.10): $100\,\Delta p_s/p_s = 100(p_{s,\mathrm{exp}} - p_{s,\mathrm{calc}})/p_{s,\mathrm{exp}}$, $100\,\Delta y_{\mathrm{Ar}} = 100(y_{\mathrm{Ar,exp}} - y_{\mathrm{Ar,calc}})$. Values calculated from the mixture model of Lemmon *et al.* (2000) are plotted for comparison at temperatures of 90 K and 120 K.

A very similar description is obtained from the multi-fluid mixture model of Lemmon *et al.* (2000), which uses a short generalised departure function composed of two polynomial terms (see Table 5.2) in addition to the reducing functions for density and temperature. In comparison, the description of thermodynamic properties of mixtures of air components by the new mixture model is (currently) only based on adjusted reducing functions for the respective binary mixtures. The already achieved quite accurate description of the *pTxy* relation for these (and also other) mixtures proves the suitability of the used reducing functions [Eqs. (7.9) and (7.10); see also Sec. 5.2] for use in multi-fluid mixture models[84].

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[84] The influence of the reducing functions for density and temperature in the description of thermodynamic properties of mixtures is considerably higher than the contribution of a departure function (see also Secs. 5.1 – 5.3). In general, the use of a departure function enables further improvement in the description of very accurate gas phase and gas-like supercritical densities and speeds of sound at reduced temperatures $T/T_r \le 1.4$, of liquid phase densities, and of *pTxy* data at low temperatures. For instance, whereas accurate gas phase densities are represented to within ±0.1% using a departure function, deviations of less than ±(0.1 – 0.3)% are typically observed without the use of a departure function. Similar behaviour is obtained for accurate liquid phase densities.

8.4 The Representation of Thermal and Caloric Properties of Natural Gases, Similar Gases, and Other Multi-Component Mixtures

As a multi-fluid mixture model, the GERG-2004 formulation is based on accurate fundamental equations for the considered pure components and equations developed for the respective binary mixtures (see Chaps. 5 and 7). This allows for an accurate description of the thermodynamic properties of natural gases, similar gases, and other multi-component mixtures over a wide range of compositions. The basis for the development of the new equation of state are experimental data for thermal and caloric properties of binary mixtures. Data for natural gases and other multi-component mixtures are only used for comparisons (no multi-component mixture data were used for the development).

The quality of the new equation of state in the description of thermal and caloric properties of various types of natural gases, similar gases, and other multi-component mixtures is presented in the following subsections. The discussions comprise comparisons with data for ordinary natural gas mixtures, natural gases rich in methane, nitrogen, carbon dioxide, ethane, or hydrogen, as well as rich natural gases, LNG-like mixtures, pure hydrocarbon mixtures, and others.

8.4.1 The $p\rho T$ Relation in the Homogeneous Gas Region

As described in Sec. 6.2, a huge amount of the $p\rho T$ measurements is available for natural gases and similar mixtures covering temperatures from 270 K to 350 K at pressures up to about 30 MPa. Comparatively few (but accurate) data were measured at temperatures below 270 K. Together with the accurate and wide ranging data for important binary mixtures strongly related to natural gases, such as methane–nitrogen and methane–ethane, the present data situation allows for a well-founded estimation of the uncertainty in gas phase densities at temperatures below 270 K.

Most of the measurements used for the following comparisons were taken from the databank GERG TM7 of Jaeschke *et al.* (1997), comprising accurate density data for synthetic multi-component mixtures, simulated and true natural gases, and natural gases with different admixtures (i.e. natural gases diluted or enriched with one or more natural gas components). The majority of these data were measured at Ruhrgas using an optical interferometry method (Op) or a Burnett apparatus (Bu). The uncertainty in density of these measurements is generally estimated to be $\Delta\rho/\rho \leq (0.07 - 0.1)\%$. A few very accurate density data were measured with a two-sinker densimeter (GDMA) at pressures up to about 8 MPa. For these measurements, the uncertainty in density is estimated to be less than 0.03%.

Table 8.1 Molar compositions of the round-robin natural gases[a]

Mixture	Composition (mole-%)									
	CH_4	N_2	CO_2	C_2H_6	C_3H_8	n-C_4	i-C_4	n-C_5	i-C_5	n-C_6
NIST1	96.522	0.260	0.596	1.819	0.460	0.101	0.098	0.032	0.047	0.066
NIST2	90.672	3.128	0.468	4.528	0.828	0.156	0.104	0.044	0.032	0.039
RG2	85.906	1.007	1.495	8.492	2.302	0.351	0.349	0.048	0.051	–
GU1	81.441	13.465	0.985	3.300	0.605	0.104	0.100	–	–	–
GU2	81.212	5.702	7.585	4.303	0.895	0.152	0.151	–	–	–

[a] The mixtures were prepared in two batches (one for laboratories in Europe and one for those in the U.S.). The values given here belong to the batch distributed to laboratories in Europe. The minor differences in the compositions between the two batches have no influence on the representation of the $p\rho T$ measurements by equations of state. For the exact molar compositions of the different data sets see Table A2.3 of the appendix.

Table 8.2 Approximate molar compositions of selected synthetic multi-component mixtures, true natural gases, natural gases with different admixtures, and simulated rich natural gas mixtures[a]

Mixture	Composition (mole-%)											
	CH_4	N_2	CO_2	C_2H_6	C_3H_8	n-C_4	i-C_4	n-C_5	i-C_5	n-C_6	H_2	CO
D17	84.78	–	2.01	8.92	3.05	1.24	–	–	–	–	–	–
D18	61.77	12.66	12.60	12.97	–	–	–	–	–	–	–	–
D21[b]	66.09	13.13	11.06	9.71	–	–	–	–	–	–	–	–
N60[c]	82.52	11.73	1.11	3.46	0.76	0.15	0.10	0.04	0.03	0.02	–	–
N61[c,d]	98.27	0.89	0.07	0.52	0.16	0.03	0.03	<0.01	<0.01	<0.01	–	–
N72[e]	73.50	9.93	1.34	3.60	0.77	0.15	0.10	0.04	0.03	0.02	9.49	0.91
N108[f]	79.95	1.13	1.02	16.01	1.40	0.26	0.13	0.03	0.03	0.02	<0.01	–
N115[g]	81.53	11.81	1.19	2.83	0.62	0.21	<0.01	0.07	<0.01	0.02	–	–
N116[h]	28.89	28.00	2.02	0.84	0.16	0.07	–	0.03	<0.01	<0.01	26.99	13.00
QUINT	80.04	9.95	1.99	5.00	3.02	–	–	–	–	–	–	–
RNG3	59.00	4.99	5.99	18.00	8.02	3.30	–	0.49	–	0.21	–	–
RNG5	63.98	2.02	7.99	11.97	10.01	3.31	–	0.51	–	0.20	–	–

[a] For the exact molar compositions of the mixtures see Table A2.3 of the appendix.

[b] The mixture contains a small fraction of oxygen.

[c] The mixture contains small fractions of n-heptane, n-octane, and helium.

[d] The mixture N62 has the same composition as N61. These two series of measurements are referred to as "N61/62" in the text.

[e] The mixture contains about 0.1 mole-% of oxygen and small fractions of n-heptane, n-octane, and n-nonane. The mixtures N73 and N74 have the same composition as N72. These three series of measurements are referred to as "N72/73/74" in the text.

[f] The mixture contains small fractions of n-heptane, n-octane, n-nonane, hydrogen, and helium.

[g] The mixture contains about 1.7 mole-% of oxygen and a small fraction of n-heptane.

[h] The mixture contains a small fraction of n-heptane.

A number of data exist for a selection of five simulated natural gases measured in a round-robin series of $p\rho T$ measurements [see Magee *et al.* (1997)] performed by different laboratories using five different experimental techniques. The gases are designated by "NIST1", "NIST2", "RG2", "GU1", and "GU2". They cover the range of compositions normally encountered in gas industry operations in North America and in Europe. Each mixture was prepared gravimetrically to the (approximate) molar compositions given in Table 8.1. Aside from the measurements carried out at Ruhrgas, further reliable data were measured by Magee *et al.* (1997) and Hwang *et al.* (1997b) using a Burnett apparatus. Measurements that appear to be associated with an increased or questionable uncertainty, such as data measured using a pycnometer method, are not included in the comparisons. In addition to the round-robin measurements, experimental data for the mixtures listed in Table 8.2 were selected for the comparisons discussed below.

The comparisons frequently focus on the representation of data at lower to medium temperatures to demonstrate important improvements compared to the previous equations of state. In general, towards higher temperatures, e.g. 330 K and 350 K, the deviations decrease.

Synthetic Five-Component Natural Gas Mixture and Pipeline Quality Natural Gases

Experimental measurements of gas phase densities for the five-component synthetic natural gas mixture "QUINT" and the round-robin gas NIST2 and their percentage deviations from the GERG-2004 formulation are shown in Fig. 8.54.

The five-component mixture consists of approximately 80% methane, 10% nitrogen, 2% carbon dioxide, 5% ethane, and 3% propane. The data were measured by Ruhrgas (1999) using an optical interferometry method (Op) and a Burnett apparatus (Bu) and are represented by the new equation of state to within their low experimental uncertainty, estimated to be $\Delta\rho/\rho \leq 0.07\%$, over the entire measured temperature and pressure range. The highest deviations occur for the lowest measured temperatures and amount to 0.06% at 270 K at about 15 MPa. Values calculated from the AGA8-DC92 equation of state of Starling and Savidge (1992), the current international standard for the calculation of natural gas compression factors, deviate from the measurements at 270 K by up to 0.09% at pressures around 11 MPa. At higher temperatures, the AGA8-DC92 equation yields similar results compared to the GERG-2004 formulation. Deviations of more than 0.1% are obtained from the multi-fluid mixture model of Lemmon and Jacobsen (1999) at 270 K. Even at higher temperatures this model is not able to represent the measurements as accurately as the new equation of state.

The round-robin gas NIST2 consists of 10 components and represents a simulated Amarillo gas. The mixture is characterised by a very typical natural gas composition with medium fractions of methane (about 90.7%), nitrogen (about 3.1%), and ethane (about 4.5%). The

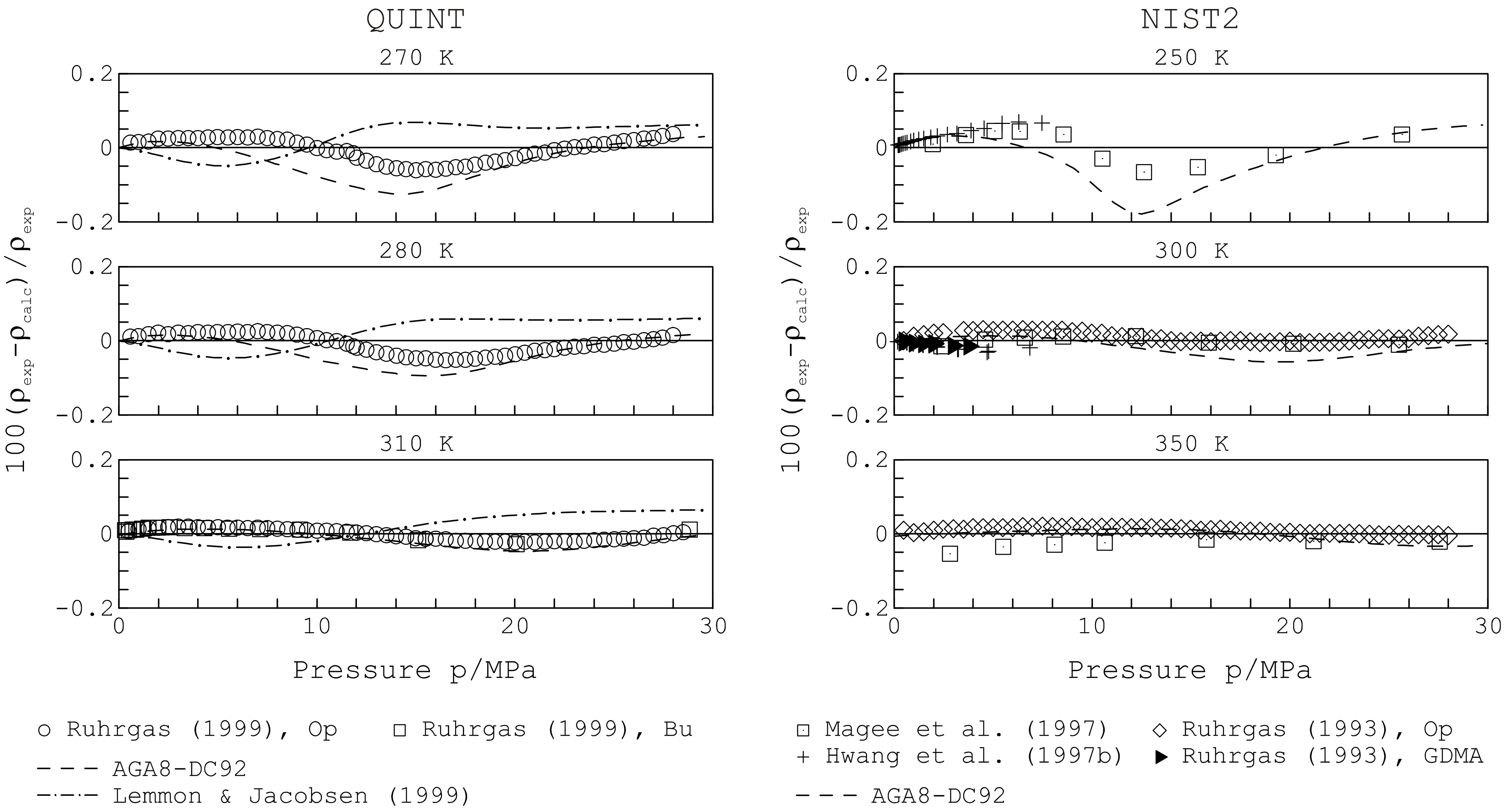

Fig. 8.54 Percentage density deviations of selected experimental $p\rho T$ data for the five-component synthetic natural gas mixture "QUINT" and the round-robin natural gas "NIST2" from values calculated from the new equation of state (GERG-2004), Eqs. (7.1) – (7.10); for the mixture compositions see Tables 8.1 and 8.2. Values calculated from the AGA8-DC92 equation of Starling and Savidge (1992) and the mixture model of Lemmon and Jacobsen (1999) are plotted for comparison. Bu: Burnett apparatus, GDMA: two-sinker densimeter, Op: optical interferometry method.

content of carbon dioxide amounts to approximately 0.5% as frequently observed in natural gases of pipeline quality. The mixture contains about 0.8% of propane and small amounts of the further alkanes from n-butane to n-hexane (see also Table 8.1). The selected data cover a wide range of temperatures from 250 K to 350 K at pressures up to 29 MPa. All of the measurements are represented by the GERG-2004 formulation well within their experimental uncertainty, estimated to be $\Delta\rho/\rho \le 0.07\%$ for Ruhrgas (1993), and $\Delta\rho/\rho \le 0.1\%$ for Magee *et al.* (1997) and Hwang *et al.* (1997b). In contrast to the new equation of state, the AGA8-DC92 equation deviates from the measurements at 250 K and pressures around 12 MPa by slightly more than 0.1%. A similar description of the data is achieved at higher temperatures. Since the multi-fluid mixture model reported by Lemmon and Jacobsen (1999) is not applicable for mixtures containing fractions of n-pentane, isopentane, and n-hexane, no comparison is possible here.

Natural Gases Rich in Methane

Figure 8.55 displays percentage deviations between experimental densities for two methane-rich natural gases and values calculated from the GERG-2004 formulation. The round-robin gas NIST1 consists of 10 components and represents a simulated Gulf Coast natural gas containing about 96.5% methane, 1.8% ethane, and low to small fractions of nitrogen, carbon dioxide, and alkanes from propane to n-hexane. The 13-component mixture designated by "N61/62" consists of about 98% methane, 0.9% nitrogen, and low to small fractions of carbon dioxide, alkanes from ethane to n-octane, and helium. Such natural gases, almost entirely composed of methane, are typical for Russian gases. The selected data cover temperatures from 250 K to 350 K for wide ranges of pressure. As shown in Fig. 8.55, all of the data are represented by the new equation of state with very low deviations of less than ±0.05%, being clearly within the uncertainty of the measurements. The AGA8-DC92 equation of state yields a quite similar accurate description for these types of natural gas mixtures.

Natural Gases Rich in Nitrogen

As mentioned in Sec. 2.1.1, a known weakness of the AGA8-DC92 equation of state is its less accurate description of natural gases containing a comparatively high fraction of nitrogen [see also Klimeck *et al.* (1996) and Jaeschke and Schley (1996)]. A nitrogen content of more than 10% is typical for Dutch natural gases of pipeline quality. Figure 8.56 shows density measurements of two nitrogen-rich natural gases and their percentage deviations from the GERG-2004 formulation. The mixture designated by GU1 consists of seven components and represents a simulated Slochteren gas. This natural gas mixture is composed of about 13.5% nitrogen, 1% carbon dioxide, 3.3% ethane, and low to small fractions of heavier alkanes. Whereas the new equation of state is able to describe all of the selected data over the entire covered temperature and pressure ranges within low deviations of ±(0.05 – 0.07)%, values

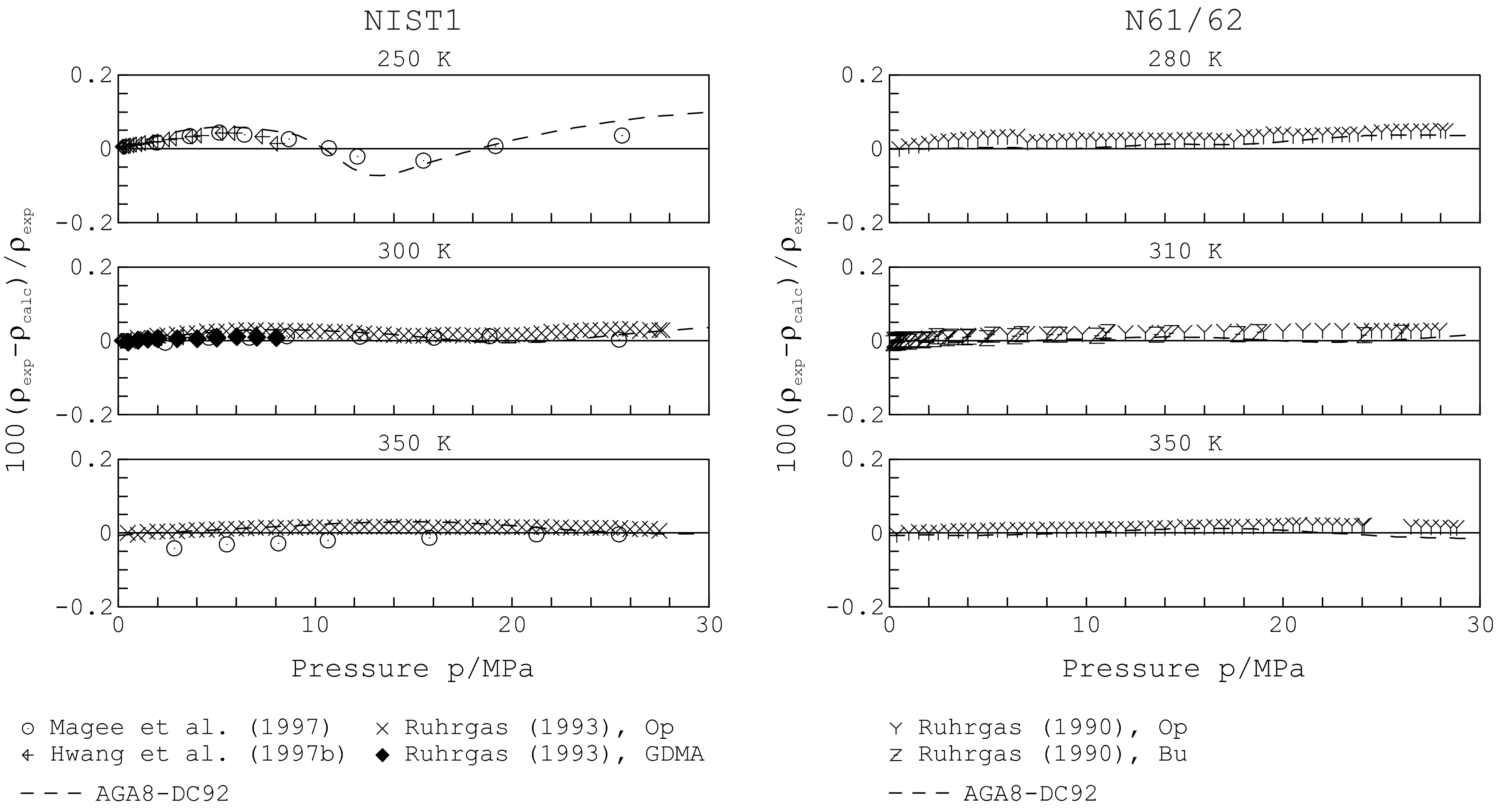

Fig. 8.55 Percentage density deviations of selected experimental $p\rho T$ data for the methane-rich natural gases “NIST1” and “N61/62” from values calculated from the new equation of state (GERG-2004), Eqs. (7.1) – (7.10); for the mixture compositions see Tables 8.1 and 8.2. Values calculated from the AGA8-DC92 equation of Starling and Savidge (1992) are plotted for comparison. Bu: Burnett apparatus, GDMA: two-sinker densimeter, Op: optical interferometry method.

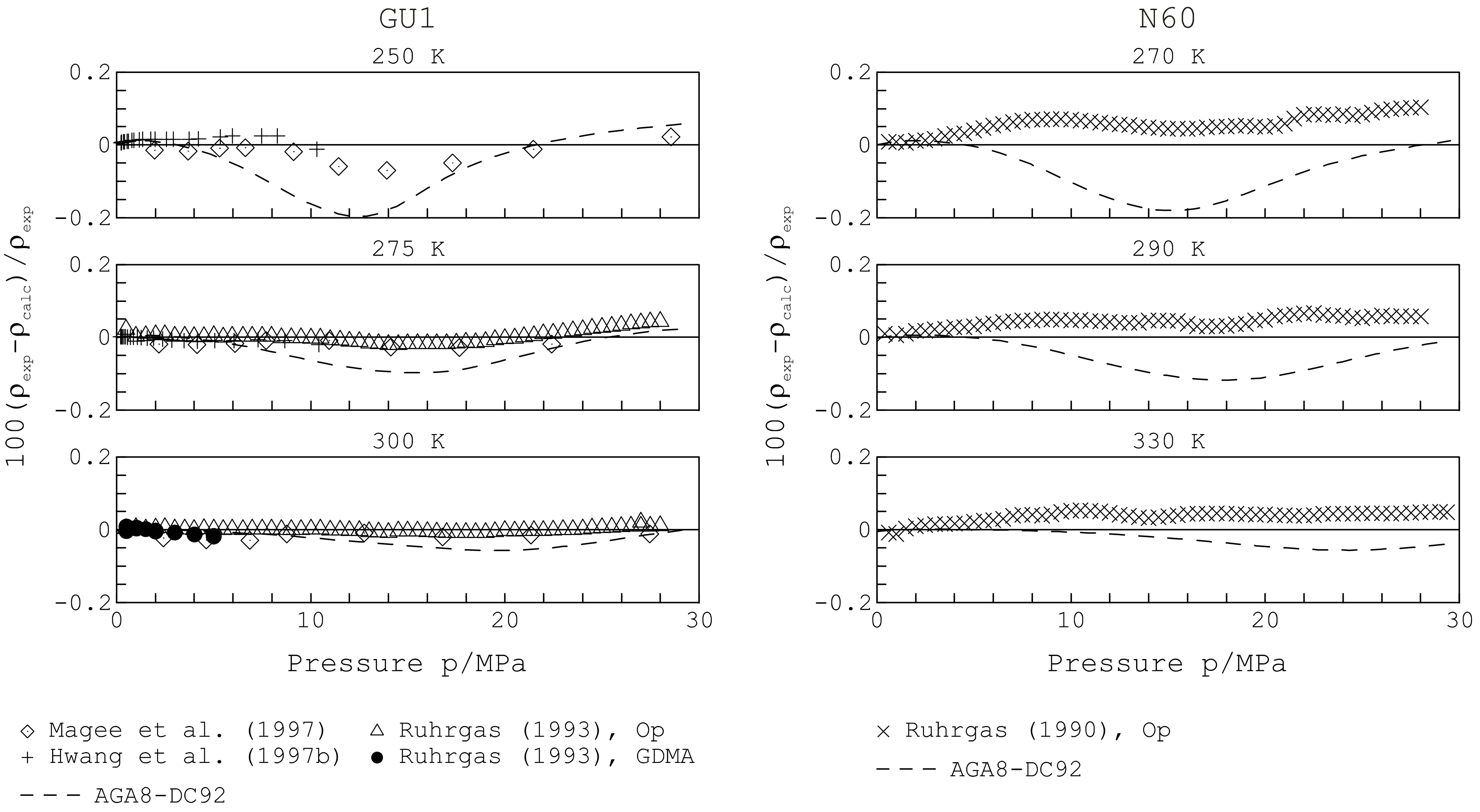

Fig. 8.56 Percentage density deviations of selected experimental $p\rho T$ data for the nitrogen-rich natural gases "GU1" and "N60" from values calculated from the new equation of state (GERG-2004), Eqs. (7.1) – (7.10); for the mixture compositions see Tables 8.1 and 8.2. Values calculated from the AGA8-DC92 equation of Starling and Savidge (1992) are plotted for comparison. GDMA: two-sinker densimeter, Op: optical interferometry method.

calculated from the AGA8-DC92 equation deviate from the measurements at 250 K by clearly more than 0.1%, thus exceeding the estimated uncertainty in density for the data. A quite similar poor description is obtained from the AGA8-DC92 equation of state for the $p\rho T$ relation of the binary mixture methane–nitrogen discussed in Sec. 8.1.1 (see the results for nitrogen concentrations of 10% and 20% displayed in Fig. 8.1), underlining the observations for this natural gas.

The AGA8-DC92 equation yields an even worse description of the measurements of Ruhrgas (1990) for the 13-component mixture designated by “N60”, exemplifying another nitrogen-rich natural gas (see Fig. 8.56). The nitrogen concentration for this mixture amounts to about 11.7%. In contrast to the mixture GU1, N60 additionally contains small fractions of the alkanes from n-pentane to n-octane, and helium. Values calculated from the AGA8-DC92 equation deviate from the data by more than 0.1% at 290 K and even exceed 0.2% at 270 K. The new equation of state represents well all measurements to within ±(0.07 – 0.1)% for all measured temperatures and pressures. The examples prove that the GERG-2004 formulation is clearly superior to the AGA8-DC92 equation in the description of nitrogen-rich natural gases. The new equation allows the calculation of the $p\rho T$ relation with a significantly lower uncertainty.

Natural Gases Rich in Carbon Dioxide

Similar to the very accurate description of the $p\rho T$ relation of the binary mixture methane–carbon dioxide discussed in Sec. 8.1.1 (see Figs. 8.5 and 8.6), important and substantial improvements compared to all previous equations of state are achieved by the GERG-2004 formulation for natural gas mixtures rich in carbon dioxide. Figure 8.57 shows density deviations between data for the round-robin gas GU2 in the temperature range from 250 K to 325 K at pressures up to 30 MPa and values calculated from the new equation of state. The mixture contains medium fractions of nitrogen (5.7%), ethane (4.3%), and propane (0.9%), and a comparatively high mole fraction of carbon dioxide of about 7.6%. All of the selected data measured by Ruhrgas (1993) and Magee *et al.* (1997) are well represented by the GERG-2004 formulation to within low deviations of ±(0.05 – 0.07)%, which agrees with the experimental uncertainty of the data.

At lower temperatures, deviations exceeding 0.1% or even 0.2% are obtained from the AGA8-DC92 equation as well as from the preliminary equation of state of Klimeck (2000). As previously observed for the binary mixture methane–carbon dioxide (see Fig. 8.5), a worse description is obtained from the mixture model of Lemmon and Jacobsen (1999), significantly deviating from the measurements over wide ranges of temperature and pressure. Values calculated from this model deviate from the experimental data by more than 0.1% at 300 K (and 325 K) and by more than 0.2% at lower temperatures.

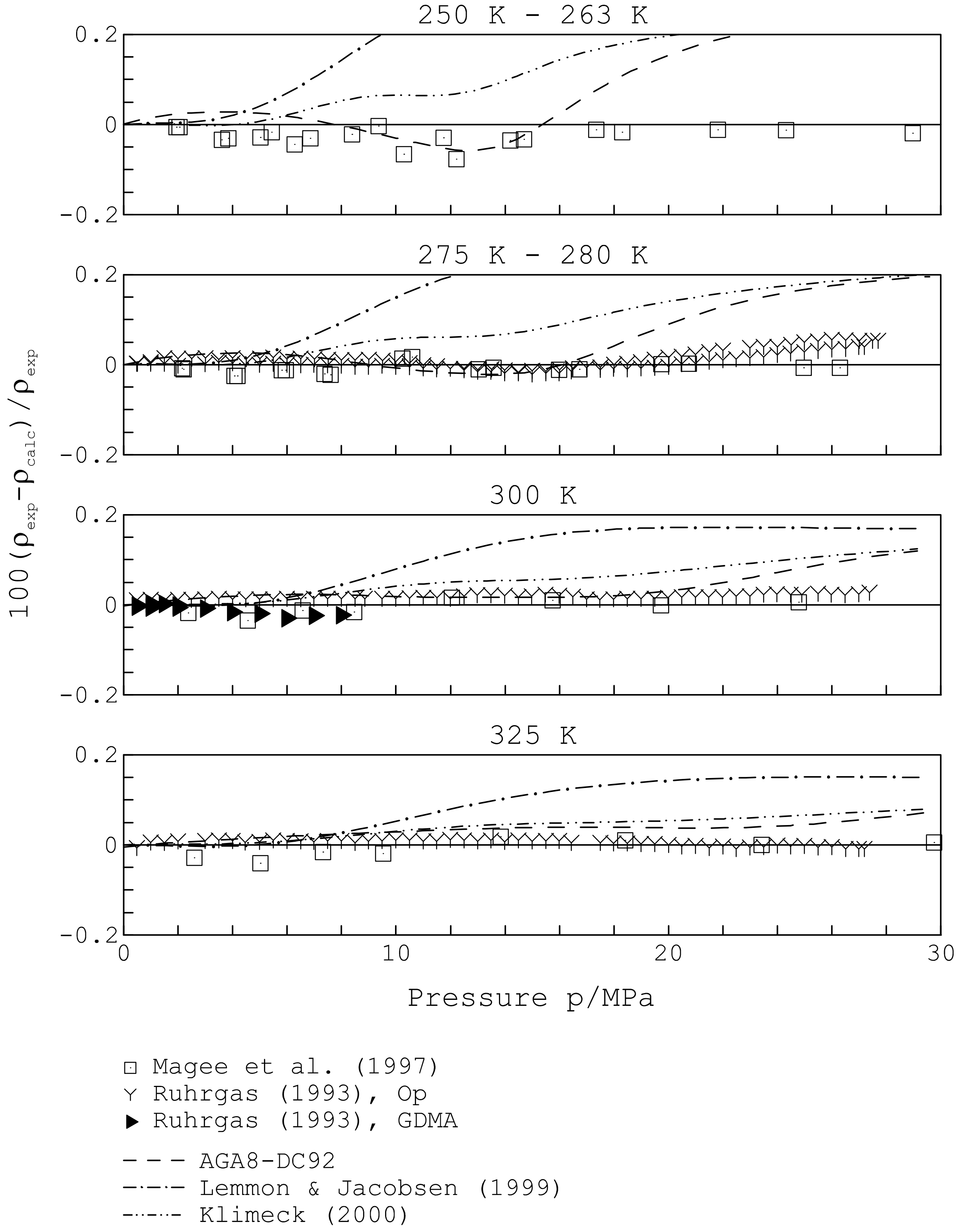

Fig. 8.57 Percentage density deviations of selected experimental $p\rho T$ data for the round-robin natural gas "GU2" from values calculated from the new equation of state (GERG-2004), Eqs. (7.1) – (7.10); for the mixture composition see Table 8.1. Values calculated from the AGA8-DC92 equation of Starling and Savidge (1992) and the mixture models of Lemmon and Jacobsen (1999) and Klimeck (2000) are plotted for comparison. GDMA: two-sinker densimeter, Op: optical interferometry method.

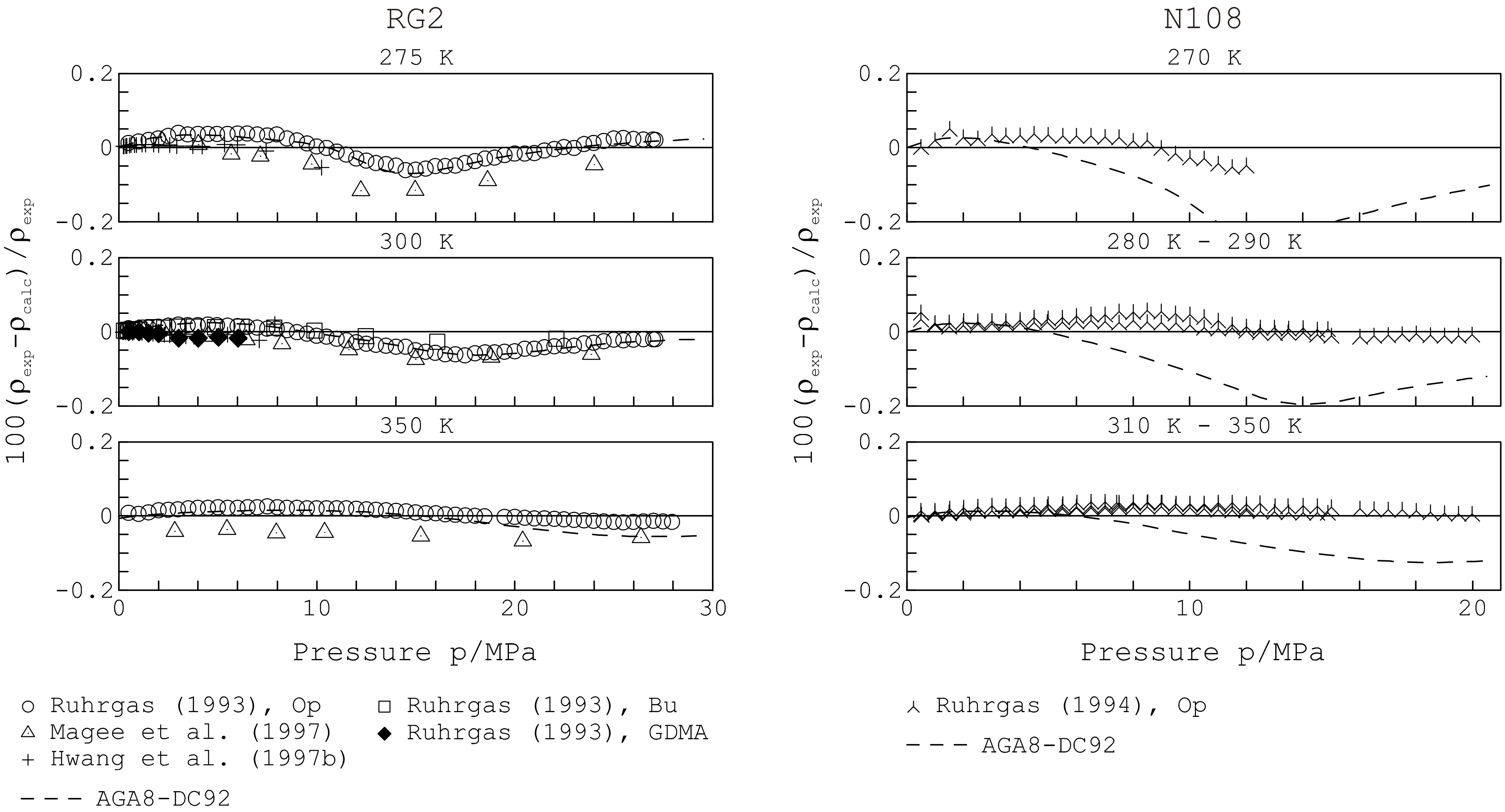

Fig. 8.58 Percentage density deviations of selected experimental $p\rho T$ data for the natural gas mixtures "RG2" and "N108" from values calculated from the new equation of state (GERG-2004), Eqs. (7.1) – (7.10); for the mixture compositions see Tables 8.1 and 8.2. Values calculated from the AGA8-DC92 equation of Starling and Savidge (1992) are plotted for comparison. Bu: Burnett apparatus, GDMA: two-sinker densimeter, Op: optical interferometry method.

Natural Gases Containing Substantial Amounts of Ethane and Propane, and Natural Gases Rich in Ethane

Natural gases containing substantial amounts of ethane and propane are typical for North Sea gas. Percentage density deviations of selected measurements for such natural gas mixtures from the GERG-2004 formulation are displayed in Fig. 8.58. The round-robin mixture designated by RG2 consists of nine components and contains about 8.5% ethane and 2.3% propane (see also Table 8.1). The mixture designated by "N108" is composed of 15 components and represents an Ekofisk gas enriched with ethane. This mixture only contains about 80% methane, but 16% ethane (see also Table 8.2).

The most reliable measurements for the mixture RG2 are represented by the GERG-2004 formulation with low deviations of less than ±(0.05 – 0.07)%, which is well within the experimental uncertainty of the data. The measurements of Magee *et al.* (1997) show a systematic offset of about 0.05% from the optical interferometry measurements of Ruhrgas (1993) at temperatures of 275 K and 350 K, and from the Burnett measurements of Ruhrgas (1993) at 300 K. Similar systematic offsets can also be observed for the data of Magee *et al.* (1997) measured for the other round-robin gases. The inconsistencies between the data sets of the different sources are, however, increased for this particular mixture. Moreover, comparisons made for a number of further data available for natural gas mixtures of nearly the same composition are accurately described by the new equation of state, supporting the impression that the measurements of Magee *et al.* (1997) seems to be associated with an increased uncertainty. The AGA8-DC92 equation of state almost exactly follows the optical interferometry measurements of Ruhrgas (1993) suggesting that the experimental data of this mixture were used for the development of the equation.

Substantial improvements are achieved by the GERG-2004 formulation for natural gas mixtures characterised by even higher amounts of ethane than contained in typical Ekofisk gases as exemplified by the comparisons shown in Fig. 8.58 for the mixture N108. The new equation of state represents all of the data measured by Ruhrgas (1994) with low deviations of less than about ±0.05%. Values calculated from the AGA8-DC92 equation of state deviate from the measurements at 310 K by up to 0.09%, and by up to about 0.2% at 280 K and 270 K.

Synthetic Five-Component Natural Gas Mixture Containing Substantial Amounts of Ethane, Propane, and n-Butane

The investigations of Klimeck *et al.* (1996) not only revealed serious weaknesses for the AGA8-DC92 equation of state in the description of natural gases containing high fractions of nitrogen (see Fig. 8.56), carbon dioxide (see Fig. 8.57), or ethane (see Fig. 8.58), but also for mixtures containing considerable amounts of the further alkanes propane and n-butane.

Figure 8.59 displays percentage deviations between density measurements of Ruhrgas (1990) for the mixture designated by “D17” and values calculated from the GERG-2004 formulation. The five-component mixture consists of about 84.8% methane, 2% carbon dioxide, 8.9% ethane, 3.1% propane, and a comparatively high content of n-butane of about 1.2%, which is about 10 times higher than commonly observed in natural gases. The data cover temperatures from 273 K to 313 K at pressures up to 29 MPa and are all represented by the new equation of state to within low deviations of ±(0.05 – 0.07)%.

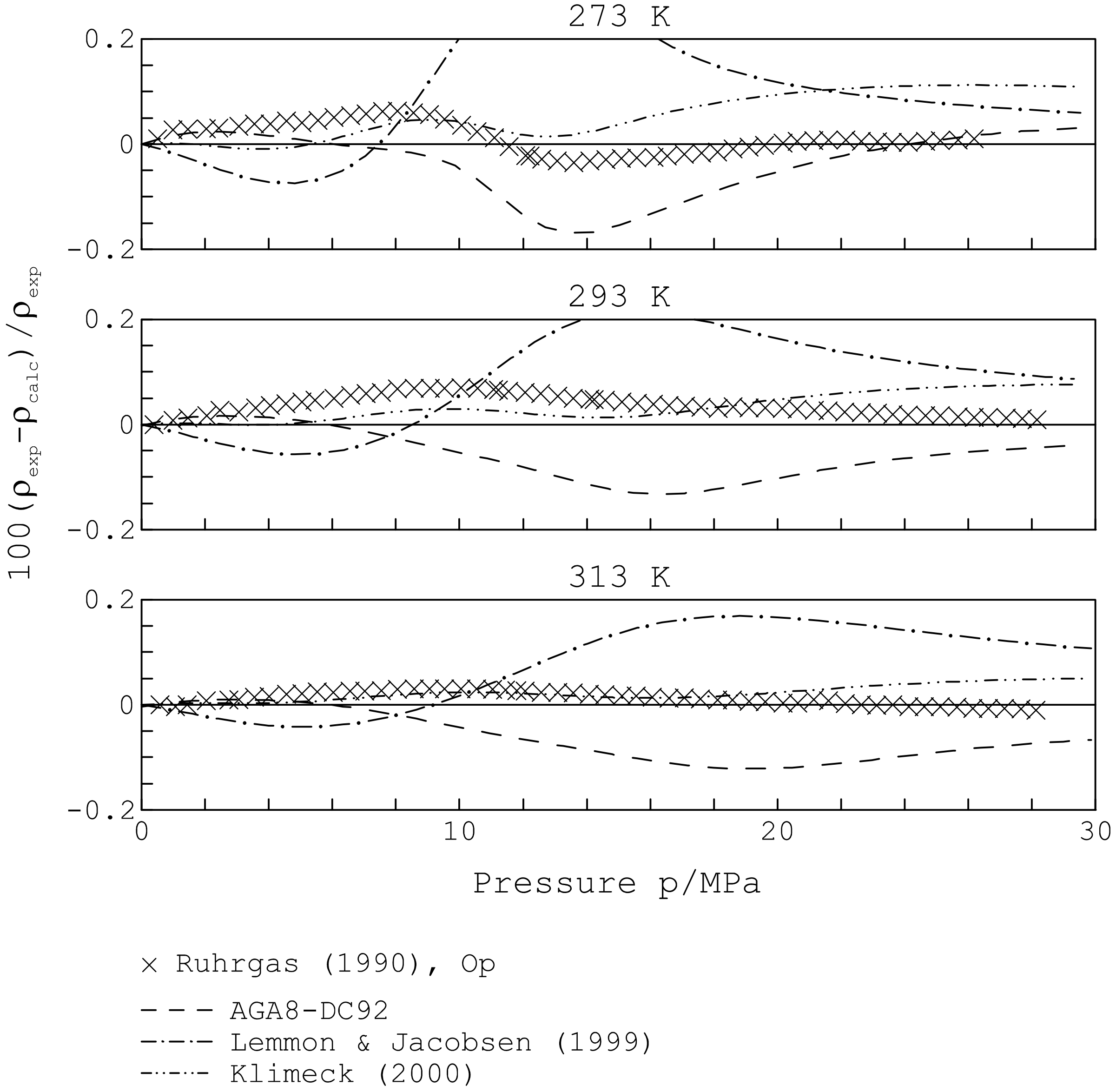

Fig. 8.59 Percentage density deviations of selected experimental $p\rho T$ data for the five-component synthetic natural gas mixture “D17” from values calculated from the new equation of state (GERG-2004), Eqs. (7.1) – (7.10); for the mixture composition see Table 8.2. Values calculated from the AGA8-DC92 equation of Starling and Savidge (1992) and the mixture models of Lemmon and Jacobsen (1999) and Klimeck (2000) are plotted for comparison.

Compared to the previous equations of state, the description of the $p\rho T$ relation of such mixtures is considerably improved by the new mixture model. The preliminary equation developed by Klimeck (2000) deviates from the measurements at 273 K by up to about 0.1%. Deviations between the experimental densities and values calculated from the AGA8-DC92 equation exceed 0.1% over the entire measured temperature range. Worse results are obtained from the mixture model of Lemmon and Jacobsen (1999), deviating by more than 0.2% from the measurements.

Synthetic Natural Gas Mixtures Rich in Nitrogen, Carbon Dioxide, and Ethane

The comparisons displayed in Figs. 8.56 – 8.58 have shown important and substantial improvements for the $p\rho T$ relation of natural gases containing high fractions of either nitrogen, carbon dioxide, or ethane. Figure 8.60 shows comparisons for two mixtures, designated by “D18” and “D21”, containing high fractions of all these components, demonstrating the enormous predictive power of the new mixture model resulting from the accurate and improved description of the respective binary subsystems. Both mixtures are characterised by comparatively low mole fractions of methane of about 61.8% (D18) and 66.1% (D21). The contents of nitrogen, carbon dioxide, and ethane all amount to approximately 13% for the four-component mixture D18, whereas the five-component gas D21 contains about 13.1% nitrogen, 11.1% carbon dioxide, 9.7% ethane, and a small amount of oxygen of 0.014%. The measurements were carried out by Ruhrgas (1990) for D18 and by Ruhrgas (1994) for D21 using an optical interferometry method.

The data for both mixtures are similarly represented by the GERG-2004 formulation with low deviations of less than ±(0.05 – 0.1)%. The AGA8-DC92 equation deviates from the measurements for the mixture D18 at 270 K by more than 0.4%, and at 290 K by more than 0.2%. Values calculated from the AGA8-DC92 equation deviate from the data of the mixture D21 by up to about 0.2% at 290 K and more than 0.2% at 280 K. Even at higher temperatures, for both mixtures, the AGA8-DC92 equation is not as accurate as the new mixture model. The comparisons for the mixture D18 show that the multi-fluid mixture models of Lemmon and Jacobsen (1999) and Klimeck (2000) yield more accurate results than the AGA8-DC92 equation of state, but both models are clearly not able to represent the measurements as accurately as the GERG-2004 formulation. The model of Klimeck (2000) deviates from the measurements at 270 K by more than 0.1%, and the model of Lemmon and Jacobsen (1999) shows deviations of more than 0.2%. Also at higher temperatures, both models are less accurate than the new equation of state.

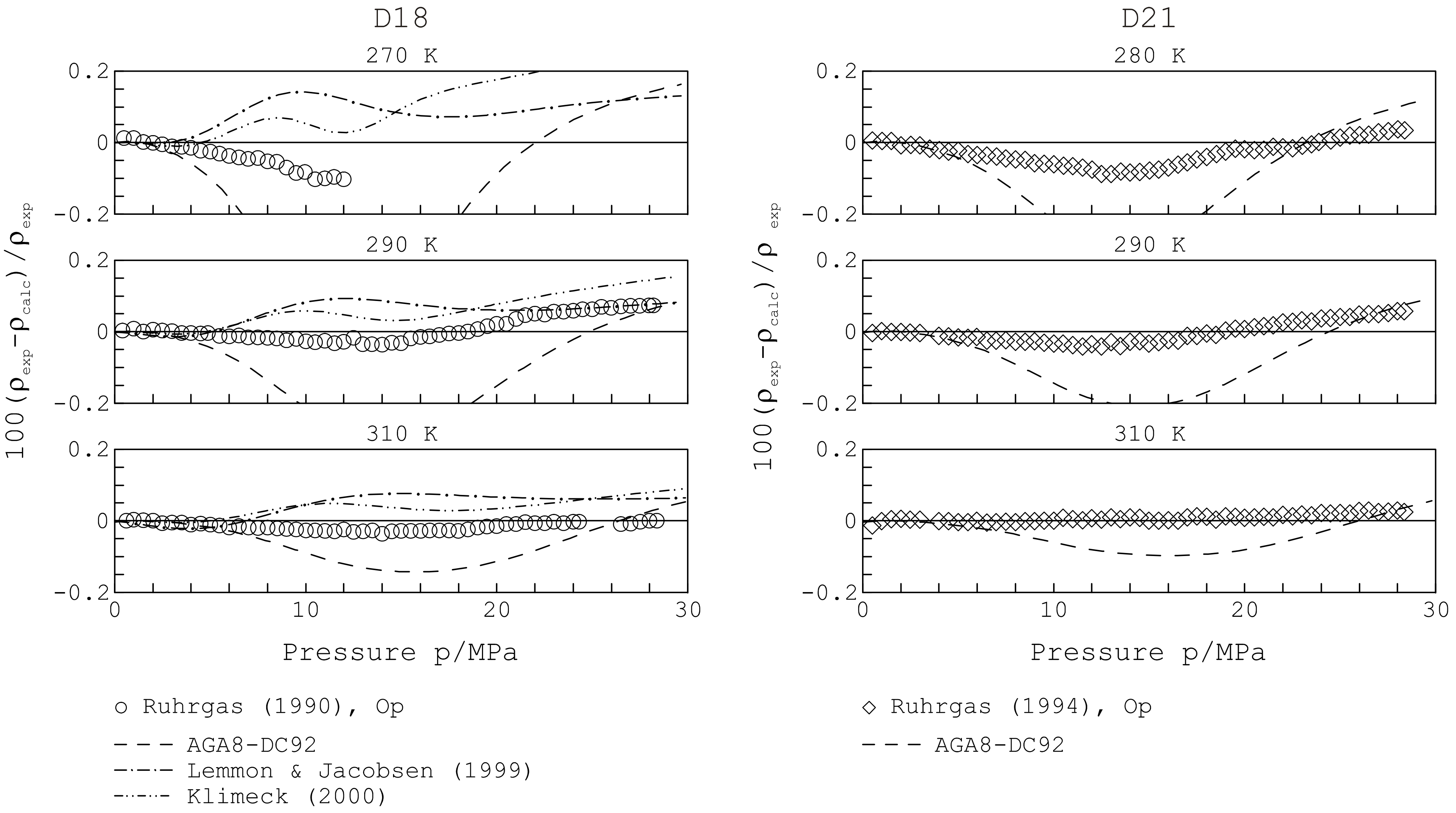

Fig. 8.60 Percentage density deviations of selected experimental $p\rho T$ data for the synthetic natural gas mixtures "D18" and "D21" from values calculated from the new equation of state (GERG-2004), Eqs. (7.1) – (7.10); for the mixture compositions see Table 8.2. Values calculated from the AGA8-DC92 equation of Starling and Savidge (1992) and the mixture models of Lemmon and Jacobsen (1999) and Klimeck (2000) are plotted for comparison.

Rich Natural Gases

In general, natural gas produced at the wellhead contains varying (large) amounts of ethane, propane, n-butane, isobutane, and heavier hydrocarbons (natural gasoline), being also called “natural gas liquids” (NGL). In its raw form, this “rich” natural gas is usually not acceptable for transportation in natural gas pipeline systems or for commercial use as a fuel. Moreover, natural gas liquids usually have more value on their own than when left in the natural gas. Therefore, rich natural gas is processed to meet pipeline quality specifications and to remove the natural gas liquids, which are then reprocessed in a fractionation unit to break them out for individual sale as ethane, propane, LPG, and other products[85]. Note that the new mixture model can be used for the calculation of such separation processes since it accurately describes the phase behaviour of natural gases and hydrocarbon mixtures, as well as their liquid phase properties (see Secs. 7.7.3 and 8.4.3 – 8.4.5).

A number of recent $p\rho T$ data for a total of seven differently composed simulated rich natural gas mixtures are available, independently measured by Jaeschke and Schley (1998) and Watson and Millington (1998). The mixtures contain up to 18% ethane, 14% propane, 6% n-butane, 0.5% n-pentane, 0.2% n-hexane, 2% or 5% nitrogen, and up to 20% carbon dioxide, whereas the comparatively low content of methane ranges from only about 52% to 64%. The measurements of Jaeschke and Schley (1998) were carried out using an optical interferometry method and cover the gas phase and gas-like supercritical region for temperatures from 280 K to 350 K at pressures up to 30 MPa. Note that the high content of the hydrocarbons from ethane to n-hexane cause the cricondentherm of the rich natural gas to be located at considerably higher temperatures (in the approximate range from 300 K to 310 K) than for typical natural gases, as shown for the simulated rich natural gas RNG5 in Fig. 7.2. Thus, the measurements at the lower temperatures are limited to pressures below the two-phase boundary. The densities of Watson and Millington (1998) complement those of Jaeschke and Schley (1998) for virtually the same mixture compositions and were measured for temperatures ranging from about 313 K to 353 K at pressures from around 8 MPa to 18 MPa using a two-sinker densimeter. The uncertainty in density of the data of Watson and Millington (1998) is claimed by the authors to be less than 0.04%. For the data measured by Jaeschke and Schley (1998), being in general in good agreement with those of Watson and Millington (1998), the uncertainty in density is assumed to be 0.1%. A systematic offset of (slightly) more than 0.1% can be observed between some data of these two sources, indicating an increased uncertainty for at least some of the measurements (see also Fig. 8.61).

The comparisons in Fig. 8.61 show selected data of these sources for two differently composed rich natural gases. The mixture designated by “RNG3” consists of about 59%

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[85] For instance, the heavier hydrocarbons n-pentane, n-hexane, etc. form a condensate (light oil), being used as an additive in motor fuel production at refineries or as replacement for LPG in making plastics at petrochemical plants.

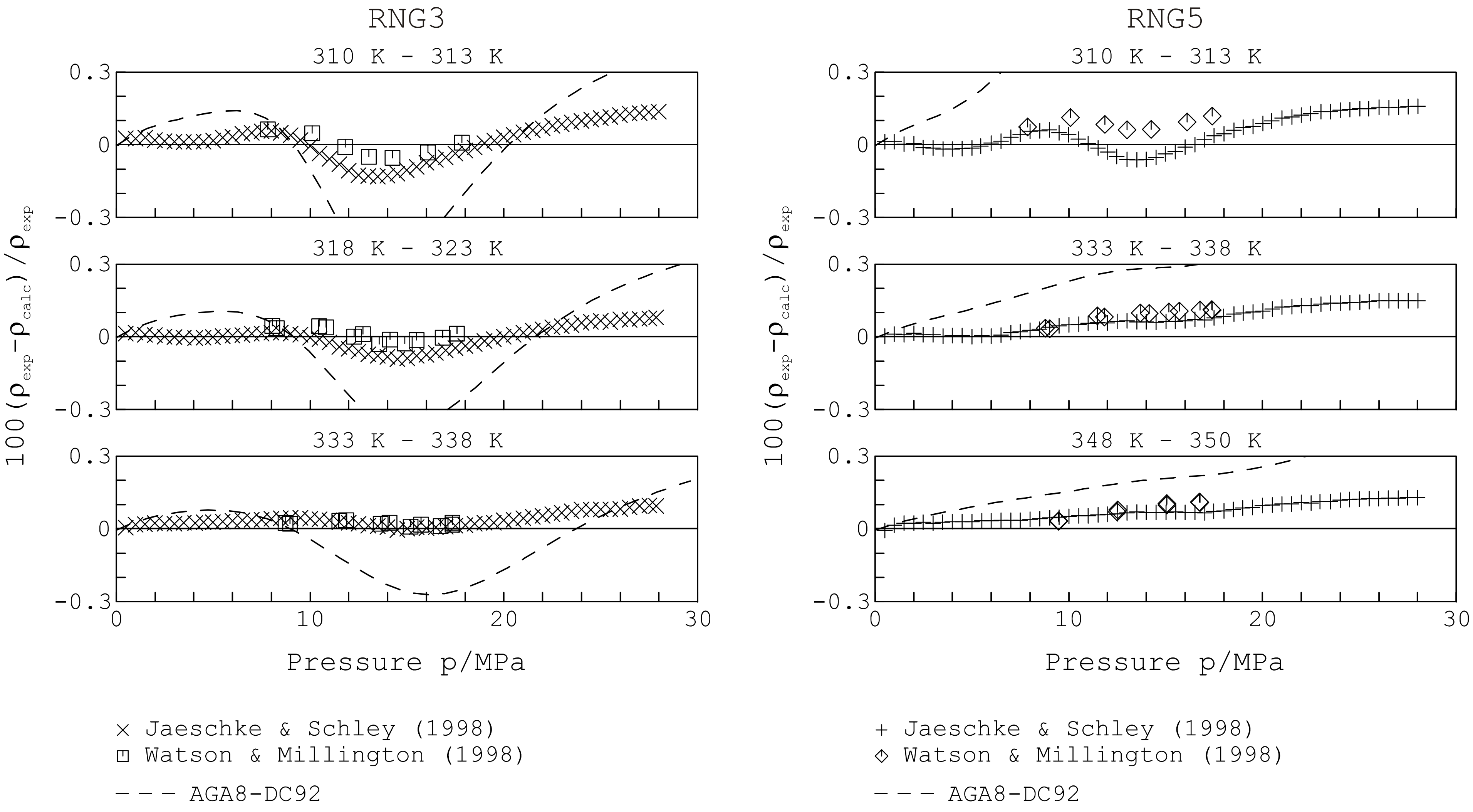

Fig. 8.61 Percentage density deviations of selected experimental $p\rho T$ data for the rich natural gases “RNG3” and “RNG5” from values calculated from the new equation of state (GERG-2004), Eqs. (7.1) – (7.10); for the mixture compositions see Table 8.2. Values calculated from the AGA8-DC92 equation of Starling and Savidge (1992) are plotted for comparison.

methane, 5% nitrogen, 6% carbon dioxide, 18% ethane, 8% propane, 3.3% n-butane, 0.5% n-pentane, and 0.2% n-hexane, whereas the mixture designated by "RNG5" contains about 64% methane, 2% nitrogen, 8% carbon dioxide, 12% ethane, 10% propane, 3.3% n-butane, 0.5% n-pentane, and 0.2% n-hexane. The GERG-2004 formulation represents the selected measurements to within deviations of ±(0.1 – 0.15)%. A similar accurate description is obtained for the measurements of Jaeschke and Schley (1998) at lower temperatures (not shown here). Comparisons with the data for additionally measured simulated rich natural gases show that the new equation of state generally yields similarly accurate results for the mixtures containing about 10% to 18% ethane, 8% to 14% propane, 3.3% to 6% n-butane, and 6% to 8% carbon dioxide (with or without the smaller fractions of n-pentane and n-hexane of 0.5% and 0.2%). Noticeably higher systematic deviations are observed for only two rich natural gas mixtures containing about 14% and 20% of carbon dioxide, being obviously more difficult to describe. However, the maximum deviations obtained for these mixtures never exceed 0.5% (see Table A2.2 of the appendix).

Although there seems to be potential for further improvements (see also Chap. 9), the current description achieved by the GERG-2004 formulation is very satisfactory and represents a major improvement compared to the AGA8-DC92 equation of state, which is not able to describe any of the data as accurately as the new mixture model. Values calculated from the AGA8-DC92 equation deviate from the measurements for the mixture RNG3 by more than 0.3% at 310 K and by more than 0.2% at even higher temperatures. For the rich natural gas mixture RNG5, deviations of up to approximately 0.7% at 310 K and of about (0.2 – 0.4)% at higher temperatures are obtained from AGA8-DC92 equation. Maximum deviations of up to 1% are obtained from the AGA8-DC92 equation for other rich natural gas mixtures.

Natural Gas–Hydrogen Mixtures and Natural Gases of Uncommon Composition

The new mixture model not only accurately describes the $p\rho T$ relation of various types of natural gases of pipeline quality and related mixtures, but also accurately handles natural gas–hydrogen mixtures, natural gases diluted with oxygen, and other special gases as exemplified in Figs. 8.62 and 8.63.

Used as an alternative fuel, natural gas–hydrogen mixtures represent the next step on the path to an ultimate hydrogen economy. Hydrogen amplifies the clean burning properties of natural gas, thus enabling the further reduction of the emission of CO, CO_2, NO_x, and hydrocarbons of gasoline or natural-gas-powered vehicles [see, for example, Akansu *et al.* (2004)]. Figure 8.62 exemplifies the description of such natural gas–hydrogen mixtures by the new equation of state. The selected mixture designated by "N72/73/74" consists of 16 components and contains only about 73.5% methane, but approximately 9.9% nitrogen, 9.5% hydrogen, 0.9% carbon monoxide, and 0.09% oxygen. The amounts of carbon dioxide (1.3%), ethane

(3.6%), propane (0.8%), and heavier hydrocarbons are similar to those obtained in ordinary natural gas mixtures. The uncertainty in density of the selected data measured by Ruhrgas (1990) is estimated to be less than (0.07 – 0.1)%. As shown in Fig. 8.62, the measurements are well represented by the GERG-2004 formulation with low deviations of less than ±(0.05 – 0.07)%. Note that most of the deviations are less than ±0.05%. Slightly higher deviations are observed only for the optical interferometry data at the lowest measured temperatures between 270 K and 283 K. Whereas the new mixture model is able to represent all measurements well within their low experimental uncertainty, values calculated from the AGA8-DC92 equation of state deviate from the data at 270 K by more than 0.1%.

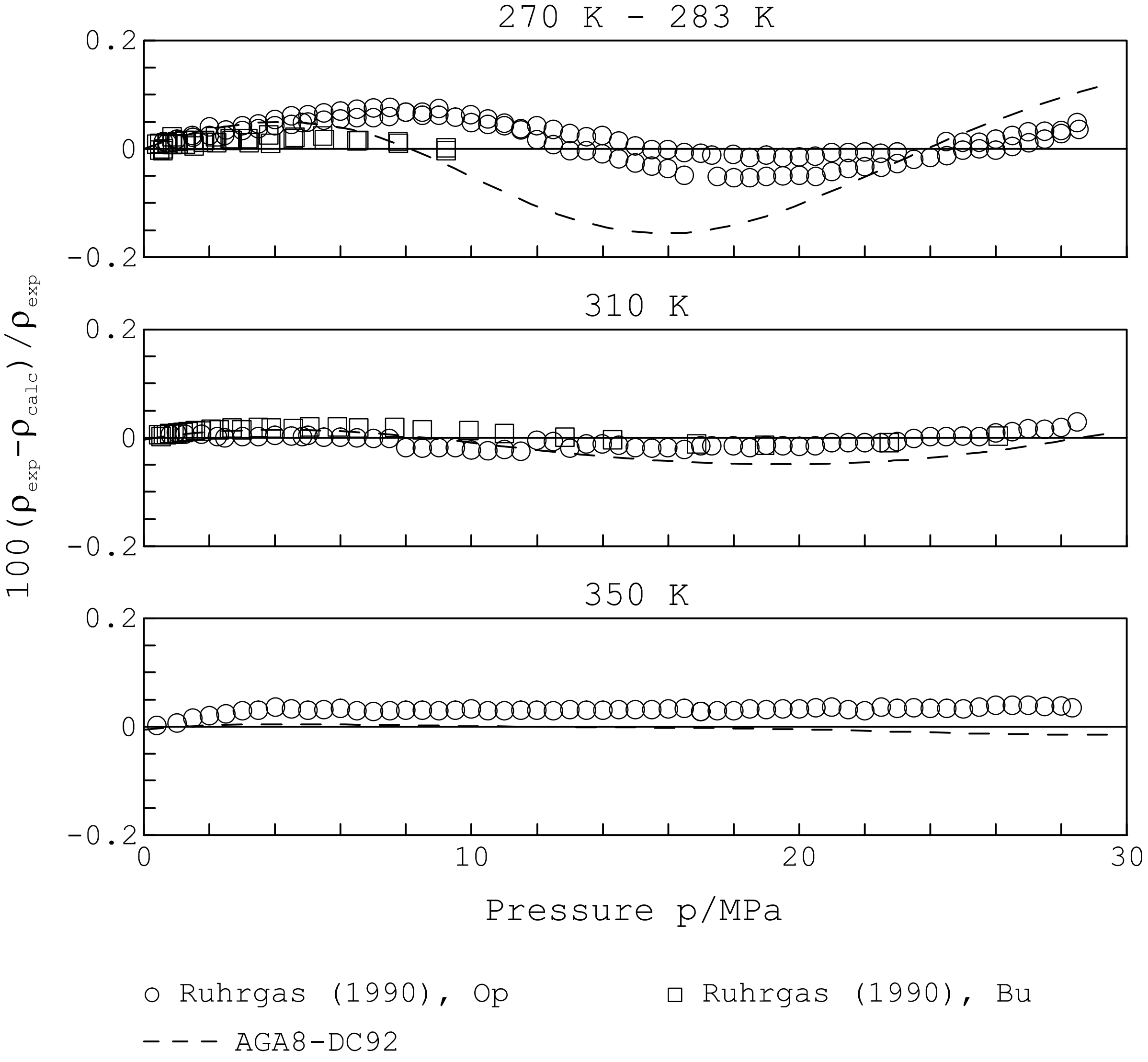

Fig. 8.62 Percentage density deviations of selected experimental $p\rho T$ data for the natural gas–hydrogen mixture "N72/73/74" from values calculated from the new equation of state (GERG-2004), Eqs. (7.1) – (7.10); for the mixture composition see Table 8.2. Values calculated from the AGA8-DC92 equation of Starling and Savidge (1992) are plotted for comparison. Bu: Burnett apparatus, Op: optical interferometry method.

Figure 8.63 shows percentage density deviations of selected measurements for the gas mixtures designated by “N115” and “N116” from the GERG-2004 formulation. Mixture N115 represents a nitrogen-rich natural gas from Gescher being further diluted with oxygen. The mixture consists of 12 components and contains about 81.5% methane, 11.8% nitrogen, and normal amounts of carbon dioxide (1.2%), ethane (2.8%), propane (0.6%), and heavier alkanes. The comparatively large content of oxygen amounts to about 1.7%. The data were measured by Ruhrgas (1994) and are represented by the new equation of state to within very low deviations over the entire measured temperature and pressure range. The majority of the data is represented clearly to within ±0.05%. Slightly higher deviations are obtained at 270 K, being, however, within ±0.07%. Values calculated from the AGA8-DC92 equation for comparison deviate from the measurements by more than 0.1% at 270 K and 290 K. Even at 330 K, the AGA8-DC92 equation is not able to represent the measurements as accurately as the GERG-2004 formulation. Here, deviations of around 0.1% are obtained from the AGA8-DC92 equation over a wide pressure range.

A similar accurate description is achieved by the GERG-2004 formulation for the rather untypical gas mixture N116 as shown in Fig. 8.63. The 12-component mixture represents a low calorific natural gas containing large amounts of coke-oven constituents. The mixture consists of only about 28.9% methane, 2% carbon dioxide, 0.8% ethane, and small fractions of heavier hydrocarbons, but 28% nitrogen, 27% hydrogen, and 13% carbon monoxide. All data, measured by Ruhrgas (1994), are represented by the new equation of state with very low deviations of less than ±0.05%, except for a few data points being, however, well within ±0.07%. Large systematic deviations are obtained from the AGA8-DC92 equation of state, which is not able to accurately describe this rather special mixture. Values calculated from this equation deviate from the measurements at 270 K by up to approximately 0.7%, and at 330 K by up to about 0.35%.

As exemplified by all of these comparisons, the new equation of state achieves a very accurate description of the $p\rho T$ relation for binary mixtures and natural gases over a much wider range of mixture conditions (temperature, pressure, and composition) than any of the previously developed equations. Since no multi-component mixture data were used for the development of the new mixture model, the improvements achieved for natural gases, similar (related) gases, and other multi-component mixtures (see also the comparisons presented in the following subsections) mainly result from the accurate description of the different binary subsystems. Furthermore, the accurate representation of multi-component data confirms the suitability of the structure of the GERG-2004 formulation in the description of multi-component mixtures.

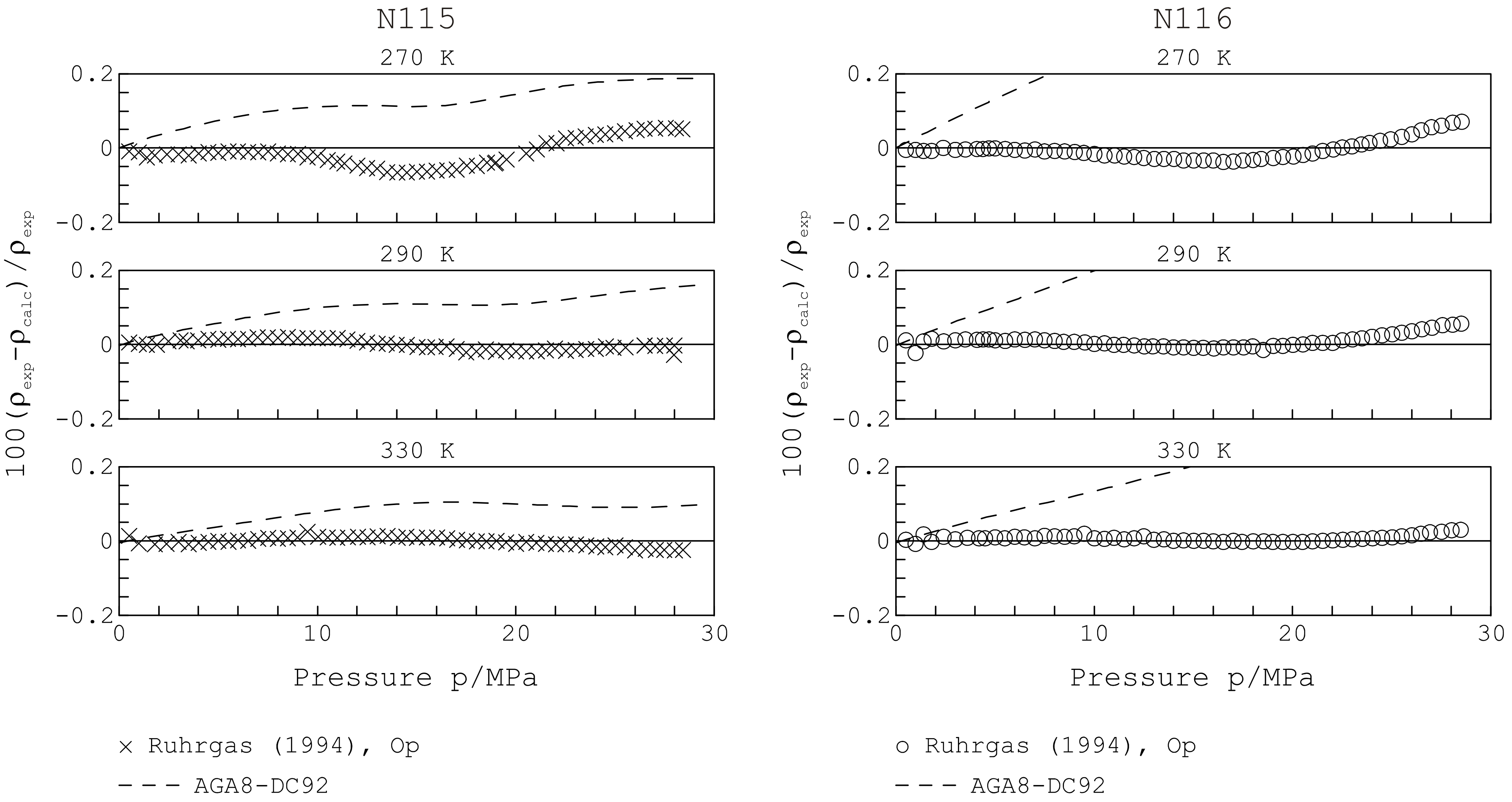

Fig. 8.63 Percentage density deviations of selected experimental $p\rho T$ data for the natural gas mixtures of uncommon composition “N115” and “N116” from values calculated from the new equation of state (GERG-2004), Eqs. (7.1) – (7.10); for the mixture compositions see Table 8.2. Values calculated from the AGA8-DC92 equation of Starling and Savidge (1992) are plotted for comparison.

8.4.2 Caloric Properties in the Homogeneous Gas Region

This subsection discusses the representation of caloric properties by the GERG-2004 formulation. Compared to the data situation present for gas phase $p\rho T$ measurements, measurements for caloric properties of natural gases are scarce. According to the demands on the accuracy of the new mixture model in the description of caloric properties of pipeline quality natural gases (see Chap. 3), the uncertainty in gas phase speed of sound was defined to be $\Delta w/w \leq 0.1\%$. Modern technical applications require the prediction of isobaric enthalpy differences to within $\Delta(\Delta h)/\Delta h \leq 1\%$. The investigations of Klimeck *et al.* (1996) showed that the AGA8-DC92 equation of state is not able to fulfil these requirements. A significant shortcoming of this equation concerns the description of caloric properties at lower temperatures. The comparisons below demonstrate the results and improvements achieved by the new equation of state.

Speed of Sound

Younglove *et al.* (1993) reported accurate caloric data for gas phase speeds of sound of different natural gas mixtures containing eight to 10 components. The data were measured over the temperature range $250\ \mathrm{K} \leq T \leq 350\ \mathrm{K}$ for pressures up to $p \leq 11\ \mathrm{MPa}$, thus covering the most interesting range in custody transfer. The mixtures are representative of commercially available or naturally occurring compositions in North America and in Europe (see Table 8.3). Comparisons between data for binary mixtures measured by these authors and those of other sources (as shown in Figs. 8.8, 8.9, and 8.14) conclude that the uncertainty in speed of sound of the multi-component data of Younglove *et al.* (1993) is likely to be (0.05 – 0.1)%.

Table 8.3 Molar compositions of the natural gas mixtures investigated by Younglove *et al.* (1993)

Mixture	Composition (mole-%)									
	CH_4	N_2	CO_2	C_2H_6	C_3H_8	n-C_4	i-C_4	n-C_5	i-C_5	n-C_6
Gulf Coast	96.561	0.262	0.597	1.829	0.410	0.098	0.098	0.032	0.046	0.067
Amarillo	90.708	3.113	0.500	4.491	0.815	0.141	0.106	0.065	0.027	0.034
Statoil Dry	83.980	0.718	0.756	13.475	0.943	0.067	0.040	0.008	0.013	–
Statfjord	74.348	0.537	1.028	12.005	8.251	3.026	–	0.575	–	0.230

Percentage speed of sound deviations from the GERG-2004 formulation and the AGA8-DC92 equation of state for three natural gases measured by Younglove *et al.* (1993) are shown in Fig. 8.64. The different mixtures represent a methane-rich natural gas (Gulf Coast), a natural gas containing medium fractions of methane, nitrogen, and ethane (Amarillo), and an ethane-rich natural gas (Statoil Dry). Table 8.3 lists the respective molar compositions (prepared gravimetrically) of these mixtures. The measurements of all three mixtures are represented by

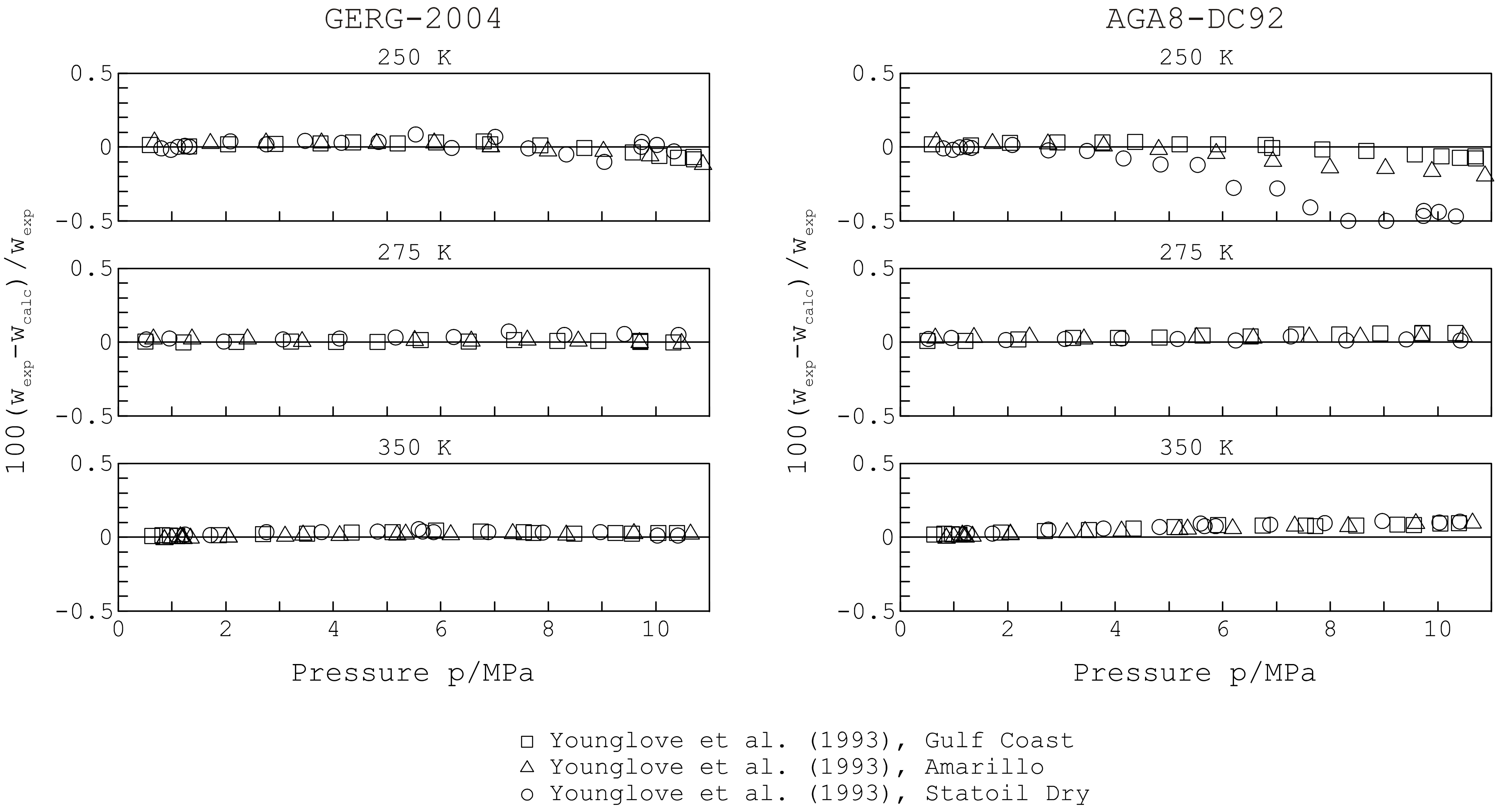

Fig. 8.64 Percentage deviations of selected experimental speed of sound data for the natural gases “Gulf Coast”, “Amarillo”, and “Statoil Dry” from values calculated from the new equation of state (GERG-2004), Eqs. (7.1) – (7.10), and the AGA8-DC92 equation of Starling and Savidge (1992); for the mixture compositions see Table 8.3.

the GERG-2004 formulation well within low deviations of ±(0.05 – 0.1)% over the entire measured temperature and pressure range, being well within the estimated uncertainty of the data. The AGA8-DC92 equation shows similar deviations at temperatures of 275 K and 350 K. At 250 K, the AGA8-DC92 equation shows weaknesses in the description of the speeds of sound for the ethane-rich natural gas mixture containing about 13.5% ethane. Here, deviations of up to 0.5% are observed. The AGA8-DC92 equation also yields less accurate results for the Amarillo gas mixture showing systematic deviations of more than 0.1% up to about 0.2% at the highest measured pressures. The comparisons show that the results achieved by the new equation of state are well within the targeted uncertainty for gas phase speeds of sound.

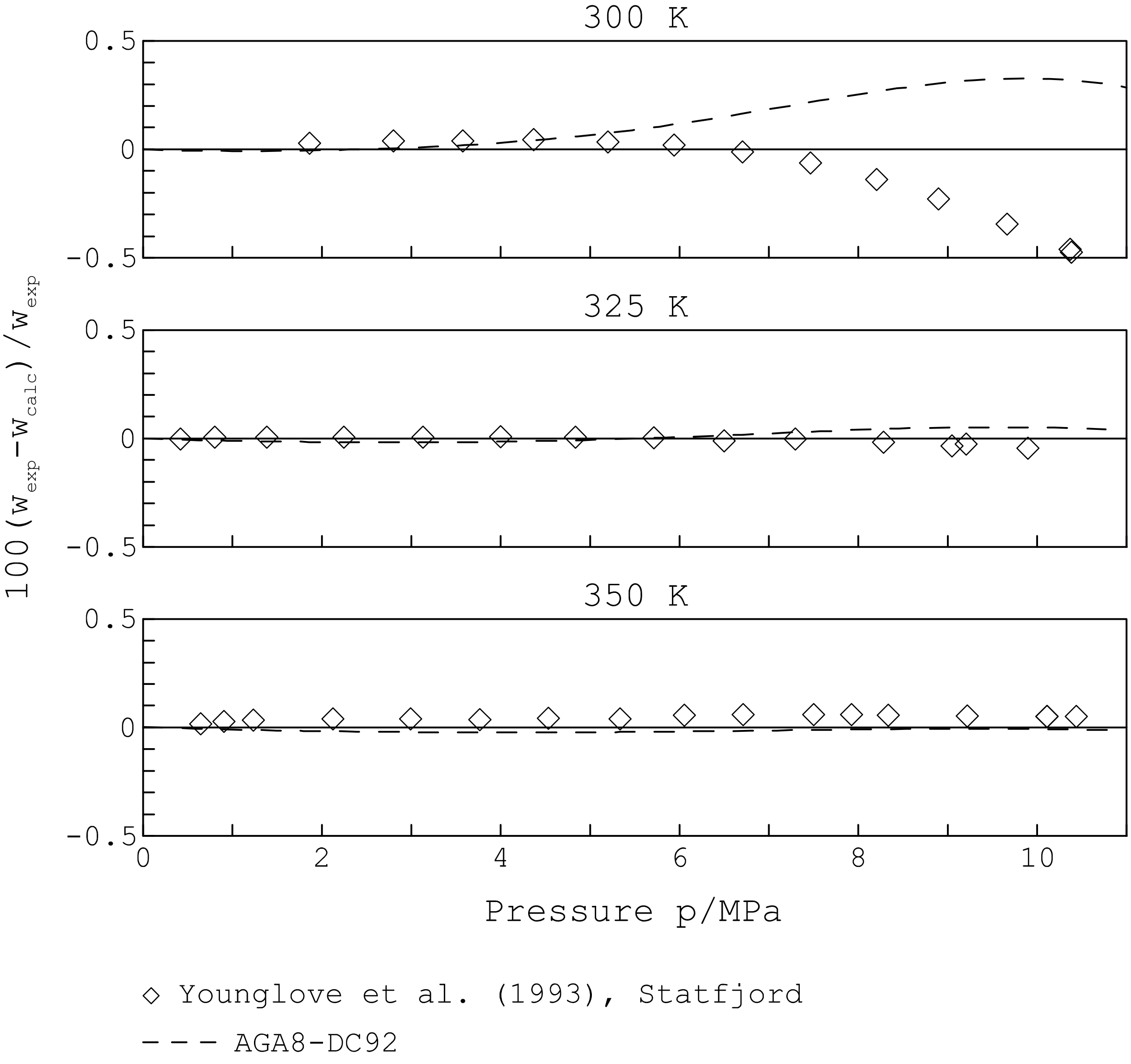

Fig. 8.65 Percentage deviations of the experimental speed of sound data for the natural gas "Statfjord" from values calculated from the new equation of state (GERG-2004), Eqs. (7.1) – (7.10); for the mixture composition see Table 8.3. Values calculated from the AGA8-DC92 equation of Starling and Savidge (1992) are plotted for comparison.

Improvements are also achieved for natural gas mixtures containing comparatively large amounts of hydrocarbons from ethane to n-hexane. Figure 8.65 shows percentage deviations of speeds of sound measured by Younglove *et al.* (1993) for an eight-component simulated Statfjord mixture from the GERG-2004 formulation. The mixture consists of about 74.3% methane, 12% ethane, 8.3% propane, 3% n-butane, and notable amounts of n-pentane (about 0.6%) and n-hexane (about 0.2%). In contrast to the rich natural gas mixtures discussed in Sec. 8.4.1, the Statfjord mixture contains only comparatively low fractions of nitrogen and carbon dioxide (see Table 8.3). The new equation of state represents most of the data to within low deviations of ±(0.05 – 0.1)%. At the lowest measured temperature of 300 K, near the cricondentherm of the mixture and corresponding to a reduced temperature of $T/T_\mathrm{r} = 1.28$, the GERG-2004 formulation shows systematically increasing deviations right up to 0.5% at pressures above 8 MPa. However, values calculated from the AGA8-DC92 equation of state deviate from the measurements at 300 K by up to about 0.8%. At higher temperatures, the AGA8-DC92 equation shows a similar description as compared to the GERG-2004 formulation.

Taking into account the rather untypical composition of the investigated mixture, the representation achieved by the GERG-2004 formulation is quite satisfactory. The poor data situation concerning speeds of sound for binary mixtures consisting of methane and propane at lower temperatures, and of methane and heavier hydrocarbons in general (see also Sec. 6.1), limits the achievable accuracy of the new mixture model. Potential further improvements would thus, first of all, require the measurement of accurate and wide-ranging speed of sound data for binary mixtures of (at least) methane with the hydrocarbons propane and n-butane at reduced temperatures $T/T_\mathrm{r} \geq 1.2$.

Enthalpy Differences

Very accurate gas phase isobaric enthalpy differences, suitable for a discussion of the description of the caloric property enthalpy, were measured by Owren *et al.* (1996) for a synthetic natural gas mixture. Similar to the data for methane–ethane of these authors previously discussed in Sec. 8.1.2 (see Fig. 8.10), the uncertainty in enthalpy differences of the measurements is estimated to be less than (0.2 – 0.5)%. The synthetic mixture consists of about 80% methane, 10% nitrogen, 2% carbon dioxide, 5% ethane, and 3% propane (see also Fig. 8.54 for the description of the $p\rho T$ relation for this mixture). Figure 8.66 shows percentage deviations of selected experimental isobaric enthalpy differences from the GERG-2004 formulation and the AGA8-DC92 equation of state. Almost all measurements are represented to within low deviations of ±(0.2 – 0.5)% by the new mixture model, thus being in good agreement with the uncertainty of the data. There are only two points located in the lower temperature range $243\ \mathrm{K} \leq T \leq 257\ \mathrm{K}$ for which the deviations obtained from the

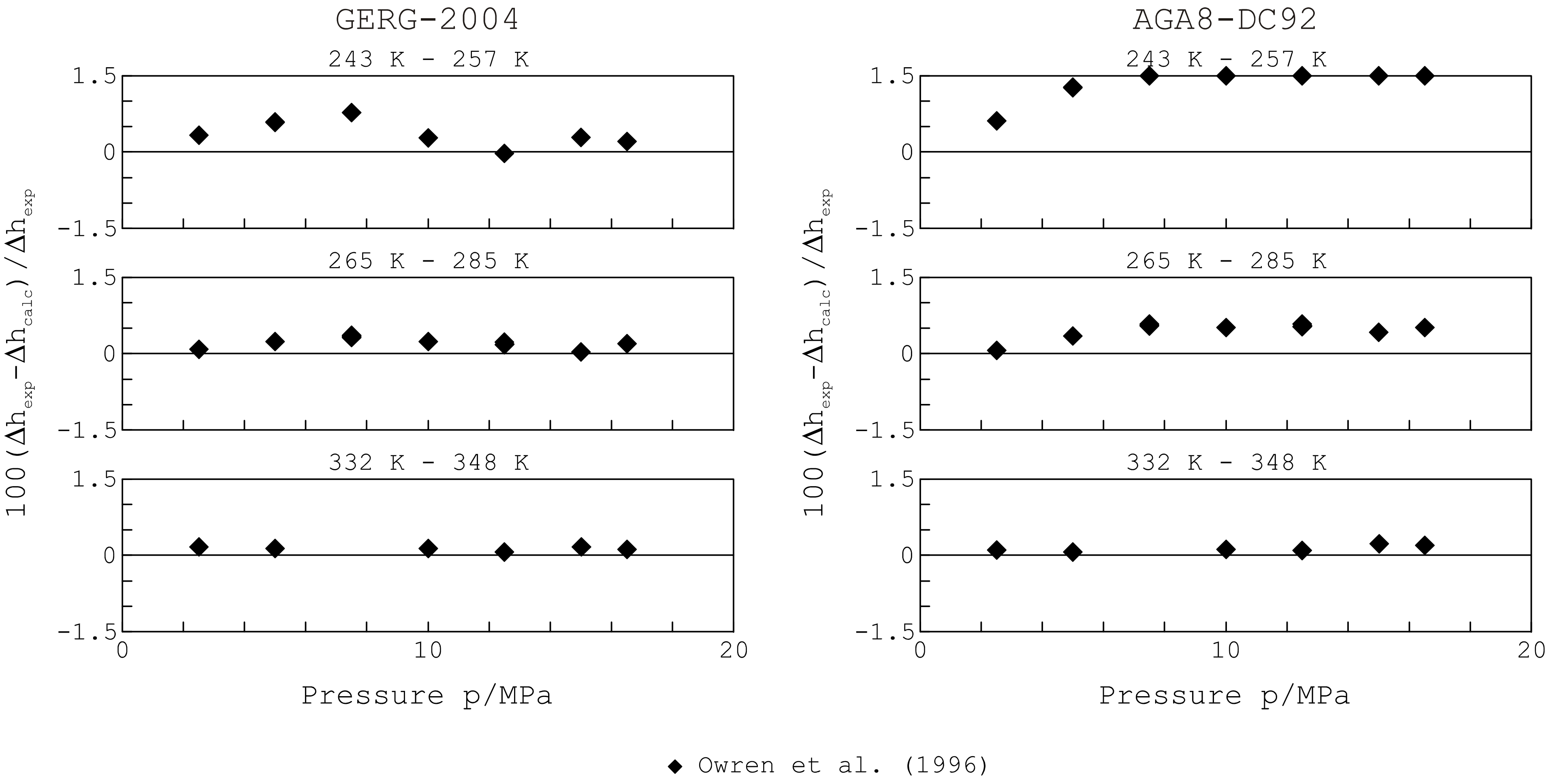

Fig. 8.66 Percentage deviations of selected experimental (isobaric) enthalpy differences measured by Owren *et al.* (1996) for a five-component synthetic natural gas mixture from values calculated from the new equation of state (GERG-2004), Eqs. (7.1) – (7.10), and the AGA8-DC92 equation of Starling and Savidge (1992); the mixture composition is as follows: 79.969% CH_4, 9.946% N_2, 2.013% CO_2, 5.065% C_2H_6, and 3.007% C_3H_8.

GERG-2004 formulation slightly exceed 0.5%, but stay clearly within the targeted uncertainty of $\Delta(\Delta h)/\Delta h \leq$ 1% for the new equation of state.

Significant weaknesses in the description of the selected isobaric enthalpy differences can be observed for the AGA8-DC92 equation of state that deviates from the data at the lower temperatures from 243 K to 257 K by (slightly) more than 1.5%. Compared to the GERG-2004 formulation, the AGA8-DC92 equation is even less accurate in the temperature range 265 K $\leq T \leq$ 285 K. Similar accurate results are only obtained at higher temperatures. The comparisons demonstrate that the new equation of state yields substantial improvements in the description of isobaric enthalpy differences in the temperature and pressure range of most interest for pipeline applications. Deviations of up to about 4% in the medium temperature range, and more than 5% at lower temperatures are obtained from the cubic equation of state of Peng and Robinson (1976) (not shown here).

Isobaric Heat Capacity

Measurements for isobaric heat capacities of natural gases and other multi-component mixtures are scarce. However, comparisons with the few available multi-component data show that the GERG-2004 formulation achieves very similar accuracy in the description of isobaric heat capacities as obtained for binary mixtures (see Secs. 8.1.2 and 8.2.2).

Figure 8.67 shows percentage deviations of isobaric heat capacities measured by Trappehl (1987) for three different ternary mixtures and a quaternary mixture consisting of methane, nitrogen, ethane, and propane from the new equation of state. The data cover the gas phase and gas-like supercritical region at temperatures from 200 K to 300 K along isobars of 2 MPa, 4 MPa, 8 MPa, and 12 MPa (data for the lowest measured temperatures are partly located near the phase boundary of the respective mixture). According to the author, the uncertainty in isobaric heat capacity of the measurements is less than 2.5%, which seems to be a quite realistic estimation. Most of the measurements are represented by the GERG-2004 formulation to within deviations of ±(1 – 2)%, thus being represented well within the experimental uncertainty claimed by the author. Slightly higher systematic deviations of up to ±3% occur for a few measurements. The achieved description is supported by the mixture model of Lemmon and Jacobsen (1999), which yields similarly accurate results (not shown here).

Sections 8.4.1 and 8.4.2 discuss the representation of data for thermal and caloric properties in the gas phase and gas-like supercritical region of natural gases, similar gases, and other multi-component mixtures by the new equation of state. Since the most important pipeline applications are located in this area of the fluid region, the highest demands on the accuracy have to be satisfied. In contrast to the AGA8-DC92 equation of state, the GERG-2004

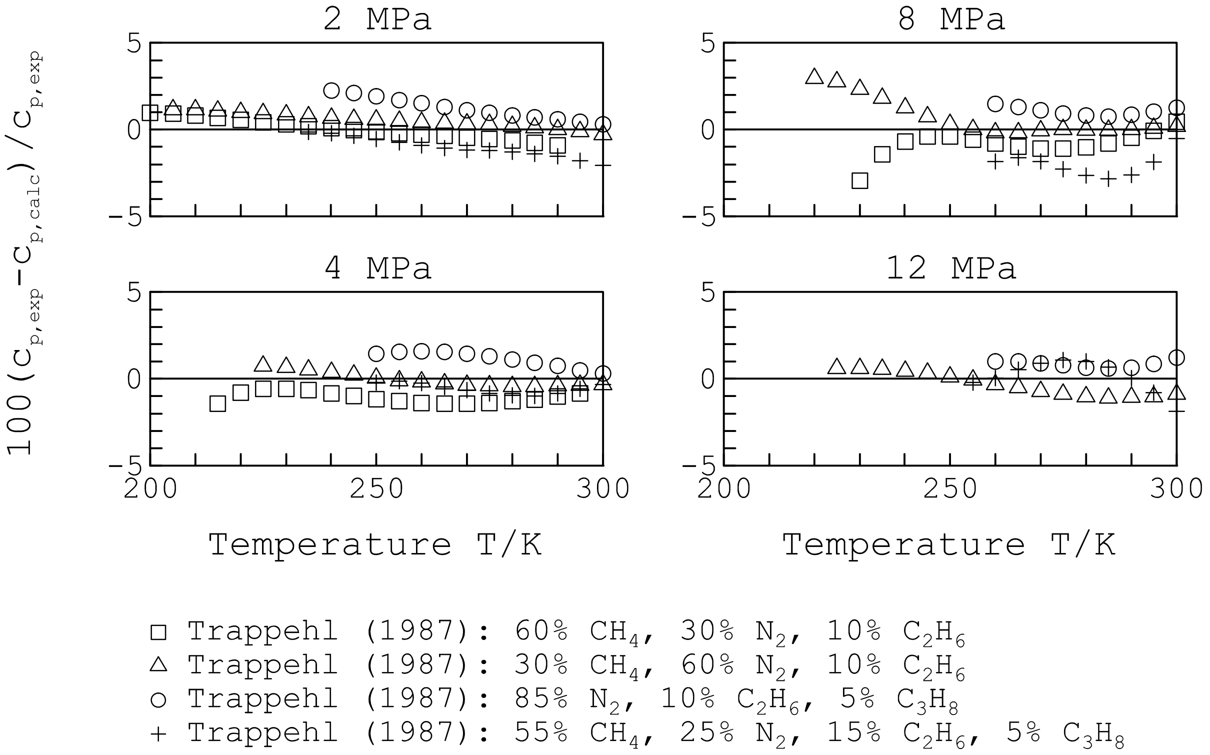

Fig. 8.67 Percentage deviations of the experimental isobaric heat capacity data measured by Trappehl (1987) for three different ternary mixtures and a quaternary mixture composed of methane, nitrogen, ethane, and propane from values calculated from the new equation of state (GERG-2004), Eqs. (7.1) – (7.10).

formulation describes the entire fluid region. Nevertheless, the new equation of state is able to represent the available most accurate experimental data for gas phase and gas-like supercritical densities, speeds of sound, and enthalpy differences mostly to within their low experimental uncertainty. This is not true for the AGA8-DC92 equation of state, which is the current internationally accepted standard for the gas region. Over wide ranges of temperature and pressure, and for natural gas compositions difficult to describe, the new equation of state achieves significant improvements. For most cases, the deviations obtained from the developed mixture model are smaller than those from the one of Lemmon and Jacobsen (1999).

8.4.3 The $p\rho T$ Relation and Caloric Properties in the Homogeneous Liquid Region

As mentioned in Chap. 6, the data situation for thermal and caloric properties of natural gases and other multi-component mixtures in the liquid phase is rather poor. For multi-component mixtures containing varying amounts of LNG components, a number of very accurate measurements were reported for saturated liquid densities as discussed in Sec. 8.4.4. Accurate density data, suitable for discussion, were measured in the homogeneous liquid region for ternary mixtures of main and secondary natural gas components.

The AGA8-DC92 equation of state is only valid in the gas region. There is no current internationally accepted standard for the description of the liquid region and the vapour-liquid equilibrium. Therefore, values calculated from the cubic equation of state of Peng and Robinson (1976) and from the multi-fluid mixture model of Lemmon and Jacobsen (1999) are used for comparison.

Liquid Phase Densities of Ternary Mixtures of Methane, Nitrogen, Ethane, and Propane

Figure 8.68 displays percentage deviations of liquid phase density data for ternary mixtures composed of methane, nitrogen, ethane, and propane from the GERG-2004 formulation, the multi-fluid mixture model of Lemmon and Jacobsen (1999), and the cubic equation of state of Peng and Robinson (1976). The measurements cover the temperature range from about 91 K to 115 K at pressures just above the phase boundary of the respective mixture. All data are represented by the new mixture model with low systematic deviations of clearly less than ±0.2%. Most of the measurements are actually within ±0.1%. For the data of Pan *et al.* (1975) and Rodosevich and Miller (1973), a very similar accurate description is observed for the model of Lemmon and Jacobsen (1999) for the ternary mixtures containing nitrogen. A different description is observed for the methane–ethane–propane system. Here, a systematic offset of around 0.1% is obtained for the measurements of Pan *et al.* (1975) and Rodosevich and Miller (1973) on the mixture containing approximately 85% methane, 10% ethane, and 5% propane. A deviation of about 0.3% is observed for the data point of Shana'a and Canfield (1968) measured for the mixture consisting of approximately 72% methane, 17% ethane, and 11% propane. The cubic equation of state of Peng and Robinson (1976) shows deviations of more than 10% for all data sets.

Liquid Phase Densities of Ternary Hydrocarbon Mixtures

Accurate liquid phase densities measured over a wide range of temperatures and pressures up to 7 MPa were recently reported by Kayukawa *et al.* (2005a) for three ternary mixtures consisting of the light hydrocarbons propane, n-butane, and isobutane, complementing the binary measurements on propane–n-butane, propane–isobutane, and n-butane–isobutane reported in the same publication (see also Figs. 8.24 and 8.25). Selected measurements and their percentage deviations from the GERG-2004 formulation as well as the multi-fluid mixture models of Lemmon and Jacobsen (1999) and Miyamoto and Watanabe (2003) are shown in Fig. 8.69. In addition, deviations between saturated liquid densities measured by the authors for the same mixture compositions are shown in the deviation plots (the saturated data are treated here as ordinary $p\rho T$ data). Similar to the measurements on the respective binary

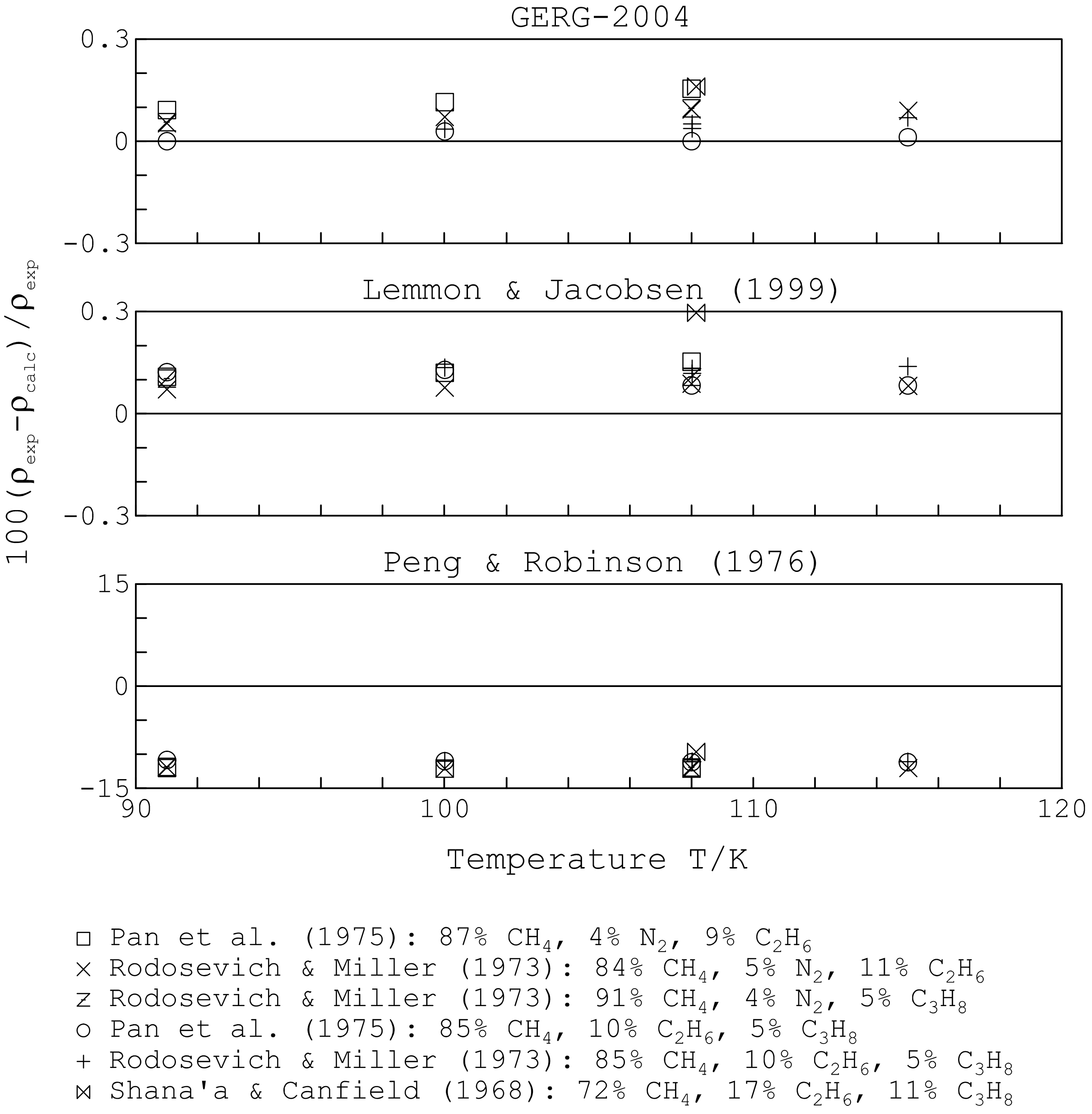

Fig. 8.68 Percentage density deviations of selected experimental $p\rho T$ data for different ternary mixtures composed of methane, nitrogen, ethane, and propane from values calculated from the new equation of state (GERG-2004), Eqs. (7.1) – (7.10), the mixture model of Lemmon and Jacobsen (1999), and the cubic equation of state of Peng and Robinson (1976).

mixtures discussed in Sec. 8.2.1, the GERG-2004 formulation accurately represents the selected ternary data to within low deviations of ±(0.1 – 0.2)%. The model of Miyamoto and Watanabe (2003) shows a less accurate description with deviations exceeding 0.3% at 240 K for the measurements on the mixture consisting of 20% propane, 60% n-butane, and 20% isobutane. The model of Lemmon and Jacobsen (1999) supports the description achieved by the GERG-2004 formulation at 240 K, but yields slightly different results at 340 K. However, all deviations are within ±0.3% for this model, which is satisfactory.

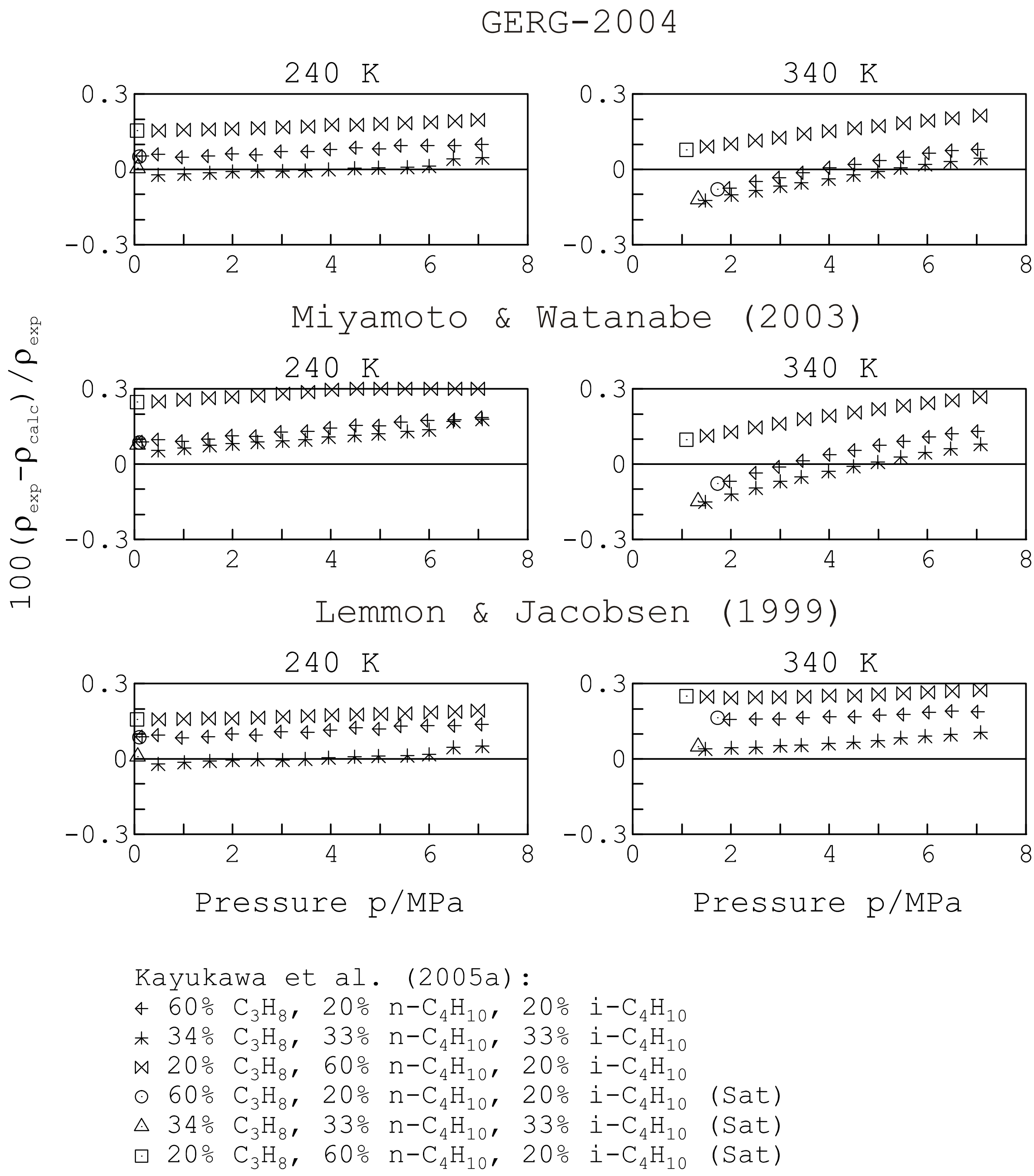

Fig. 8.69 Percentage density deviations of selected experimental $p\rho T$ data measured by Kayukawa *et al.* (2005a) for the propane–n-butane–isobutane ternary mixture from values calculated from the new equation of state (GERG-2004), Eqs. (7.1) – (7.10), the mixture model of Miyamoto and Watanabe (2003), and the mixture model of Lemmon and Jacobsen (1999). Sat: saturated liquid densities.

A number of liquid phase densities were measured by Pecar and Dolecek (2003) for the n-pentane–n-hexane–n-heptane ternary system for a variety of distinct mixture compositions. The measurements complement those reported by the same authors for the binary mixtures n-pentane–n-hexane, n-pentane–n-heptane, and n-hexane–n-heptane (see also Fig. 8.27). Similar to the binary measurements, the ternary data cover temperatures from 298 K to

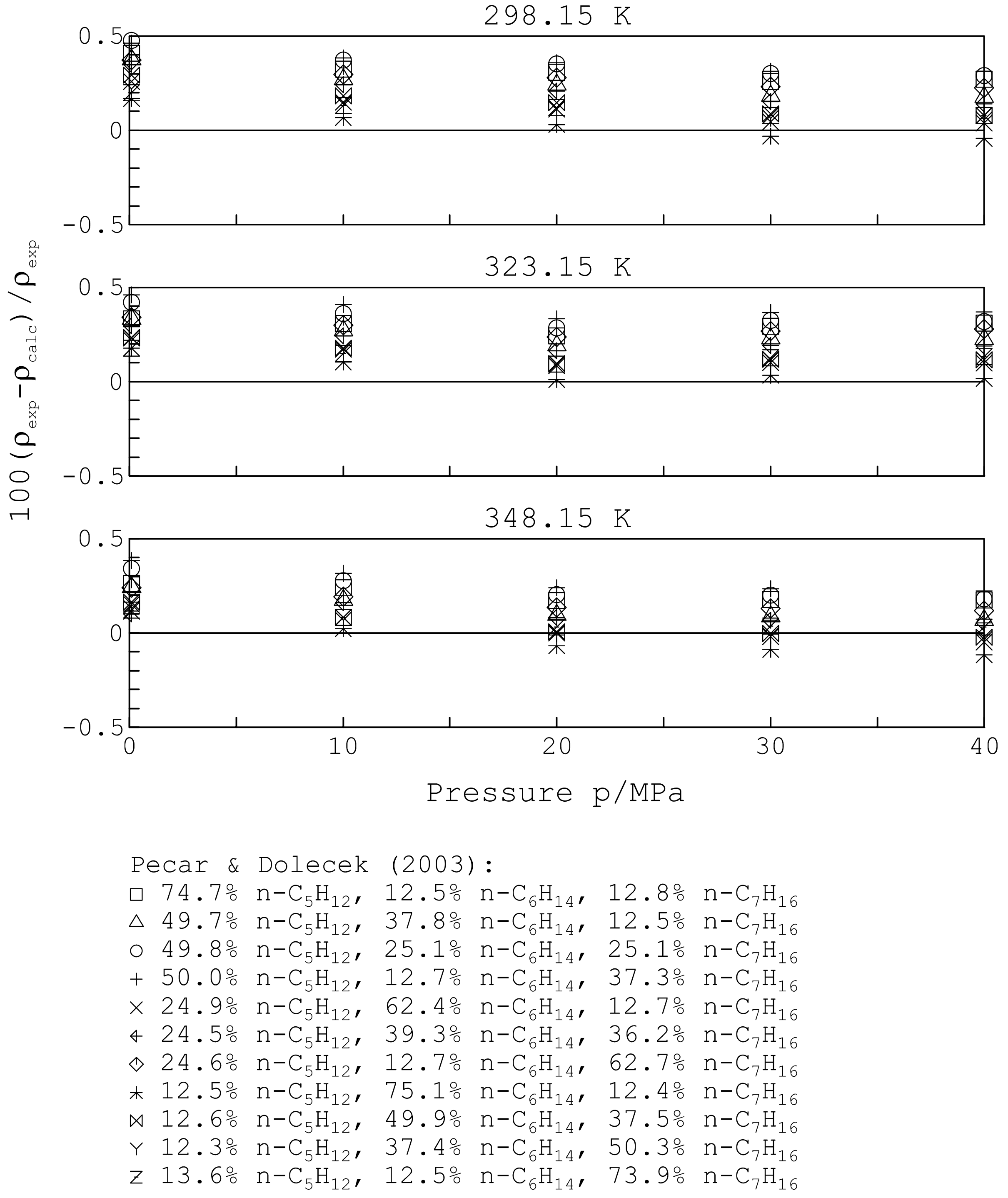

Fig. 8.70 Percentage density deviations of selected experimental *pρT* data measured by Pecar and Dolecek (2003) for the n-pentane–n-hexane–n-heptane ternary mixture from values calculated from the new equation of state (GERG-2004), Eqs. (7.1) – (7.10).

348 K at pressures up to 40 MPa. All of the data reported by these authors are well represented by the GERG-2004 formulation to within deviations of ±(0.1 – 0.5)% as exemplified by the selected measurements displayed in Fig. 8.70. The uncertainty in density of the ternary measurements is estimated by the authors to be less than 1%.

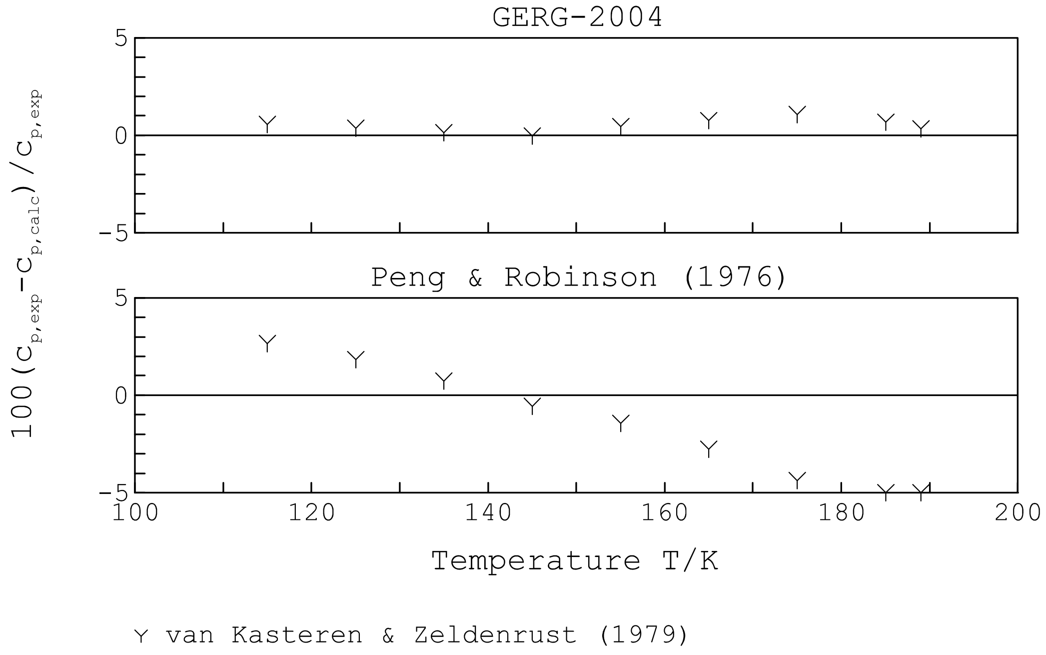

Fig. 8.71 Percentage deviations of selected experimental isobaric heat capacity data measured by van Kasteren and Zeldenrust (1979) for an eight-component LNG-like mixture at a pressure of 5.07 MPa from values calculated from the new equation of state (GERG-2004), Eqs. (7.1) – (7.10), and the cubic equation of state of Peng and Robinson (1976); the mixture composition is as follows: 89.94% CH_4, 0.78% N_2, 4.52% C_2H_6, 3.35% C_3H_8, 0.63% n-C_4H_{10}, 0.74% i-C_4H_{10}, 0.03% n-C_5H_{12}, and 0.01% i-C_5H_{12}.

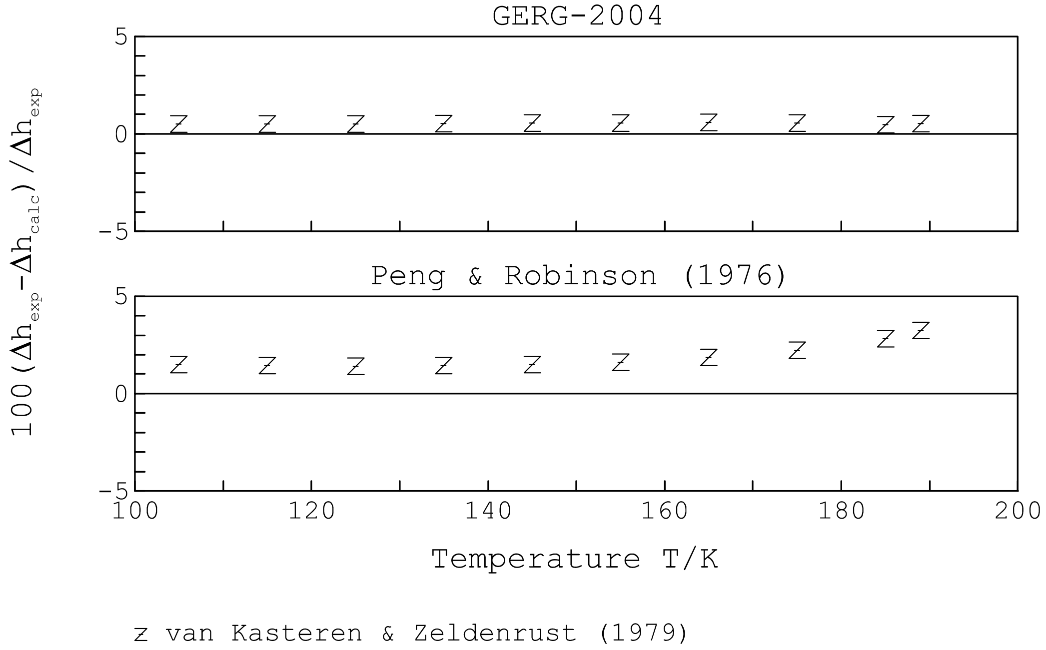

Fig. 8.72 Percentage deviations of selected experimental (isobaric) enthalpy differences measured by van Kasteren and Zeldenrust (1979) for an eight-component LNG-like mixture at a pressure of 5.07 MPa from values calculated from the new equation of state (GERG-2004), Eqs. (7.1) – (7.10), and the cubic equation of state of Peng and Robinson (1976); the mixture composition is as follows: 89.94% CH_4, 0.78% N_2, 4.52% C_2H_6, 3.35% C_3H_8, 0.63% n-C_4H_{10}, 0.74% i-C_4H_{10}, 0.03% n-C_5H_{12}, and 0.01% i-C_5H_{12}.

Isobaric Heat Capacity and Enthalpy Differences

Figure 8.71 displays percentage deviations between selected liquid phase isobaric heat capacities for an eight-component LNG-like mixture measured by van Kasteren and Zeldenrust (1979) and values calculated from the GERG-2004 formulation and the cubic equation of state of Peng and Robinson (1976). The mixture consists of about 89.9% methane, 0.8% nitrogen, 4.5% ethane, 3.4% propane, 0.6% n-butane, 0.7% isobutane, 0.03% n-pentane, and 0.01% isopentane. The selected data cover temperatures from 115 K to 189 K at a pressure of 5.07 MPa and are represented well by the new equation of state to within deviations of ±1%. Significantly larger systematic deviations exceeding values of even 5% when approaching the phase boundary of the mixture are observed for the cubic equation of state of Peng and Robinson (1976).

Aside from gas and liquid phase isobaric heat capacities, the accurate description of the enthalpy-temperature relation of natural gases, including the total enthalpy change from room temperature down to 110 K, is of considerable importance for the economic design of liquefaction and regasification plants. For the same mixture discussed above, van Kasteren and Zeldenrust (1979) also reported liquid phase isobaric enthalpy data. The percentage deviations between selected experimental enthalpy differences $\Delta h = h_2(T_2, p, \bar{x}) - h_1(T_1, p, \bar{x})$ (with T_2 = 270 K and T_1 according to Fig. 8.72) and values calculated from the GERG-2004 formulation and the cubic equation of state of Peng and Robinson (1976) are shown in Fig. 8.72. The new equation of state represents all of the data to within deviations of around ±0.5%. The cubic equation shows systematic deviations ranging from around 1.5% at temperatures below 150 K to more than 3% when approaching the phase boundary of the mixture.

8.4.4 Saturated Liquid Densities of LNG-Like Mixtures

Experimental data for liquid phase densities of multi-component natural gas mixtures are scarce. Very accurate data, however, exist for saturated liquid densities of a variety of LNG-like mixtures consisting of up to eight components, including simulated commercial LNG mixtures, over the temperature range from 100 K to 140 K, corresponding to reduced temperatures ranging from about 0.4 to 0.6. The measurements were performed as part of an extensive experimental program carried out at the National Bureau of Standards (NBS) in Boulder, Colorado, USA [Haynes *et al.* (1983)]. The uncertainty of the data is claimed by the authors to be $\Delta\rho'/\rho' \leq 0.1\%$. Since the pressure dependence of the $p\rho T$ relation in the liquid phase is small for reduced temperatures such as these, the accurately measured saturated liquid densities also provide a suitable basis for the approximate evaluation of the quality of the new equation of state in the description of homogeneous liquid phase densities of LNG-like mixtures. Table 8.4 summarises the data sets being discussed in the following passages (see Figs. 8.73 and 8.74) and lists the compositions of the corresponding mixtures.

Table 8.4 Molar compositions of selected multi-component LNG-like mixtures

Author	Composition (mole-%)							
	CH_4	N_2	C_2H_6	C_3H_8	n-C_4	i-C_4	n-C_5	i-C_5
	Five- to six-component mixtures (see Fig. 8.74)							
◫ Haynes (1982)	90.613	0.601	6.026	2.154	0.306	0.300	–	–
⊲ Haynes (1982)	88.225	0.973	7.259	2.561	0.492	0.490	–	–
○ Haynes (1982)	85.934	1.383	8.477	2.980	0.707	0.519	–	–
⋈ Haynes (1982)	85.892	–	11.532	1.341	0.705	0.530	–	–
Y Hiza & Haynes (1980)	85.442	–	5.042	4.038	2.901	2.577	–	–
⚹ Haynes (1982)	84.558	–	8.153	4.778	1.252	1.259	–	–
Ƶ Hiza & Haynes (1980)	81.300	4.250	4.750	4.870	2.420	2.410	–	–
	Seven- to eight-component mixtures (see Fig. 8.73)							
□ Haynes (1982)	90.068	0.599	6.537	2.200	0.284	0.291	0.011	0.010
◇ Haynes (1982)	85.341	–	7.898	4.729	0.992	0.854	0.089	0.097
+ Haynes (1982)	75.713	0.859	13.585	6.742	1.326	1.336	0.216	0.223
⊙ Haynes (1982)	75.442	–	15.401	6.950	1.057	0.978	0.083	0.089
× Haynes (1982)	74.275	0.801	16.505	6.547	0.893	0.843	0.067	0.069

Mixtures Consisting of Seven to Eight LNG Components

Figure 8.73 exemplifies the high quality of the new equation of state in the description of saturated liquid densities for multi-component LNG-like mixtures. Displayed are percentage deviations between the selected measurements of Haynes (1982) for five different mixtures and values calculated from the GERG-2004 formulation as well as the cubic equation of state of Peng and Robinson (1976). The seven- to eight-component mixtures are composed of methane, nitrogen, ethane, propane, n-butane, isobutane, n-pentane, and isopentane, and are representative for compositions encountered in commercial LNG[86]. The new equation of state describes all measurements well within deviations of ±(0.1 – 0.4)%. Most of the measurements are actually represented to within ±(0.1 – 0.3)%. Slightly higher systematic deviations up to about 0.4% are only obtained for the data of the mixture containing comparatively large amounts of n-butane and isobutane (about 1.3% each), and n-pentane and isopentane (about 0.2% each). The cubic equation of state of Peng and Robinson (1976) is not able to represent the data within acceptable deviations and deviates from the measurements for the five selected mixtures by approximately 10% or more. On average, the new mixture model is about 50 times more accurate than an ordinary cubic equation of state, which is still

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[86] Note that the mixtures do not contain any carbon dioxide. To prevent it from freezing to dry ice and plugging the heat exchangers, this component is generally removed from the natural gas before liquefaction.

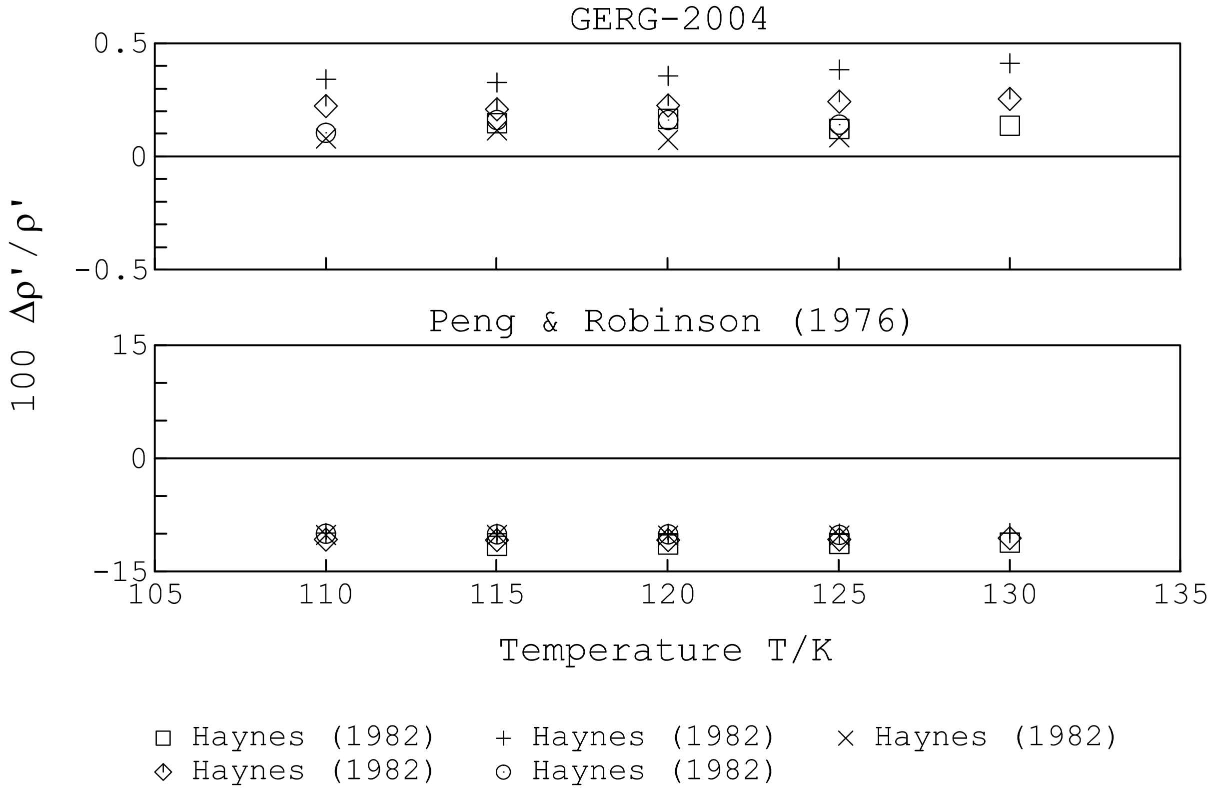

Fig. 8.73 Percentage deviations $100\Delta\rho'/\rho' = 100(\rho'_{\text{exp}} - \rho'_{\text{calc}})/\rho'_{\text{exp}}$ of the experimental saturated liquid densities measured by Haynes (1982) for different LNG-like mixtures consisting of seven to eight components from values calculated from the new equation of state (GERG-2004), Eqs. (7.1) – (7.10), and the cubic equation of state of Peng and Robinson (1976); for the mixture compositions see Table 8.4.

widely applied in the natural gas industry. The GERG-2004 formulation thus enables a substantial improvement in the description of natural gases in the liquid phase. The comparisons with the data measured by Hiza *et al.* (1977) for binary mixtures of LNG components showed similar results (see Fig. 8.16 and also Fig. 8.17).

Mixtures Consisting of Five to Six LNG Components

Comparisons with the cubic equation of state of Peng and Robinson (1976) are thus of minor value for further discussions. Figure 8.74 shows deviations of selected experimental saturated liquid densities of Hiza and Haynes (1980) and Haynes (1982) for LNG-like mixtures consisting of five to six components from the GERG-2004 formulation as well as the multi-fluid mixture model of Lemmon and Jacobsen (1999). The new mixture model represents almost all of the measurements to within deviations of ±(0.1 – 0.3)% (maximum deviations are clearly below 0.4%). Larger systematic deviations, partially exceeding 0.4%, are observed for the multi-fluid mixture model of Lemmon and Jacobsen (1999) for the nitrogen containing mixtures as well as for those only consisting of hydrocarbons. For the latter, systematic

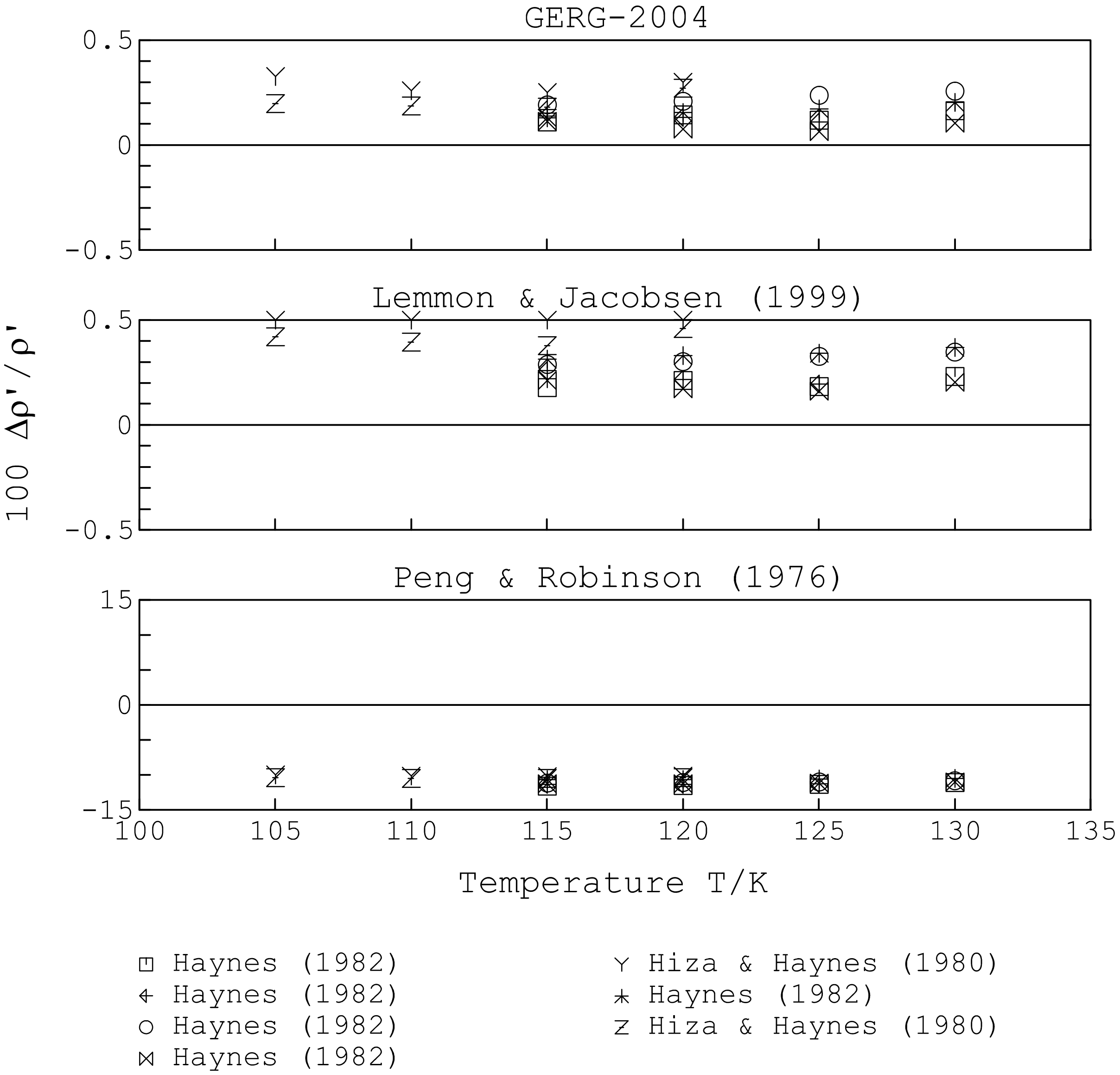

Fig. 8.74 Percentage deviations $100\Delta\rho'/\rho' = 100(\rho'_{\mathrm{exp}} - \rho'_{\mathrm{calc}})/\rho'_{\mathrm{exp}}$ of selected experimental saturated liquid densities for different LNG-like mixtures consisting of five to six components from values calculated from the new equation of state (GERG-2004), Eqs. (7.1) – (7.10), the mixture model of Lemmon and Jacobsen (1999), and the cubic equation of state of Peng and Robinson (1976); for the mixture compositions see Table 8.4.

deviations of more than 0.5% are observed. The cubic equation of Peng and Robinson (1976) again deviates from the measurements for the seven selected mixtures by approximately 10% or more.

The new multi-fluid mixture model satisfies the demands concerning the representation of the saturated liquid densities, underlined by the comparisons given here. The data situation for experimental liquid phase densities of natural gases is not sufficient to show this accurate representation by multi-component data in the homogeneous (compressed) liquid region. Due to the small pressure dependence in liquid phase densities and the very accurate description of compressed liquid densities for binary mixtures shown in Secs. 8.1.1 and 8.2.1, a comparable uncertainty can be assumed. As shown by the comparisons, densities of natural gases in the liquid region are represented by the new equation of state more accurately by an order of magnitude than cubic equations of state widely in use in technical applications.

8.4.5 The *pTxy* Relation

Measurements on the *pTxy* relation of natural gases or other multi-component mixtures are rather scarce. Moreover, virtually no accurate experimental information is available for bubble point pressures of natural gases. Compared to the very accurate saturated liquid densities of Hiza and Haynes (1980) and Haynes (1982) discussed in the previous subsection, their reported pressure measurements are much less accurate and can only be considered as approximate vapour pressures (see also Chap. 6). The data show quite large systematic deviations from different equations of state as demonstrated by the investigations of Klimeck (2000).

A number of comparatively accurate dew point data were recently measured by several authors and are accurately represented by the GERG-2004 formulation as shown in the comparisons given in Sec. 7.7.3, for selected natural gas mixtures. Various, but in general not wide ranging, measurements are available for the *pTxy* relation of ternary mixtures of natural gas and air components. The representation of a selection of these data is discussed in the following passages. The accurate description of the *pTxy* relation is of indispensable importance for the design of any separation processes as encountered in the processing and liquefaction of natural gas or air.

Methane–Carbon Dioxide–Ethane

Figure 8.75 shows percentage deviations of experimental vapour pressures for the ternary system methane–carbon dioxide–ethane from values calculated from the GERG-2004 formulation, the multi-fluid mixture model of Lemmon and Jacobsen (1999), and the cubic equation of state of Peng and Robinson (1976). The data were measured by Wei *et al.* (1995) at a temperature of 230 K and at pressures from about 1.2 MPa to 6.6 MPa. The data complement those measured by the same authors for the *pTxy* relation of the constituent binaries methane–carbon dioxide, methane–ethane, and carbon dioxide–ethane (see Figs. 8.20 – 8.22 and Figs. 7.16 and 7.17). The new equation of state represents all of the vapour pressures with deviations of clearly less than ±4%. Most of the measurements are actually within ±(1 – 3)%, which is in good agreement with the representation obtained for the respective binary mixtures. Larger maximum deviations exceeding 5% are obtained from both the mixture model of Lemmon and Jacobsen (1999) and the cubic equation of Peng and Robinson (1976).

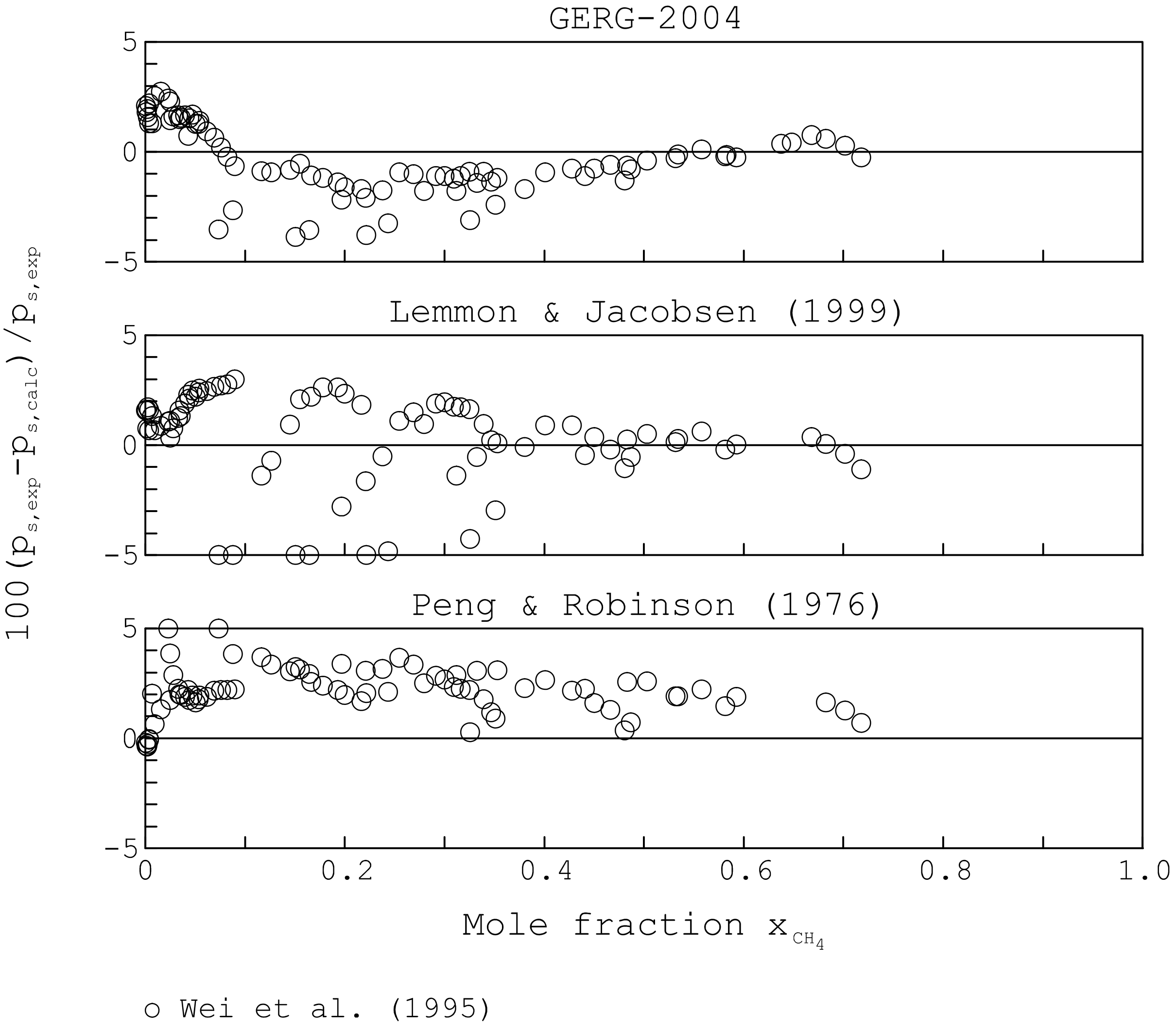

Fig. 8.75 Percentage deviations of the experimental vapour pressures measured by Wei *et al.* (1995) for the methane–carbon dioxide–ethane ternary mixture at a temperature of 230 K from values calculated from the new equation of state (GERG-2004), Eqs. (7.1) – (7.10), the mixture model of Lemmon and Jacobsen (1999), and the cubic equation of state of Peng and Robinson (1976).

The comparisons in Fig. 8.76 display deviations between the experimentally determined vapour phase fractions of each mixture component, corresponding to the simultaneously measured set of *pTxy* data of Wei *et al.* (1995) and values calculated from the GERG-2004 formulation. The vapour fractions for methane and carbon dioxide are represented by the new equation of state well within deviations of ±(1 – 2) mole-% with only a few exceptions with slightly higher deviations. However, the measured ethane fractions are all within ±(0.5 – 1) mole-%, indicating a less sensitive pressure dependence for this component. This achieved accurate description is very satisfactory and agrees well with the results obtained for the respective binary mixtures. Similar to the vapour pressure measurements shown in Fig. 8.75, larger but acceptable systematic deviations are obtained from the mixture model of Lemmon and Jacobsen (1999) and the cubic equation of Peng and Robinson (1976) (not shown here).

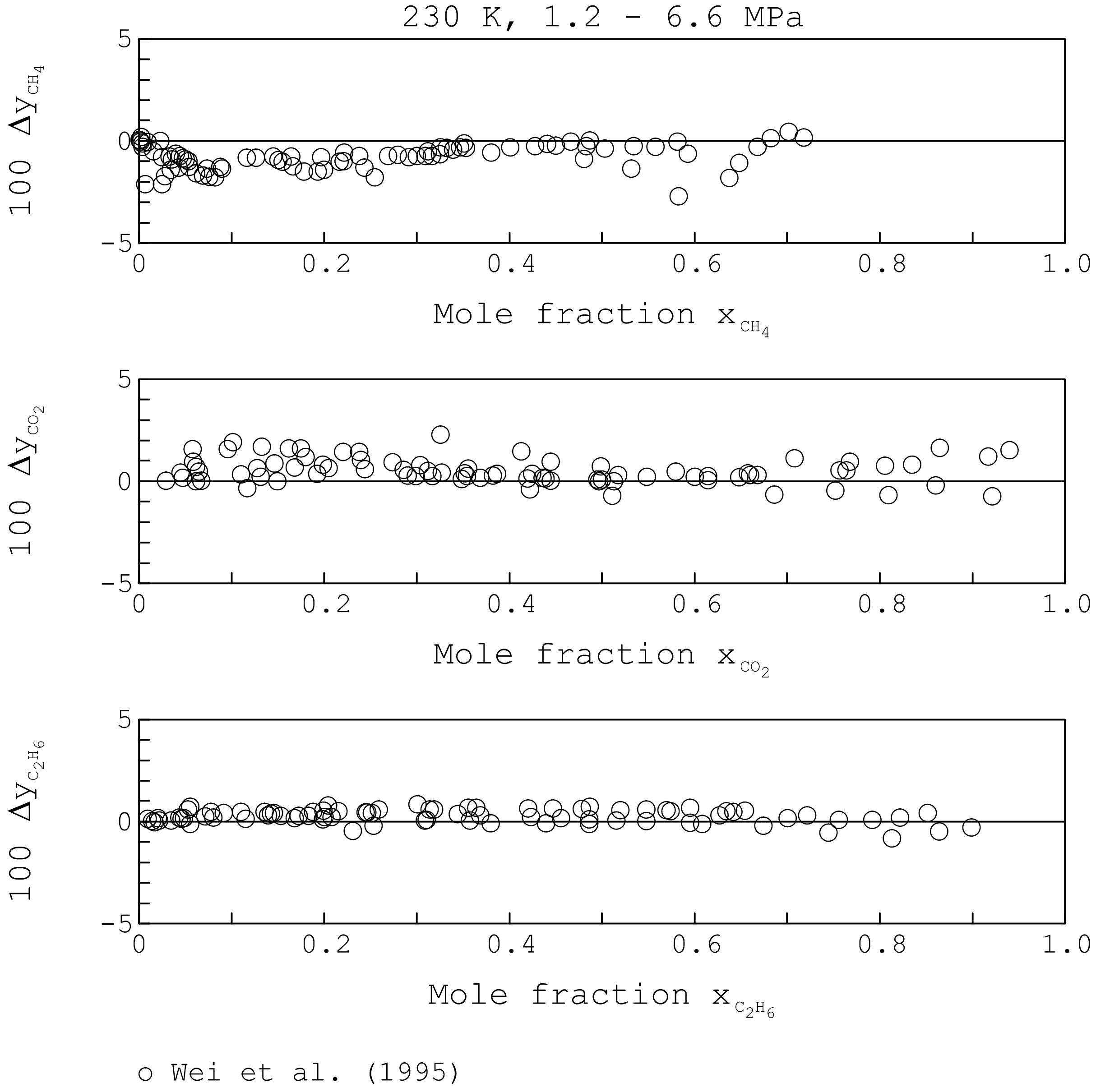

Fig. 8.76 Deviations of the experimental methane, carbon dioxide, and ethane mole fractions in the saturated vapour phase measured by Wei *et al.* (1995) for the methane–carbon dioxide–ethane ternary mixture at a temperature of 230 K from values calculated from the new equation of state (GERG-2004), Eqs. (7.1) – (7.10): $100\,\Delta y_{\mathrm{CH_4}} = 100(y_{\mathrm{CH_4,exp}} - y_{\mathrm{CH_4,calc}})$, $100\,\Delta y_{\mathrm{CO_2}} = 100(y_{\mathrm{CO_2,exp}} - y_{\mathrm{CO_2,calc}})$, $100\,\Delta y_{\mathrm{C_2H_6}} = 100(y_{\mathrm{C_2H_6,exp}} - y_{\mathrm{C_2H_6,calc}})$.

Ethane–Propane–n-Butane

Figure 8.77 displays deviations of the *pTxy* measurements by Lhoták and Wichterle (1983) for the ternary hydrocarbon system ethane–propane–n-butane from values calculated from the GERG-2004 formulation. The data cover pressures from 0.7 MPa to 4.9 MPa in the rather narrow temperature range from about 304.6 K to 306.5 K enclosing the critical temperature of

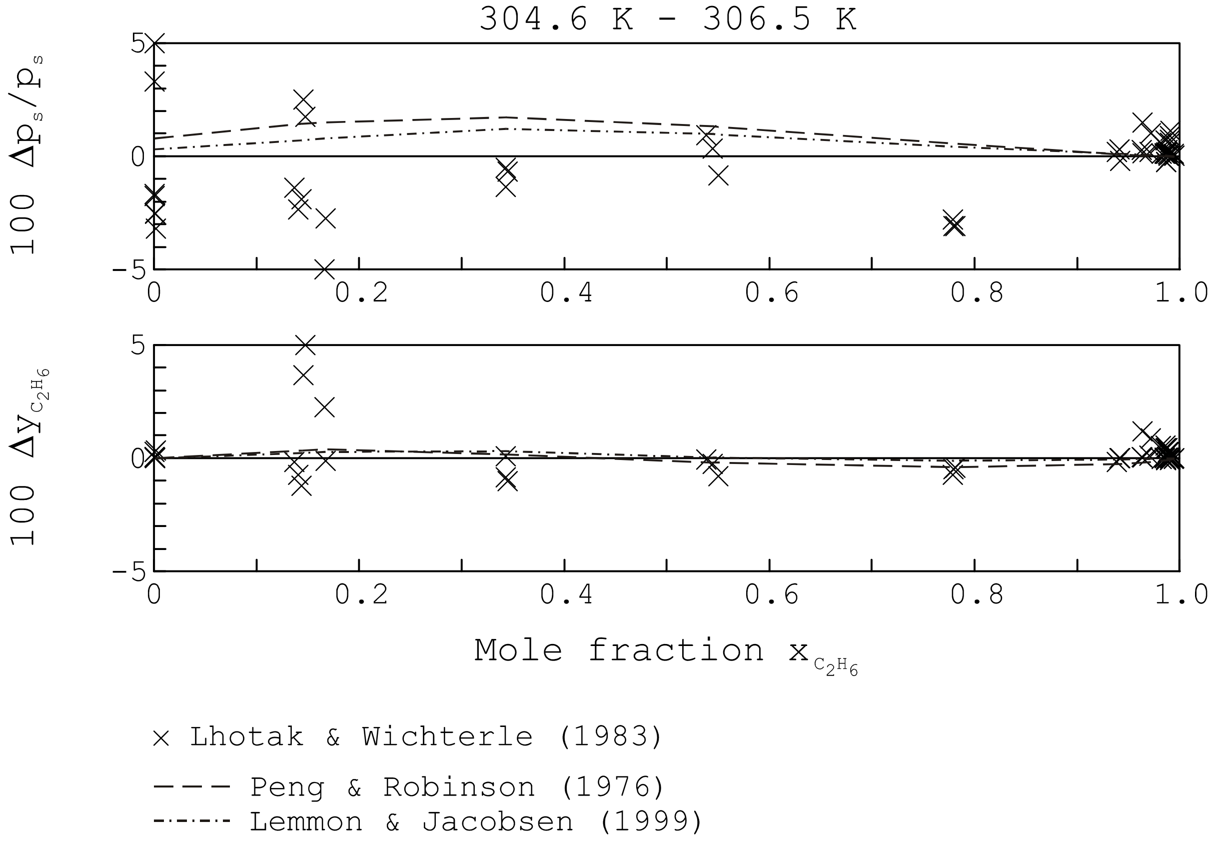

Fig. 8.77 Representation of the experimental vapour pressures and ethane mole fractions in the saturated vapour phase measured by Lhoták and Wichterle (1983) for the ethane–propane–n-butane ternary mixture by the new equation of state (GERG-2004), Eqs. (7.1) – (7.10): $100\,\Delta p_s/p_s = 100\,(p_{s,\mathrm{exp}} - p_{s,\mathrm{calc}})/p_{s,\mathrm{exp}}$, $100\,\Delta y_{C_2H_6} = 100\,(y_{C_2H_6,\mathrm{exp}} - y_{C_2H_6,\mathrm{calc}})$. Values calculated from the mixture model of Lemmon and Jacobsen (1999) and the cubic equation of state of Peng and Robinson (1976) are plotted for comparison at a temperature of 305 K.

pure ethane. Most of the measured vapour pressures are represented by the new equation of state to within deviations of ±(1 – 3)%. The smallest deviations are observed in the vicinity of pure ethane, while the scatter in the deviations increases towards lower ethane concentrations. The simultaneously measured vapour phase compositions are accurately described as well. As shown for the ethane fractions, most of the data are within ±(0.5 – 1) mole-%. The mixture model of Lemmon and Jacobsen (1999) as well as the cubic equation of Peng and Robinson (1976) yield quite similar results in the representation of the experimental vapour phase compositions. For vapour pressures, a slightly different but still acceptable description is observed.

Multi-Component Mixtures of Hydrocarbons from Ethane to n-Hexane

A number of accurate VLE measurements on mixtures of hydrocarbons from ethane through n-hexane, related to the design of depropanisers (depropanisation is a continuous distillation process), were reported by VonNiederhausern and Giles (2001). The measurements were performed on the binary mixtures propane–n-butane and propane–isobutane (see also Figs. 8.32 – 8.34), and three multi-component mixtures (a ternary mixture of propane, n-butane, and isobutane, a four-component mixture of ethane, propane, n-butane, and isobutane, and a five-component mixture of propane, n-butane, isobutane, n-pentane, and n-hexane). Although the authors only measured one data point at a defined temperature and pressure (and overall mixture composition) for each multi-component system, the data provide accurate and valuable information for testing the quality of the new equation of state in flash operations for multi-component hydrocarbon mixtures. Table 8.5 lists the results of the *pTxy* measurements of VonNiederhausern and Giles (2001) on the four- and five-component mixtures and the values calculated from the GERG-2004 formulation using the flash program of the software package developed in this work (see Secs. 7.6 and 7.14). The deviations between the experimentally determined and the calculated liquid and vapour molar compositions are small (in general much less than ±1 mole-%).

Table 8.5 Comparisons between the VLE measurements of VonNiederhausern and Giles (2001) on two multi-component hydrocarbon mixtures and values calculated from the GERG-2004 formulation

Component	Experimental overall and phase compositions (mole fractions)			Calculated phase compositions and total differences (mole fractions)[a]			
i	x_i	$x'_{i,\mathrm{exp}}$	$x''_{i,\mathrm{exp}}$	$x'_{i,\mathrm{calc}}$	$x''_{i,\mathrm{calc}}$	$\Delta x'_i$	$\Delta x''_i$
			Four-component mixture at 322.04 K and 1.713 MPa				
Ethane	0.02	0.0197	0.0467	0.0193	0.0458	0.0004	0.0009
Propane	0.96	0.9567	0.9423	0.9604	0.9448	−0.0037	−0.0025
n-Butane	0.01	0.0112	0.00461	0.0102	0.00424	0.0010	0.00037
Isobutane	0.01	0.0124	0.00639	0.0101	0.00511	0.0023	0.00128
			Five-component mixture at 366.48 K and 1.039 MPa				
Propane	0.01	0.0089	0.0229	0.0089	0.0240	0.0000	−0.0011
n-Butane	0.50	0.5008	0.6032	0.4927	0.5921	0.0081	0.0111
Isobutane	0.15	0.1436	0.2169	0.1444	0.2206	−0.0008	−0.0037
n-Pentane	0.20	0.2061	0.1159	0.2063	0.1200	−0.0002	−0.0041
n-Hexane	0.14	0.1406	0.0411	0.1477	0.0433	−0.0071	−0.0022

[a] The total mole fraction differences are calculated as $\Delta x'_i = x'_{i,\mathrm{exp}} - x'_{i,\mathrm{calc}}$ and $\Delta x''_i = x''_{i,\mathrm{exp}} - x''_{i,\mathrm{calc}}$.

Nitrogen–Oxygen–Argon

A huge amount of (comparatively) accurate *pTxy* measurements exists for the ternary system nitrogen–oxygen–argon. The accurate description of the VLE behaviour of this system is of great importance for the design of air separation plants. Figures 8.78 and 8.79 display comparisons between various measurements of several authors covering a wide range of

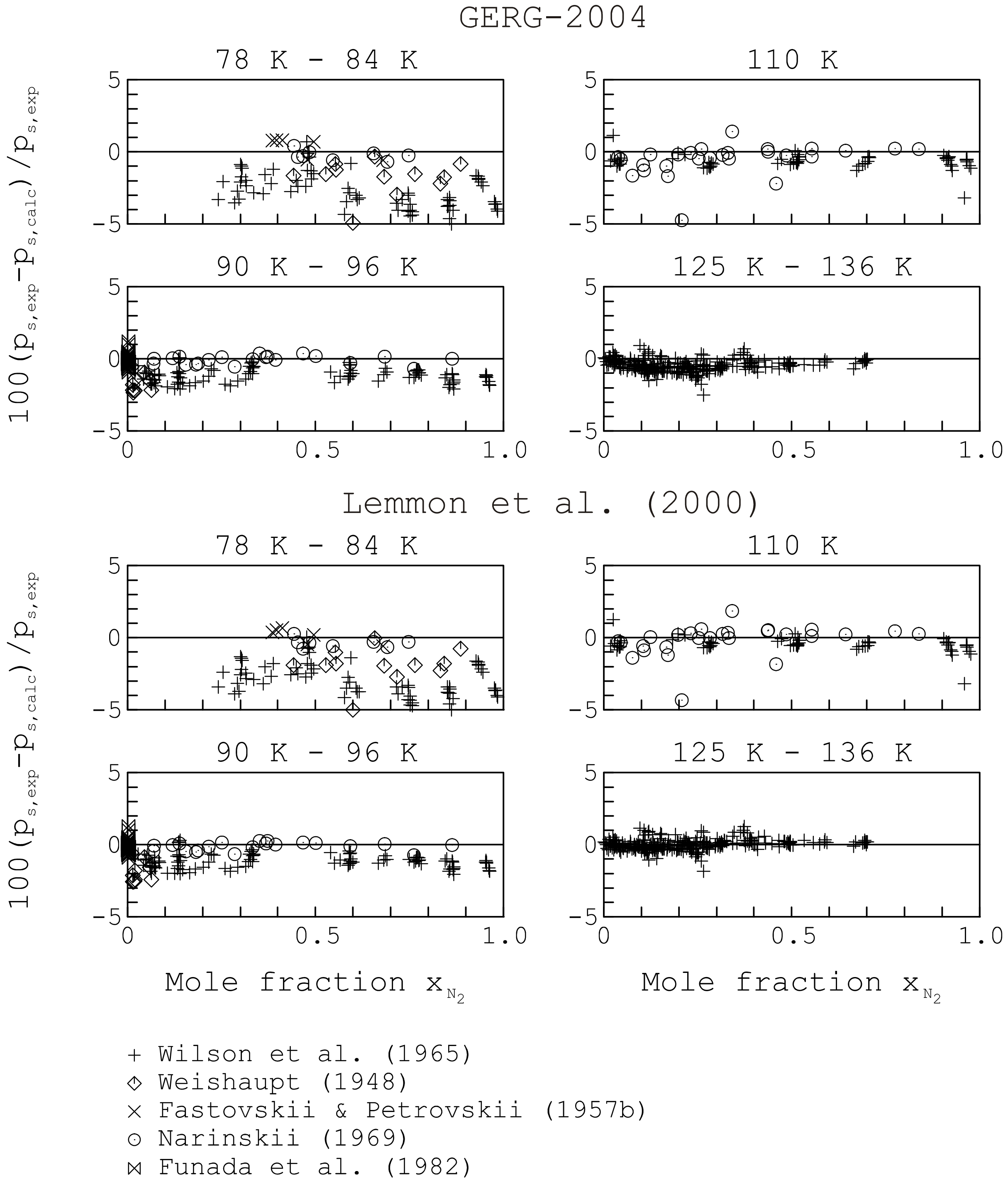

Fig. 8.78 Percentage deviations of selected experimental vapour pressures for the nitrogen–oxygen–argon ternary mixture from values calculated from the new equation of state (GERG-2004), Eqs. (7.1) – (7.10), and the mixture model of Lemmon *et al.* (2000).

mixture conditions in the temperature range from 78 K to 136 K and values calculated from the GERG-2004 formulation as well as the multi-fluid mixture model of Lemmon *et al.* (2000). For vapour pressures, a comparatively large scatter in the deviations is observed for the lower temperatures from 78 K to 84 K. In this range, the GERG-2004 formulation represents the measurements to within deviations of ±(1 – 5)%. At higher temperatures, most

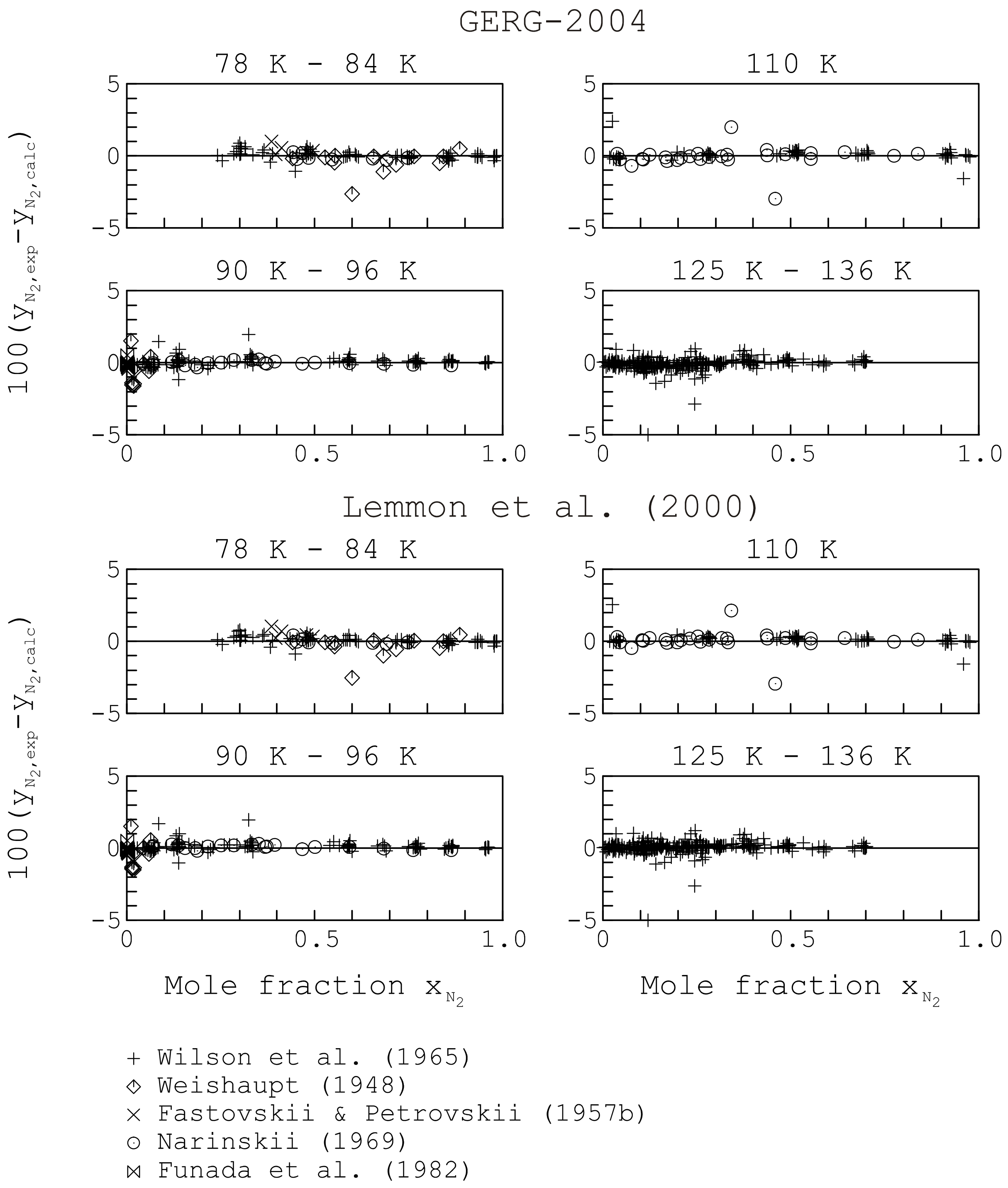

Fig. 8.79 Deviations of selected experimental nitrogen mole fractions in the saturated vapour phase for the nitrogen–oxygen–argon ternary mixture from values calculated from the new equation of state (GERG-2004), Eqs. (7.1) – (7.10), and the mixture model of Lemmon *et al.* (2000).

of the vapour pressures are represented to within ±(1 – 2)%. The simultaneously measured vapour phase compositions are, however, accurately described over the complete temperature range. Most of the data are represented by the new mixture model with deviations of clearly less than ±(0.5 – 1) mole-%.

The description achieved by the new equation of state is supported by the results obtained from the multi-fluid mixture model of Lemmon *et al.* (2000). As mentioned before, this model uses a generalised departure function in addition to the adjusted reducing functions for density and temperature. However, the model achieves a quite similar accurate description compared to the GERG-2004 formulation. Noticeable but minor differences are only observed for the measured vapour pressures in the critical region of the ternary system. In the temperature range from 125 K to 136 K, the model of Lemmon *et al.* (2000) yields a slightly different and perhaps more accurate representation for the vapour pressures of Wilson *et al.* (1965) as shown in Fig. 8.78. However, since these data do not seem to be the most accurate values available for this system, as shown from the comparisons for subcritical temperatures, the achieved description of the new equation of state is very satisfactory. Moreover, virtually no differences are obtained in the description of the vapour phase compositions as demonstrated for the deviations in the experimentally determined nitrogen fractions. Note that the cubic equation of state of Peng and Robinson (1976) is clearly less accurate in the description of the *pTxy* relation of nitrogen–oxygen–argon than the two multi-fluid mixture models (not shown here; see also the statistical comparisons in Table A2.4 of the appendix).

8.5 General Conclusions of the Comparisons for Binary and Multi-Component Mixtures

As underlined by the comparisons and discussions above, the new equation of state clearly satisfies the requirements on the accuracy and range of validity defined prior to its development (see Chap. 3). The new mixture model achieves a very accurate description of the thermal and caloric properties of natural gases, similar gases, and other multi-component mixtures, as well as of their constituent binaries over a much wider range of temperatures, pressures, and compositions than any of the previously developed equations of state.

The statements on the range of validity as well as the conservative uncertainty estimations for the different thermodynamic properties given in Sec. 7.13, are based on detailed graphical comparisons with all available experimental data (see Chap. 6). The following passages briefly summarise the main conclusions that follow from the above selected comparisons.

Binary Mixtures

Substantial improvements are achieved by the new mixture model, for example, in the description of gas phase densities and speeds of sound (including gas-like supercritical states), of binary mixtures consisting of methane and further important natural gas components. Very accurate experimental gas phase densities and speeds of sound are represented by the GERG-2004 formulation to within their low experimental uncertainty of less than (0.05 – 0.1)% in density and speed of sound. The new equation of state achieves a very accurate description of these properties over a much wider range of temperatures, pressures, and compositions than any of the previously developed equations, including the AGA8-DC92 equation of state of Starling and Savidge (1992) and the multi-fluid mixture model of Lemmon and Jacobsen (1999). Accurate experimental gas phase enthalpy differences are represented by the new equation of state to within deviations of ±(0.2 – 0.5)%, which is in agreement with the experimental uncertainty of the measurements.

The GERG-2004 formulation accurately represents the properties in the liquid phase and liquid-like supercritical region. Typical deviations between experimental compressed liquid densities and values calculated from the new mixture model are within ±(0.1 – 0.2)% (e.g. methane–nitrogen, methane–ethane, ethane–propane, and binary mixtures of propane, n-butane, and isobutane), or ±(0.1 – 0.3)% (e.g. n-pentane–n-hexane, n-hexane–n-heptane), or ±(0.1 – 0.5)% (e.g. n-pentane–n-heptane). In general, the deviations obtained from the mixture model developed in this work are smaller than those from the model of Lemmon and Jacobsen (1999). Isobaric and isochoric heat capacities are well represented by the new model to within ±(1 – 2)% in the homogeneous gas, liquid, and supercritical regions.

The vapour-liquid phase equilibrium is accurately described as well. It is interesting to note that the deviations observed for saturated liquid densities are very consistent to those obtained for compressed liquid densities. The achieved description for the *pTxy* relation is in agreement with the experimental uncertainty of the measurements (being often of comparatively poor quality). Accurate vapour pressure data for binary mixtures consisting of the main natural gas components or light hydrocarbons are represented to within ±(1 – 2)%. However, frequently a scatter in the measurements of ±(1 – 3)% or more can be observed. Typical deviations between the simultaneously measured vapour phase compositions and values calculated from the GERG-2004 formulation are within ±(0.5 – 1) mole-% or ±(1 – 2) mole-% depending on the accuracy of the corresponding measurements.

The new equation of state not only accurately represents the properties of binary mixtures of the main natural gas components or binary hydrocarbon mixtures, but also many binary mixtures containing the secondary natural gas components hydrogen, oxygen, carbon monoxide, water, helium, and argon.

Multi-Component Mixtures

The GERG-2004 formulation fulfils the high demands on the accuracy in the description of thermal and caloric properties of natural gases and related mixtures in the custody transfer region. Important improvements compared to the AGA8-DC92 equation of state are particularly achieved for temperatures below 290 K as well as for mixtures of unusual composition. Thus, the known weaknesses of the current internationally accepted standard for this region are eliminated by the new development.

In contrast to the AGA8-DC92 equation of state, the GERG-2004 formulation is valid (and yields very accurate results) in the extended fluid region (homogeneous gas, liquid, and supercritical regions, and vapour-liquid equilibrium states). Additionally, the new equation of state is able to represent the available most accurate experimental data for gas phase and gas-like supercritical densities, speeds of sound, and enthalpy differences mostly to within their low experimental uncertainty, which is not true for the AGA8-DC92 equation of state. Accurate experimental gas phase densities for a broad variety of natural gases and related mixtures are represented by the GERG-2004 formulation to within ±(0.05 – 0.1)% for temperatures down to 250 K and at pressures up to 30 MPa. The same is observed for gas phase speeds of sound covering temperatures from 250 K to 350 K at pressures up to 11 MPa. Accurate experimental enthalpy differences covering almost the same temperature range at pressures up to 17 MPa are mostly represented by the new equation of state to within ±(0.2 – 0.5)%. Accurate experimental gas phase densities of rich natural gases are in general described with deviations of less than ±(0.1 – 0.3)% over a wide temperature range and at pressures up to 30 MPa. In addition to that, and as obtained for binary mixtures, isobaric heat capacities of natural gases and other multi-component mixtures are well represented to within ±(1 – 2)%, which is in agreement with the experimental uncertainty of the available data.

All in all, compared to the AGA8-DC92 equation of state, the GERG-2004 formulation achieves important and fundamental improvements in the description of gas phase and gas-like supercritical densities of natural gas mixtures containing

- high fractions of nitrogen,
- high fractions of carbon dioxide,
- high fractions of ethane,
- substantial amounts of ethane, propane, and heavier hydrocarbons,
- high fractions of hydrogen,
- considerable amounts of carbon monoxide, and
- noticeable fractions of oxygen.

The new equation of state is much more accurate for rich natural gases and in the description of all caloric properties.

The new multi-fluid mixture model also satisfies the 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. The GERG-2004 formulation well represents accurate experimental saturated liquid densities to within ±(0.1 – 0.5)%, being on average about 50 times more accurate than results obtained from ordinary cubic equations of state. A comparable and very accurate description can be expected for compressed liquid densities of natural gas mixtures due to the small pressure dependence of the $p\rho T$ relation in the temperature range from 100 K to 140 K. This assumption is supported by the very accurate description achieved for compressed liquid densities of important binary mixtures such as methane–nitrogen and methane–ethane. Moreover, experimental liquid phase densities of ternary mixtures consisting of natural gas main constituents or only hydrocarbons are accurately described as well. For many cases, the deviations obtained from the new mixture model are smaller than those from the model of Lemmon and Jacobsen (1999).

For liquid phase isobaric and isochoric heat capacities, a similar accurate description as that for binary mixtures can also be expected for multi-component mixtures. Experimental liquid phase isobaric enthalpy differences are represented to within ±(0.5 – 1)%.

For vapour pressures and vapour phase compositions of multi-component mixtures, a similar accurate description as that for binary mixtures is achieved by the GERG-2004 formulation. Accurate vapour pressures are represented to within ±(1 – 3)% and vapour phase compositions to within ±(1 – 2) mole-%. The achieved description is supported by the results obtained from the still widely applied cubic equation of state of Peng and Robinson (1976). Cubic equations generally achieve a quiet accurate description of (only) the $pTxy$ relation of mixtures. In general, the new equation of state yields similar or even more accurate results as shown in the comparisons.

General Comments

Due to the basic structure of the new multi-fluid mixture model, the representation of multi-component mixture data is based on the description of thermal and caloric properties of binary mixtures. Thus, the model only considers the binary interactions of the molecules in the multi-component mixture. This restriction, mostly resulting from the limited data situation, obviously does not affect the accuracy in the description of multi-component mixtures, implying that ternary and higher order interactions between molecules in the mixture are negligible for the components considered in the developed model (this is confirmed by comparisons with ternary and quaternary data). For an accurate description of the properties of multi-component mixtures, the development of accurate equations for the constituent binaries is necessary and sufficient.

In general, the quality and the extent of the available experimental data limit the achievable accuracy of any empirical equation of state. Many of the improvements achieved in this work are due to the use of recently measured accurate experimental data. However, the structure of the mixture model is also of considerable importance for the accurate description of binary and multi-component mixtures. Thus, aside from the use of suitable flexible and thus very efficient reducing functions for density and temperature, the development of binary specific departure functions is indispensable to represent the most accurate binary data to within their low experimental uncertainty. Generalised departure functions allow an improved description of binary mixtures characterised by limited data. The combined strategy pursued in this work proved to be clearly superior to the one of Lemmon and Jacobsen (1999) using a single generalised departure function for all considered binary mixtures. However, their work provided a foundation from which this work was able to build on, and a basis on which the new model could be compared to in order to supersede it with increased accuracies and a more fundamental functional form.

9 Outlook and Future Challenges

The new equation of state for thermal and caloric properties of natural gases, similar gases, and other mixtures developed in this work fulfils all of the requirements defined prior to its development as shown by the comparisons presented in the previous chapter (see also Chap. 3). However, based on experiences gained during this work, it is worthwhile to discuss the further extension of the current mixture model as well as the corresponding property calculation software. Some of the main ideas and recommendations, including those mentioned at several places in the previous chapters, will be summarised in the following passages.

Extension to Further Components

One of the main recommendations concerns the extension of the developed multi-fluid mixture model to further components. As mentioned before, the structure of the new equation of state basically allows for an extension to any arbitrary number of components without affecting the representation of mixtures consisting of the 18 natural gas components already considered.

Table 9.1 List of available accurate technical equations of state for selected further components[a]

Pure substance	Reference	Range of validity Temperature T/K	 Pressure $p_{\max}$/MPa	Number of terms
Further important components				
n-Nonane	Lemmon & Span (2006)	219 – 575	800	12
n-Decane	Lemmon & Span (2006)	243 – 675	800	12
Hydrogen sulphide	Lemmon & Span (2006)	187 – 760	170	12
Further optional components				
Ethylene	Span & Wagner (2003b)	104 – 473	100	12
Cyclohexane	Span & Wagner (2003b)	279 – 473	100	12
Toluene	Lemmon & Span (2006)	178 – 700	500	12
n-Dodecane	Lemmon & Huber (2004)	263 – 700	500	12
Sulphur dioxide	Lemmon & Span (2006)	197 – 523	35	12

[a] See the literature for further technical and also reference quality equations of state.

Aside from the extension of the new equation of state to the heavier hydrocarbons n-nonane and n-decane, the implementation of hydrogen sulphide is of particular interest. Hydrogen sulphide is important in the processing of raw natural gases and the injection of acid gases (mainly consisting of carbon dioxide and hydrogen sulphide) into deep saline aquifers and depleted hydrocarbon reservoirs driven by the need to dispose of hydrogen sulphide produced with natural gas from sour gas reservoirs (see also Chap. 3). These processes occur over a wide range of mixture compositions and operating conditions, frequently requiring the separation of one or more components from the mixture. Furthermore, natural gases may also contain small amounts of ethylene, propylene, benzene, and toluene. To inhibit the undesired formation of gas hydrates (hydrocarbon ice) that can lead to blockage of transport pipelines, alcohols such as methanol and monoethylene glycol are commonly used as an anti-freeze added to the wellstream. Fortunately, accurate technical equations of state in the form of fundamental equations well fitting to the currently pursued structure of the multi-fluid mixture model are available for a number of these components and are listed in Table 9.1.

Aside from the pure substance equations of state, binary data are required to (at least) fit the parameters of the reducing functions for density and temperature. However, the representation of mixtures with limited or poor data can be taken into account by only using different combining rules for the critical parameters of the components without any fitting (see Sec. 5.2). For binary mixtures consisting of the current 18 components and n-nonane, n-decane, and hydrogen sulphide, a comprehensive data set of more than 15,000 data points has been compiled within the framework of this work. Preliminary investigations have shown that there are a number of data available for binary mixtures containing one of the 18 considered components with ethylene, propylene, benzene, or toluene.

Extension of the Mixture Model to User-Definable (Pseudo-)Components

In addition to the number of considered distinct and well defined mixture components, the implementation of one or more pseudo-components that can be individually defined by the user seems to be worthwhile. Such a development is relevant for many applications in the chemical and petrochemical industry. Uncommon mixture constituents and heavy hydrocarbons, which have a great influence on the phase behaviour of natural gases even when only present in very small amounts, can be handled in this way.

For this development, a generalised equation of state in the form of fundamental equations with substance specific (adjustable) parameters is required which can be used like a usual substance specific equation of state. Such an equation was developed by Span (2000b) and can be expressed as follows:

$$\frac{a(\rho,T)}{RT} = \alpha^{\mathrm{o}}(\rho,T) + \alpha^{\mathrm{r}}(\delta,\tau) = \alpha^{\mathrm{o}}(\rho,T) + \sum_{i=1}^{5} n_i\,\delta^{d_i}\tau^{t_i} + \sum_{i=6}^{10} n_i\,\delta^{d_i}\tau^{t_i} e^{-\delta^{p_i}} \tag{9.1}$$

with

$$n_i = c_{1,i} + c_{2,i}\,w + c_{3,i}\,w^4, \quad \delta = \rho/\rho_{\mathrm{r}}, \quad \text{and} \quad \tau = T_{\mathrm{r}}/T. \tag{9.2}$$

In Eq. (9.2), ρ_r, T_r, and w are substance dependent adjustable parameters. The structure of the equation for α^r in Eq. (9.1) was determined by the simultaneous optimisation method (see Sec. 4.5) considering data sets for 13 non- and weakly polar substances. The generalised coefficients $c_{j,i}$ in Eq. (9.1) were determined by a fit to data sets for methane, ethane, propane, n-butane, isobutane, n-pentane, n-hexane, n-heptane, n-octane, oxygen, and argon. The values for the exponents d_i, t_i, and p_i, and the coefficients $c_{j,i}$ are tabulated in Span (2000b). With these parameters, Eq. (9.1) becomes an empirical three parameter equation of state for nonpolar fluids.

To specify a pseudo-component, values for ρ_r (an approximate critical density), T_r (an approximate critical temperature), and w (an approximate acentric factor) are required. Normally, these parameters can be fitted to experimental data to compensate for the limited accuracy of this kind of corresponding states approach. Due to the numerically very stable simultaneously optimised functional form of the three parameter approach, a very small number of accurate experimental results is sufficient to adjust the substance specific parameters and to obtain equations of state yielding satisfyingly accurate results for a variety of substances. When data are not available, the critical density ρ_c, the critical temperature T_c, and the acentric factor ω can be used for ρ_r, T_r, and w. Whether the limited accuracy of this corresponding states approach, without fitting the parameters to experimental data, is sufficient to obtain at least reasonably accurate results for the properties of the desired substance and those for mixtures containing small amounts of such a component remains still to be investigated.

Development of Further Binary Departure Functions

The present mixture model uses equations of state in the form of fundamental equations for each considered mixture component along with binary correlation equations to take the residual mixture behaviour into account. Most of the binary mixtures are represented only by using adjusted reducing functions for density and temperature. Binary specific and generalised departure functions were additionally developed for binary mixtures consisting of important main and secondary natural gas components (see Sec. 7.10). This approach enabled a very accurate description of the properties of various types of natural gases, similar gases, and other mixtures in over wide range of mixture conditions (temperature, pressure, and composition) as underlined by the comparisons presented in the preceding chapter. Potential further improvements were identified during the development of the new equation of state, also resulting from very recent data or other data that were not available at the time the mixture model was developed.

A very accurate description of the thermal and caloric properties of binary mixtures is achieved by the use of binary specific departure functions. Such a development, however, requires a sufficiently comprehensive and comparatively accurate data set. Since this precondition is not fulfilled for most of the considered binary systems, aside from the measurement of mixture properties where data are currently not available, potential improvements can be achieved by the development of further generalised departure functions. Based on experiences gained during this work, it seems to be worthwhile to develop different generalised departure functions for the following groups of (somehow) related binary mixtures:

- Binary mixtures of the air components nitrogen, oxygen, and argon (i.e. nitrogen–oxygen, nitrogen–argon, and oxygen–argon).
- Binary mixtures of carbon dioxide with the hydrocarbons ethane, propane, n-butane, etc.
- Binary hydrocarbon mixtures consisting of or containing the heavier hydrocarbons from n-pentane to n-octane.
- Binary mixtures containing helium (e.g. nitrogen–helium, carbon dioxide–helium, and helium–argon).

Although the developed mixture model already yields a fairly accurate description of the thermal and caloric properties of (dry) air by using only adjusted reducing functions for density and temperature[87], investigations have shown that a very accurate description of densities and speeds of sound similar to that achieved for natural gases can be obtained by developing a short generalised departure function for the binary mixtures of the main air constituents nitrogen, oxygen, and argon. Such a development would offer the opportunity to calculate the thermal and caloric properties of natural gases and air very accurately in the homogeneous gas, liquid, and supercritical regions, as well as for vapour-liquid equilibrium states using a single and consistent mixture model. The most accurate and wide-ranging equations of state for air and mixture of nitrogen, oxygen, and argon were developed by Lemmon et al. (2000)[88]. The accuracy of these equations is superior to the one achieved by the mixture model developed in this work in particular for gas and liquid phase densities and speeds of sound, being represented to within ±0.1% for densities and within ±0.2% for speeds of sound in the homogeneous gas, liquid, and supercritical regions. Compared to these equations, a quite similar accurate description is obtained from the new mixture model for

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[87] The uncertainty of the mixture model in gas phase and gas-like supercritical densities for air is less than (0.1 – 0.2)% for temperatures up to 900 K and pressures to 90 MPa, and less than (0.2 – 0.5)% in liquid phase and liquid-like supercritical densities for temperatures down to 60 K. For the speed of sound, similar uncertainties are estimated. The uncertainty in isobaric and isochoric heat capacity is estimated to be less than (1 – 2)% in the homogeneous gas, liquid, and supercritical regions.

[88] The authors actually published two equations. An equation of state in the form of a fundamental equation treating ternary air as a pseudo pure component with a fixed composition (which does not allow for the calculation of saturation properties needed in separation processes), and a multi-fluid mixture model using adjusted reducing functions for density and temperature along with a generalised two-term departure function for the constituent binaries.

isobaric and isochoric heat capacities, and for the *pTxy* relation as demonstrated in Secs. 8.3.2 and 8.4.5.

As mentioned in Sec. 8.4.1, potential further improvements might be achievable for the description of the $p\rho T$ relation of rich natural gases containing large amounts of carbon dioxide of 14% or more. The developed mixture model achieves a very accurate description for the $p\rho T$ relation of natural gases rich in carbon dioxide as well as of synthetic natural gas mixtures containing high fractions of nitrogen, carbon dioxide, and ethane. Therefore, the higher deviations mentioned in Sec. 8.4.1 are most likely due to the comparatively large amounts of propane, n-butane, n-pentane, and n-hexane found in rich natural gases. The development of a generalised departure function for binary mixtures of carbon dioxide with these hydrocarbons seems to be worthwhile testing.

In general, data for binary hydrocarbon mixtures consisting of or containing heavier hydrocarbons is lacking. However, for certain binary hydrocarbon mixtures, a number of recently published and comparatively accurate measurements are available, covering a fairly wide range of mixture conditions. Binary hydrocarbon mixtures for which only limited experimental information is available could benefit from the development of a generalised departure function for hydrocarbon mixtures containing the heavier hydrocarbons from n-pentane to n-octane, or the extension of the existing generalised departure function for secondary alkanes to these mixtures.

Extension of the Property Calculation Software

In addition to the new mixture model, the corresponding property calculation algorithms, including the tangent-plane stability analysis and the *pT* flash and phase envelope algorithms, of the new software package can easily be extended to further components. The development of Gibbs free energy based (or rather Helmholtz free energy based) minimisation procedures according to the approaches reported by Michelsen (1999) is recommended for future extensions of the calculation software as described in Sec. 7.9. This would allow for solving other flash situations of technical relevance aside from the implemented and well-known isothermal flash calculation, such as the isenthalpic flash and the isentropic flash (see Sec. 7.9.3 and also Sec. 5.4.4).

Liquid-Liquid and Multi-Phase Equilibrium Calculations

Multi-fluid mixture models are capable of accurately describing the two-phase vapour-liquid equilibrium of binary and multi-component mixtures as shown in the various comparisons with experimental data in Chaps. 7 and 8. Individual investigations carried out in the course of this work have shown that such models are also able to predict binary and multi-component liquid-liquid equilibrium (see also Sec. 7.7.3) as well as binary and multi-component multi-phase equilibrium (tested for the vapour-liquid-liquid equilibrium). Detailed and comprehensive comparisons with experimental data and other models concerning the accuracy of this prediction remain for future work.

The development of robust and efficient multi-phase algorithms seems to be a general challenge to be taken.

10 Summary

In cooperation with 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), a new equation of state for natural gases and other mixtures was developed in this work. The new formulation is a fundamental equation explicit in the Helmholtz free energy as a function of density, temperature, and composition.

There is currently an internationally accepted standard only for the $p\rho T$ relation in the homogeneous gas region of natural gases, namely the AGA8-DC92 equation of state of Starling and Savidge (1992). Aside from the restriction to the homogeneous gas phase, the AGA8-DC92 equation of state shows significant weaknesses in the description of natural gas properties and covers only a limited temperature, pressure, and composition range [Jaeschke and Schley (1996), Klimeck *et al.* (1996), Klimeck (2000)]. Cubic equations of state, which show poor accuracy in the description of many thermodynamic properties, are commonly used in the natural gas industry for phase equilibrium calculations, with further correlation equations applied in the liquid phase, typically applicable only in the subcritical range for very limited mixture conditions. As a result of the use of individual equations for different fluid regions, there are inconsistencies in calculations when moving from one region to another and when more than one phase is involved.

The new formulation, adopted by GERG in 2004 and called GERG-2004 equation of state or GERG-2004 for short, overcomes the weaknesses and limitations of the previous equations and is valid for wide ranges of temperature, pressure, and composition and covers the gas phase, the liquid phase, the supercritical region, and vapour-liquid equilibrium states for natural gases and other mixtures consisting of the 18 components methane, nitrogen, carbon dioxide, ethane, propane, n-butane, isobutane, n-pentane, isopentane, n-hexane, n-heptane, n-octane, hydrogen, oxygen, carbon monoxide, water, helium, and argon.

The basis for the development of this fully consistent mixture model and its evaluation is the continuously updated database composed of more than 100,000 experimental data for multiple thermodynamic properties in different fluid regions. About 75% of the collected data accounts for binary mixtures and the remaining 25% accounts for multi-component mixtures, including various types of natural gases, hydrocarbon mixtures, and other mixtures. Almost 70% of the available mixture data describe the $p\rho T$ relation, more than 20% of the data are vapour-liquid equilibrium state points, and less than 10% account for caloric properties.

As a multi-fluid correlation, the new mixture model uses accurate equations of state in the form of fundamental equations for each mixture component along with several functions developed for the binary mixtures of the components that take into account the residual mixture behaviour. This allows for an accurate description of the properties of multi-component mixtures over a wide range of compositions. The different functional forms of the binary equations have been determined by using a state-of-the-art linear structure-optimisation method and nonlinear multi-property fitting techniques in an iterative procedure. Most of the binary systems for the 153 combinations resulting from the 18 components studied in this work are taken into account by using adjusted reducing functions for density and temperature. For a number of well-measured binary mixtures of important natural gas components, binary specific or generalised departure functions were additionally developed. Binary mixtures characterised by poor data, allowing for neither the development of a departure function nor the fitting of the parameters of the reducing functions, are taken into account by using different combining rules for the pure component critical parameters. This combined strategy pursued in this work proved to be clearly superior to the early model for mixtures of natural gas components developed by Lemmon and Jacobsen (1999) using a single generalised departure function for all considered binary mixtures.

Special interest has been focused on achieving physically correct behaviour along the vapour-liquid phase boundary. A new functional form was introduced in this work resulting in a fundamentally improved formulation as compared to the natural gas model developed by Klimeck (2000) that showed physically unreasonable shapes in the description of vapour-liquid equilibrium states. Equations developed here using the new terms do not show any bumps and are in the description of all thermodynamic properties superior to the equations developed by Klimeck (2000).

The GERG-2004 formulation is able to represent the most accurate experimental binary and multi-component data for gas phase and gas-like supercritical densities, speeds of sound, and enthalpy differences mostly to within their low experimental uncertainties, which is not true for the AGA8-DC92 equation of state. The new wide-range formulation achieves an accuracy never obtained before by an equation of state for mixtures. The normal range of validity covers temperatures from 90 K to 450 K and pressures up to 35 MPa. The uncertainties in gas phase density and speed of sound for a broad variety of natural gases and related mixtures are less than 0.1% over the temperature range from 250 K to 450 K at pressures up to 35 MPa. Accurate data for isobaric enthalpy differences of binary and multi-component mixtures are reproduced to within their experimental uncertainty, which is less than (0.2 – 0.5)%. In the liquid phase of many binary and multi-component mixtures, the uncertainty of the equation in density amounts to generally less than (0.1 – 0.5)%, which is again in agreement with the experimental uncertainty of the data. The vapour-liquid equilibrium of binary and multi-component mixtures, including the dew points of natural gases, is accurately described as well. For instance, accurate vapour pressure data for binary and ternary mixtures of the main natural gas constituents or of hydrocarbons are reproduced to within their experimental uncertainty, which is generally less than (1 – 3)%.

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 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 natural gas liquids 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.

Along with the new mixture model, robust and efficient property calculation routines, resulting in a comprehensive and user-friendly software package, were developed. They allow for the calculation of several single- and two-phase properties at arbitrary mixture conditions (temperature, pressure, and composition) where the prior knowledge of the number of phases is not required, including pT flash, phase envelope, dew point, and bubble point calculations without any user-provided initial estimates. The algorithms are based on modern numerical procedures using various partial derivatives to solve the set of equations for the equilibrium and secondary conditions for the unknown variables, to perform second order Gibbs free energy minimisation, and to verify the (phase) stability of the solution by means of minimising the tangent plane distance. Due to the increased complexity of the mixture model, a systematic and modular approach, where all required derivatives were analytically determined including the very sophisticated composition derivatives, was used to avoid inefficient and incorrect computer codes. Moreover, the solution to other flash situations of technical relevance, such as the isenthalpic flash and the isentropic flash, was described.

The structure of the new mixture model was kept as simple as possible to allow for the development of computing-time saving algorithms and an easy extension to further components.

With the development of the new wide-range equation of state, the final assembly of a property database with applications for natural gases and other mixtures over the entire fluid region has been accomplished. The GERG-2004 formulation should be established as a standard international reference equation for all natural gas applications where thermodynamic properties are required.

A1 Estimated Uncertainties in Calculated Density and Speed of Sound for Methane, Nitrogen, Carbon Dioxide, and Ethane

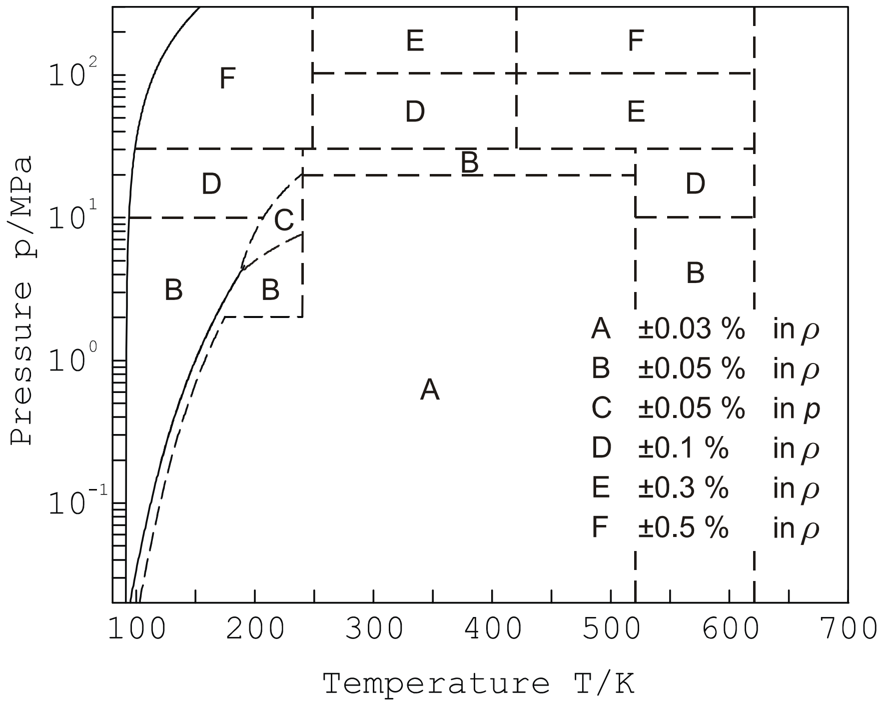

Fig. A1.1 Tolerance diagram for densities calculated from the new equation of state for methane, see Sec. 4.8. For region C, the uncertainty in pressure is given.

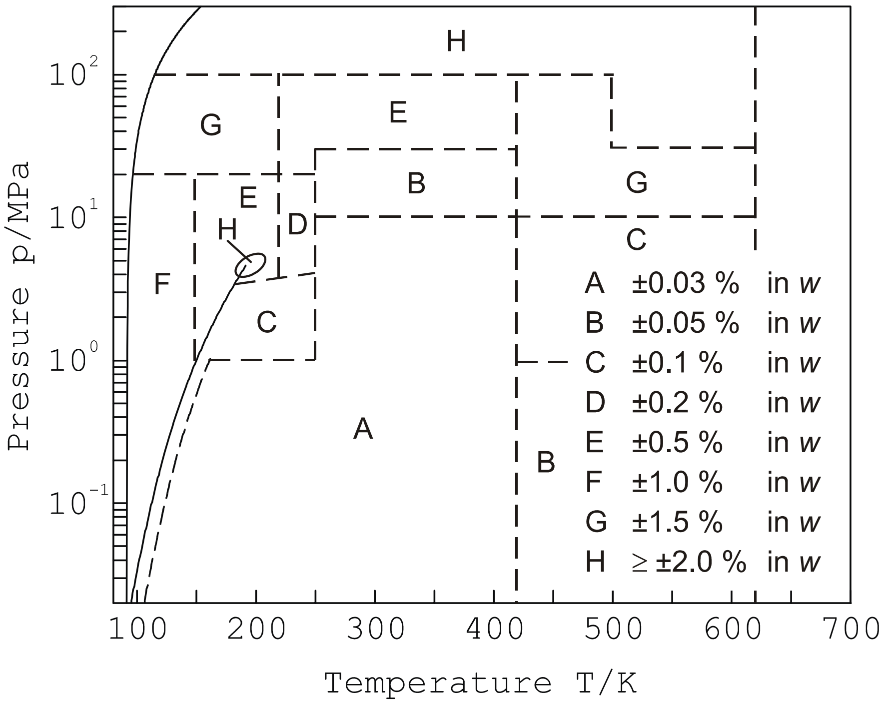

Fig. A1.2 Tolerance diagram for speed of sound data calculated from the new equation of state for methane, see Sec. 4.8.

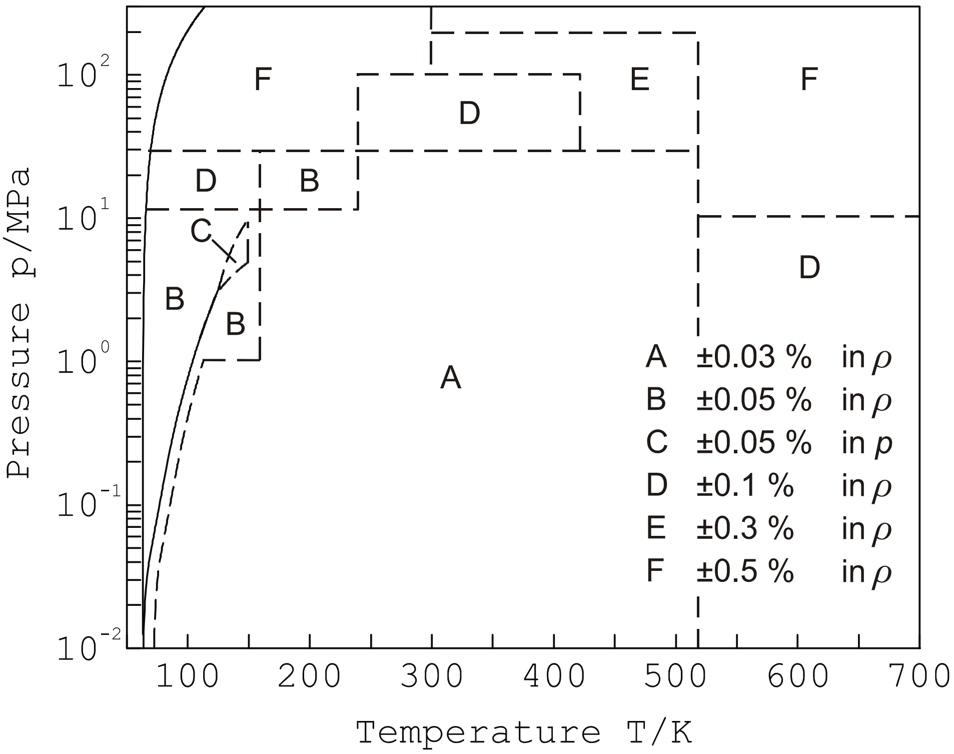

Fig. A1.3 Tolerance diagram for densities calculated from the new equation of state for nitrogen, see Sec. 4.8. For region C, the uncertainty in pressure is given.

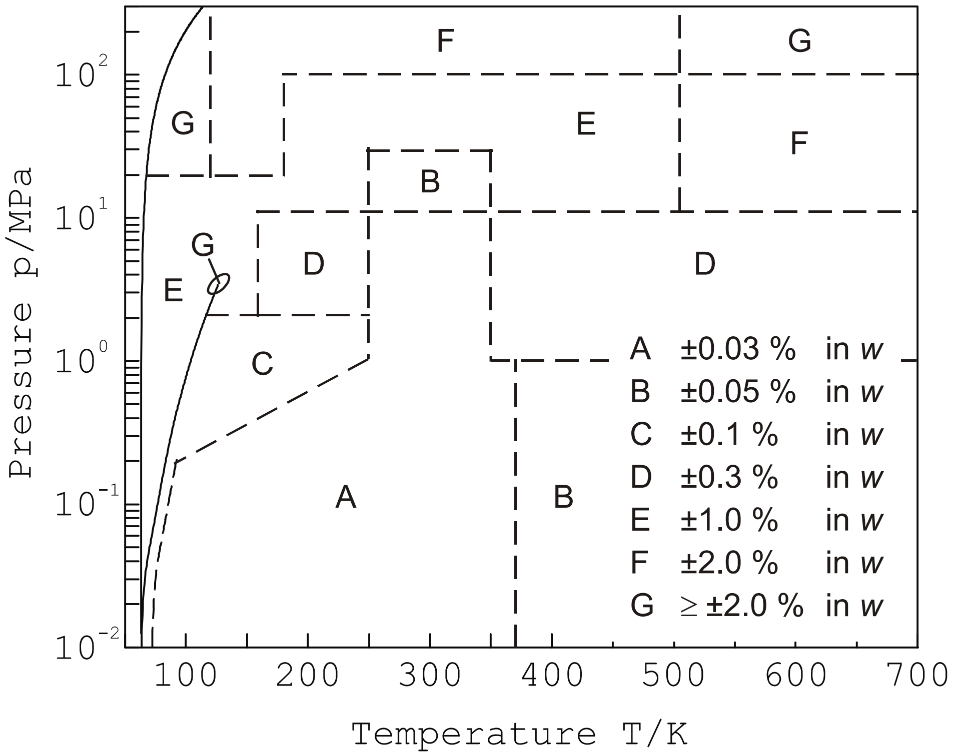

Fig. A1.4 Tolerance diagram for speed of sound data calculated from the new equation of state for nitrogen, see Sec. 4.8.

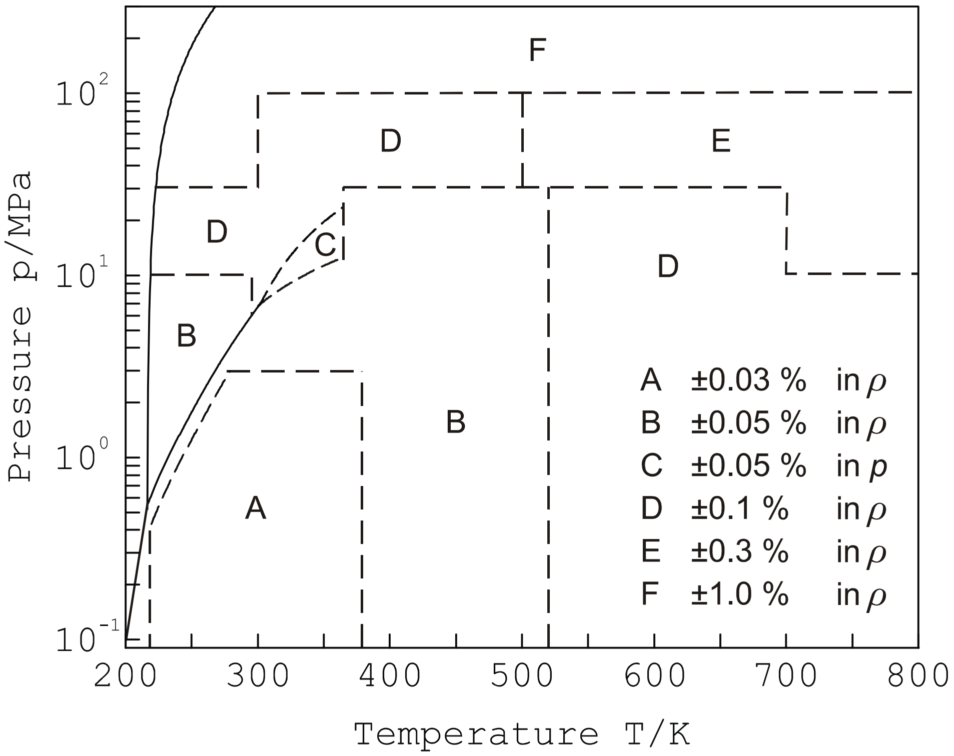

Fig. A1.5 Tolerance diagram for densities calculated from the new equation of state for carbon dioxide, see Sec. 4.8. For region C, the uncertainty in pressure is given.

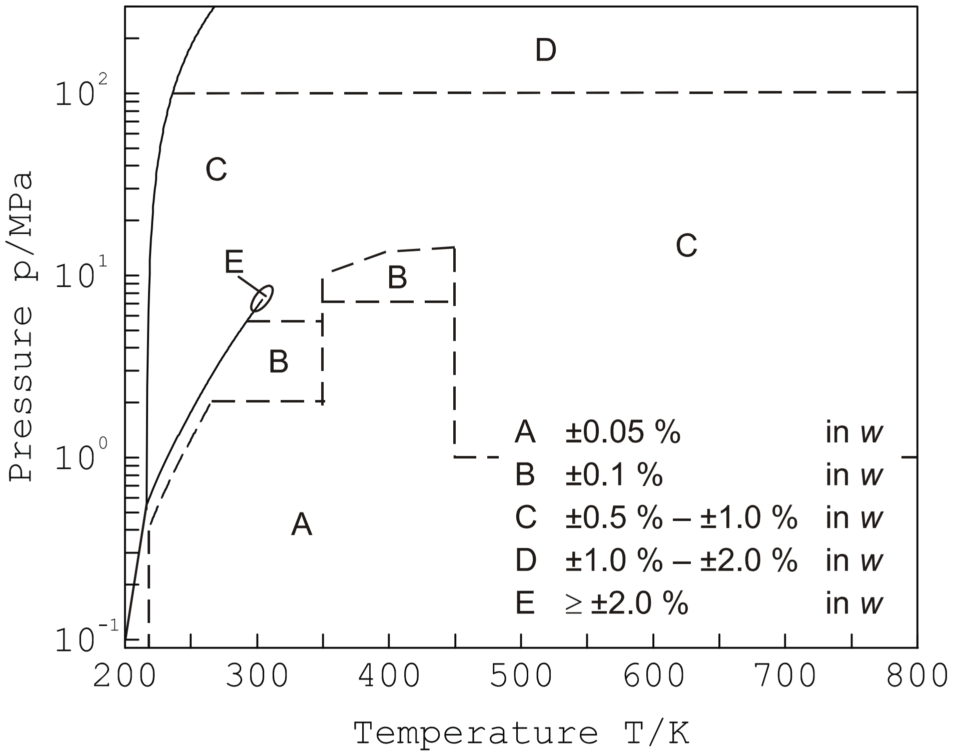

Fig. A1.6 Tolerance diagram for speed of sound data calculated from the new equation of state for carbon dioxide, see Sec. 4.8.

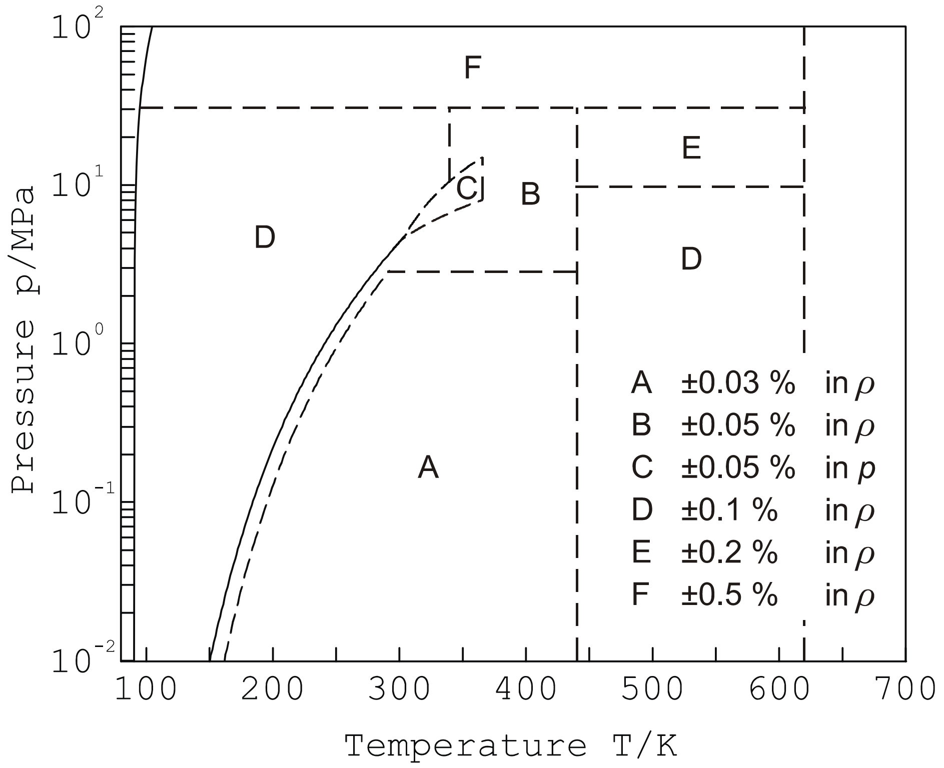

Fig. A1.7 Tolerance diagram for densities calculated from the new equation of state for ethane, see Sec. 4.8. For region C, the uncertainty in pressure is given.

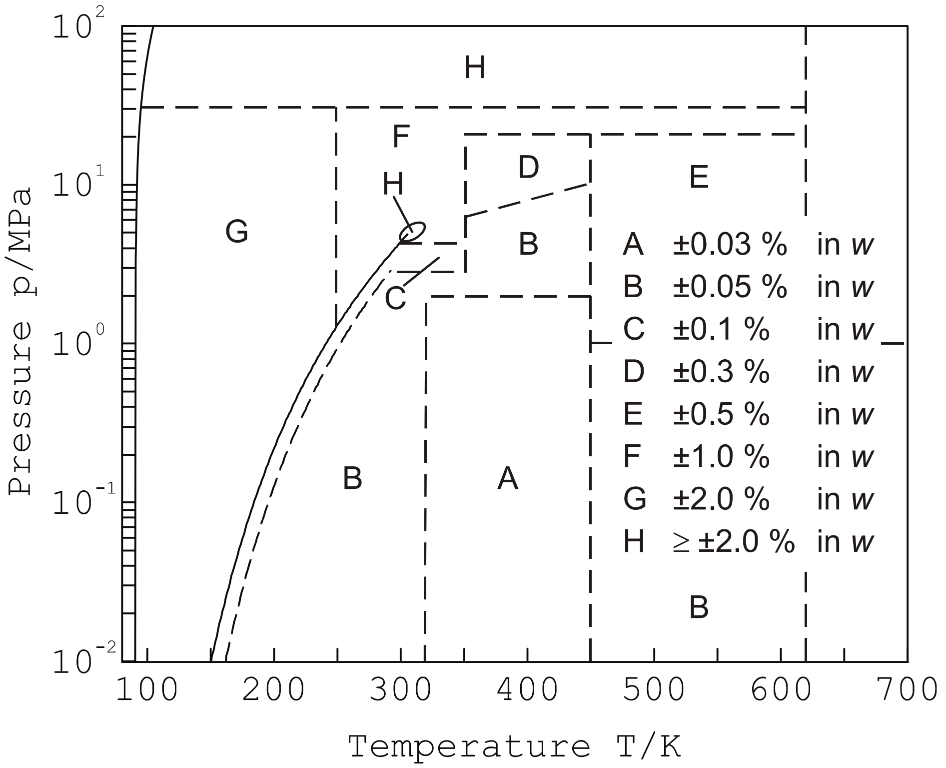

Fig. A1.8 Tolerance diagram for speed of sound data calculated from the new equation of state for ethane, see Sec. 4.8.

A2 Data Sets for Binary and Multi-Component Mixtures and Statistical Analysis

The data presented in Chap. 6 were used to assess the accuracy of the mixture model developed in this work. The accuracies of calculated values of various properties are determined by comparing them to measured values. Graphical deviation plots illustrate these comparisons and demonstrate random errors and relative consistency among different experimental data as shown in Chap. 8 for a number of selected examples for binary and multi-component mixtures. Statistical analyses of all of the collected data sets (used for either fitting the parameters and optimising the structure of the different binary equations or only for comparison) are used to determine the overall estimated accuracy of the mixture model and to define the ranges of estimated accuracies for various properties calculated with the new formulation (see Sec. 7.13). To compare the results, statistical analyses using the AGA8-DC92 equation of state of Starling and Savidge (1992) and the cubic equation of state of Peng and Robinson (1976) are provided additionally where possible[1].

The definitions of the statistics used to evaluate an equation are based on the percent deviation for any property *z*:

$$\Delta z_m = \left[\frac{z_{\mathrm{exp}} - z_{\mathrm{calc}}}{z_{\mathrm{exp}}}\right]_m . \tag{A2.1}$$

According to this definition, the statistics are defined as:

$$\mathrm{AAD} = \frac{1}{M}\sum_{m=1}^{M}\left|\Delta z_m\right|, \tag{A2.2}$$

$$\mathrm{Bias} = \frac{1}{M}\sum_{m=1}^{M}\Delta z_m , \tag{A2.3}$$

$$\mathrm{SDV} = \sqrt{\frac{1}{M-1}\sum_{m=1}^{M}\left(\Delta z_m - \mathrm{Bias}\right)^2} , \tag{A2.4}$$

$$\mathrm{RMS} = \sqrt{\frac{1}{M}\sum_{m=1}^{M}\left(\Delta z_m\right)^2} . \tag{A2.5}$$

Equation (A2.2) defines the average absolute deviation (AAD) of a data set from property values calculated from an equation. High values of AAD indicate either a systematic or large random difference between the data and the equation. The average deviation of the data set is

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[1] The AGA8-DC92 equation of state is only valid for properties in the homogeneous gas phase and gas-like supercritical region. The cubic equation of state of Peng and Robinson (1976) is used for comparison for liquid and saturated liquid densities as well as for VLE data.

quantified by the bias value in Eq. (A2.3). Large positive or negative values of the bias indicate systematic differences between the data and the equation. The SDV from Eq. (A2.4) is the standard deviation for a data set and gives an indication of the systematic or random dispersion of the data set about the bias value. The root-mean-squared (RMS) deviation in Eq. (A2.5) provides another indication of the systematic or random dispersion of the data from the equation. When all four statistical parameters are near zero, data sets are accurately represented by an equation. Therefore, the values of these parameters should be small. For the following tabular listings and comparisons, the SDV is not included.

The label "MaxD" indicates the maximum value of Δz_m in a data set. The data points above a certain percentage can be considered as outliers ("bad" points) and are not included in the statistics, as even one very large deviation which is based upon an error in the data or a weakness in the computer program can greatly change the values of the statistics. These outliers are often typographical errors in the database or points for which the algorithm failed to find a solution (e.g. some data points claimed to be homogeneous are, however, located within the two-phase region of the equation). For this work, data points for density and speed of sound which deviate by more than 10% from the equation are classified as outliers. For isobaric and isochoric heat capacities as well as enthalpy differences, this maximum limit amounts to 20%. For VLE calculations, data points which deviate by more than 30% from the equation are considered as outliers. The algorithm for the calculation of many of these VLE points failed for various numerical reasons and, therefore, these points were not included in the statistics. Most of these points are located in the critical region or are poor data and with that provide bad initial estimates for the iterative VLE calculation. However, for individual data sets known to be very accurate, considerably lower limits were used. Therefore, along with the maximum limits, additional statistics were calculated (and analysed) for several intermediate lower limits.

Along with the statistical parameters, the tabular listings in this appendix provide detailed information on the covered temperature, pressure, and composition ranges of all data sets used for the development and evaluation of the new wide-range equation of state. Table A2.1 lists the data sets collected for thermal and caloric properties of binary mixtures consisting of the 18 natural gas components considered in this work (see Table 4.2). The data sets available for thermal and caloric properties of natural gases, similar gases, and other multi-component mixtures are provided in Table A2.2, and their compositions are listed in Table A2.3. Table A2.4 lists supplementary $p\rho T$ and VLE data for ternary and quaternary mixtures. The mixture compositions of the supplementary $p\rho T$ data are given in Table A2.5. In addition to Table 6.4, a differently ordered summary of the available data for binary mixtures is presented in Table A2.6. Table A2.7 summarises the available VLE data for binary mixtures and provides detailed information on the covered liquid and vapour phase compositions. Finally, Table A2.8 summarises the supplementary ternary and quaternary data.

Table A2.1 Data sets for thermal and caloric properties of binary mixtures used for the development and evaluation of the new equation of state (GERG-2004), Eqs. (7.1) – (7.10), and statistical analysis

Authors	Number of data points total[a]	used[b]	Temp. T/K	Covered ranges Pressure p/MPa	Compos.[c,d] x	Statistical analysis[n] N_1	N_2	AAD_1 %	AAD_2 %	Bias_1 %	Bias_2 %	RMS_1 %	RMS_2 %	MaxD_1 %	MaxD_2 %
(1 − x) CH_4 + x N_2															
***pρT* data**						**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA
Ababio *et al.* (2001)	11	–	333	1.0 – 11.5	0.22	11	11	0.096	0.096	0.010	0.007	0.108	0.107	0.173	0.168
Ababio *et al.* (2001)	11	–	308	1.3 – 10.4	0.23	11	11	0.067	0.064	0.007	0.010	0.097	0.095	0.267	0.264
Ababio *et al.* (2001)	9	–	313	2.8 – 11.1	0.25	9	9	0.069	0.070	−0.041	−0.038	0.081	0.081	−0.142	−0.140
Ababio *et al.* (2001)	10	–	308	0.6 – 10.1	0.47	10	10	0.247	0.236	0.247	0.236	0.256	0.245	0.375	0.364
Ababio *et al.* (2001)	10	–	313	1.5 – 10.9	0.49	10	10	0.168	0.183	−0.168	−0.183	0.179	0.195	−0.297	−0.320
Ababio *et al.* (2001)	12	–	323	0.9 – 11.6	0.49	12	12	0.088	0.102	−0.083	−0.099	0.113	0.128	−0.268	−0.293
Ababio *et al.* (2001)	10	–	333	2.1 – 12.0	0.49	10	10	0.101	0.120	−0.101	−0.120	0.111	0.128	−0.196	−0.208
Ababio *et al.* (2001)	10	–	333	1.7 – 11.2	0.49	10	10	0.185	0.203	−0.185	−0.203	0.191	0.210	−0.277	−0.301
Achtermann *et al.* (1986)	66	–	323	1.0 – 33.5	0.10	66	66	0.095	0.096	0.095	0.096	0.103	0.103	0.148	0.140
Achtermann *et al.* (1986)	66	–	323	1.0 – 33.5	0.50	66	66	0.085	0.060	0.085	0.060	0.087	0.061	0.117	0.079
Achtermann *et al.* (1986)	66	–	323	1.0 – 33.5	0.61	66	66	0.030	0.006	0.030	−0.004	0.031	0.007	0.049	−0.014
Achtermann *et al.* (1986)	66	–	323	1.0 – 33.5	0.75	66	66	0.035	0.067	−0.035	−0.067	0.036	0.070	−0.043	−0.085
Achtermann *et al.* (1986)	66	–	323	1.0 – 33.5	0.86	66	66	0.024	0.007	0.024	0.007	0.025	0.009	0.040	0.016
Blake *et al.* (1965)	15	–	299	35.5 – 507	0.02	15	15	0.319	0.297	0.297	0.265	0.369	0.349	0.699	0.764
Blake *et al.* (1965)	15	–	299	35.5 – 507	0.26	15	15	0.613	0.483	0.520	0.373	0.675	0.537	1.061	0.938
Blake *et al.* (1965)	16	–	299	30.4 – 507	0.50	16	16	0.575	0.313	0.575	0.313	0.678	0.400	1.129	0.767
Boomer *et al.* (1938a)	26	–	298 – 334	0.1 – 37.4	0.06	26	26	3.091	3.080	3.091	3.080	3.128	3.118	4.262	4.265
British Gas (1989)	39	–	283 – 313	1.0 – 7.0	0.50	39	39	0.018	0.027	−0.016	−0.027	0.022	0.031	−0.046	−0.061
Brugge *et al.* (1989a)	39	–	280 – 300	0.2 – 10.5	0.50	39	39	0.013	0.017	−0.009	−0.017	0.019	0.027	−0.053	−0.070
Chamorro *et al.* (2000)	95	95	250 – 400	2.0 – 19.2	0.20	95	95	0.012	0.040	0.010	0.037	0.016	0.052	0.045	0.125
Chamorro *et al.* (2006)	108	–	240 – 400	0.9 – 20.1	0.10	108	108	0.012	0.028	0.011	0.028	0.014	0.042	0.025	0.139
Chamorro *et al.* (2006)	134	–	240 – 400	2.0 – 19.2	0.20	134	134	0.008	0.040	−0.003	0.036	0.010	0.057	−0.031	0.153
Distrigaz (1989)	20	–	283 – 293	3.1 – 7.7	0.50	20	20	0.017	0.028	−0.017	−0.028	0.020	0.029	−0.044	−0.052
Gasunie (1989)	22	–	280 – 290	2.9 – 7.0	0.50	22	22	0.064	0.067	−0.038	−0.047	0.072	0.076	−0.114	−0.122
Gasunie (1990)	52	–	280 – 300	3.7 – 6.5	0.09	52	52	0.043	0.032	−0.043	−0.032	0.048	0.037	−0.083	−0.072

Table A2.1 (continued)

Authors	Number of data points total[a]	used[b]	Covered ranges Temp. T/K	Pressure p/MPa	Compos.[c,d] x	N_1	N_2	Statistical analysis[n] AAD_1 %	AAD_2 %	$Bias_1$ %	$Bias_2$ %	RMS_1 %	RMS_2 %	$MaxD_1$ %	$MaxD_2$ %
(1 − *x*) CH_4 + *x* N_2 (continued)															
***pρT* data (continued)**						**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA
Gasunie (1990)	32	–	279 – 308	3.7 – 6.3	0.20	32	32	0.044	0.032	−0.044	−0.031	0.053	0.040	−0.103	−0.089
Gasunie (1990)	33	–	280 – 308	3.7 – 6.4	0.30	33	33	0.036	0.028	−0.036	−0.028	0.047	0.039	−0.090	−0.081
Gasunie (1990)	32	–	279 – 308	3.7 – 6.4	0.50	32	32	0.046	0.056	−0.046	−0.056	0.053	0.061	−0.104	−0.110
Gaz de France (1989)	14	–	280 – 290	1.0 – 7.0	0.50	14	14	0.013	0.019	−0.010	−0.019	0.019	0.024	−0.056	−0.062
Haynes & McCarty (1983)	27	26	150 – 320	1.1 – 15.2	0.29	27	27	0.025	0.181	0.015	0.174	0.035	0.387	0.116	1.749
Haynes & McCarty (1983)	28	26	140 – 320	1.0 – 15.5	0.50	28	28	0.040	0.131	0.027	0.109	0.064	0.314	0.208	1.498
Haynes & McCarty (1983)	30	26	140 – 320	1.0 – 16.4	0.68	29	27	0.048	0.037	0.044	−0.020	0.066	0.048	0.199	−0.148
Hiza *et al.* (1977)	8	8	105 – 140	0.1 – 0.9	0.05	8	–	0.110		0.110		0.118		0.160	
Hiza *et al.* (1977)	5	5	100 – 120	0.3 – 1.0	0.30	5	–	0.095		0.095		0.097		0.134	
Hiza *et al.* (1977)	8	8	95.0 – 130	0.3 – 2.1	0.49	8	–	0.070		0.070		0.080		0.142	
Jaeschke & Hinze (1991), Bu	29	29	313 – 353	0.4 – 18.3	0.20	29	29	0.006	0.008	−0.005	−0.007	0.007	0.009	−0.016	−0.019
Jaeschke & Hinze (1991), Bu	33	33	290	0.3 – 26.1	0.50	33	33	0.017	0.008	0.015	0.002	0.019	0.009	0.031	−0.017
Jaeschke & Hinze (1991), Bu	16	–	310	0.4 – 26.2	0.50	16	16	0.006	0.010	0.004	−0.010	0.007	0.012	0.013	−0.029
Jaeschke & Hinze (1991), Bu	25	25	310	0.9 – 26.1	0.75	25	25	0.009	0.016	0.008	−0.016	0.011	0.022	0.018	−0.051
Jaeschke & Hinze (1991), Op	271	271	270 – 353	0.4 – 28.6	0.20	271	271	0.010	0.018	−0.001	0.009	0.013	0.025	0.056	0.077
Jaeschke & Hinze (1991), Op	153	153	280 – 310	0.5 – 28.0	0.50	153	153	0.025	0.012	0.025	0.003	0.027	0.014	0.045	0.033
Jaeschke & Hinze (1991), Op	397	–	270 – 350	0.4 – 31.1	0.50	397	397	0.018	0.013	0.018	−0.009	0.023	0.015	0.068	−0.034
Jaeschke & Hinze (1991), Op	281	281	270 – 350	0.4 – 28.1	0.75	281	281	0.010	0.034	0.006	−0.034	0.013	0.041	0.027	−0.084
Liu & Miller (1972)	7	–	91.2 – 115	0.3 – 1.2	0.51	7	–	0.361		−0.361		0.362		−0.420	
Nunes da Ponte *et al.* (1978)	46	–	110 – 120	1.7 – 138	0.32	46	–	0.250		0.247		0.275		0.428	
Nunes da Ponte *et al.* (1978)	88	–	110 – 120	1.5 – 138	0.50	84	–	0.208		0.207		0.245		0.467	
Nunes da Ponte *et al.* (1978)	45	–	110 – 120	2.0 – 137	0.71	44	–	0.174		0.172		0.192		0.328	
Pan *et al.* (1975)	3	–	91.0 – 108	0.1 – 0.4	0.14	3	–	0.082		0.082		0.085		0.115	
Pan *et al.* (1975)	4	–	91.0 – 115	0.3 – 1.1	0.50	4	–	0.072		0.036		0.077		0.110	
Rodosevich & Miller (1973)	4	–	91.0 – 115	0.04 – 0.2	0.05	4	–	0.058		0.058		0.072		0.124	
Rodosevich & Miller (1973)	4	–	91.1 – 115	0.1 – 0.5	0.16	4	–	0.070		0.070		0.074		0.111	

Table A2.1 (continued)

Authors	Number of data points		Covered ranges			Statistical analysis^{n}									
	total^{a}	used^{b}	Temp. T/K	Pressure p/MPa	Compos.^{c,d} x	N_1	N_2	AAD$_1$ %	AAD$_2$ %	Bias$_1$ %	Bias$_2$ %	RMS$_1$ %	RMS$_2$ %	MaxD$_1$ %	MaxD$_2$ %
(1 − x) CH_4 + x N_2 (continued)															
pρT **data (continued)**						**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA
Roe (1972)	23	23	219 – 291	0.3 – 9.6	0.28	23	23	0.026	0.029	−0.024	0.013	0.035	0.063	−0.063	0.255
Roe (1972)	24	20	219 – 291	0.3 – 9.6	0.52	24	24	0.022	0.025	−0.020	−0.025	0.034	0.037	−0.094	−0.114
Ruhrgas, ADH (1989)	24	–	280 – 310	2.0 – 7.0	0.50	24	24	0.015	0.013	0.004	−0.007	0.017	0.019	−0.042	−0.053
Sault (1952)	46	–	139 – 273	0.6 – 18.8	0.11	43	43	0.442	0.565	0.442	0.565	0.529	0.683	1.466	1.707
Sault (1952)	52	–	139 – 273	0.7 – 20.9	0.30	52	52	0.219	0.470	−0.180	0.195	0.284	0.887	−0.610	4.024
Sault (1952)	52	–	139 – 273	0.8 – 22.7	0.50	50	49	0.168	0.196	−0.094	−0.015	0.320	0.356	1.407	1.382
Sault (1952)	58	–	139 – 273	0.5 – 23.6	0.74	58	58	0.161	0.209	0.118	−0.013	0.204	0.284	−0.522	−1.197
Seitz & Blencoe (1996)	3	–	673	29.9 – 99.9	0.10	3	3	0.159	0.096	−0.108	−0.079	0.170	0.109	−0.219	−0.144
Seitz & Blencoe (1996)	5	–	673	29.9 – 99.9	0.20	5	5	0.147	0.114	−0.147	−0.114	0.150	0.124	−0.191	−0.207
Seitz & Blencoe (1996)	5	–	673	29.9 – 99.9	0.30	5	5	0.146	0.097	−0.146	−0.097	0.158	0.114	−0.233	−0.185
Seitz & Blencoe (1996)	5	–	673	29.9 – 99.9	0.40	5	5	0.138	0.068	−0.138	−0.064	0.140	0.097	−0.169	−0.196
Seitz & Blencoe (1996)	5	–	673	29.9 – 99.9	0.50	5	5	0.123	0.050	−0.123	−0.015	0.128	0.073	−0.171	−0.152
Seitz & Blencoe (1996)	5	–	673	29.9 – 99.9	0.60	5	5	0.095	0.097	−0.095	0.056	0.103	0.104	−0.145	0.157
Seitz & Blencoe (1996)	5	–	673	29.9 – 99.9	0.70	5	5	0.096	0.145	−0.096	0.105	0.111	0.148	−0.160	0.186
Seitz & Blencoe (1996)	5	–	673	29.9 – 99.9	0.80	5	5	0.088	0.176	−0.088	0.170	0.095	0.196	−0.114	0.247
Seitz & Blencoe (1996)	5	–	673	29.9 – 99.9	0.90	5	5	0.090	0.237	−0.082	0.237	0.097	0.261	−0.119	0.332
Seitz *et al.* (1996a)	17	–	323 – 573	9.9 – 99.9	0.10	17	17	0.765	0.739	0.725	0.698	0.812	0.790	1.288	1.260
Seitz *et al.* (1996a)	19	–	323 – 573	9.9 – 99.9	0.20	19	19	0.643	0.611	0.608	0.576	0.727	0.707	1.600	1.603
Seitz *et al.* (1996a)	22	–	323 – 573	9.9 – 99.9	0.30	22	22	0.564	0.522	0.514	0.472	0.631	0.608	1.292	1.288
Seitz *et al.* (1996a)	24	–	323 – 573	9.9 – 99.9	0.40	24	24	0.449	0.409	0.402	0.355	0.537	0.519	1.286	1.272
Seitz *et al.* (1996a)	24	–	323 – 573	9.9 – 99.9	0.50	24	24	0.358	0.343	0.298	0.249	0.456	0.453	1.130	1.108
Seitz *et al.* (1996a)	24	–	323 – 573	9.9 – 99.9	0.60	24	24	0.295	0.315	0.231	0.186	0.389	0.406	1.013	0.985
Seitz *et al.* (1996a)	22	–	323 – 573	9.9 – 99.9	0.70	22	22	0.187	0.256	0.136	0.095	0.280	0.333	0.770	0.744
Seitz *et al.* (1996a)	20	–	323 – 573	9.9 – 99.9	0.80	20	20	0.180	0.269	0.114	0.093	0.225	0.310	0.555	0.578
Seitz *et al.* (1996a)	18	–	323 – 573	9.9 – 99.9	0.90	18	18	0.120	0.234	−0.011	−0.005	0.133	0.273	0.255	−0.534
SNAM (1989)	12	–	284 – 300	2.1 – 7.1	0.50	12	12	0.012	0.009	0.007	−0.003	0.013	0.011	0.027	−0.019

Table A2.1 (continued)

Authors	Number of data points		Covered ranges			Statistical analysis[n]									
	total[a]	used[b]	Temp. T/K	Pressure p/MPa	Compos.[c,d] x	N_1	N_2	AAD$_1$ %	AAD$_2$ %	Bias$_1$ %	Bias$_2$ %	RMS$_1$ %	RMS$_2$ %	MaxD$_1$ %	MaxD$_2$ %
(1 − x) CH_4 + x N_2 (continued)															
***pρT* data (continued)**						**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA
Straty & Diller (1980)	80	72	100 – 320	0.9 – 35.1	0.29	78	–	0.077		−0.013		0.203		−1.215	
Straty & Diller (1980)	312	281	82.0 – 320	0.6 – 35.6	0.50	305	–	0.095		−0.077		0.252		−1.760	
Straty & Diller (1980)	86	83	92.0 – 310	0.9 – 34.7	0.68	85	–	0.080		−0.056		0.244		−1.345	
Speed of sound						**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA
Estela-Uribe (1999)	106	–	220 – 400	0.1 – 20.1	0.20	104	104	0.013	0.049	−0.004	0.032	0.018	0.067	−0.053	−0.231
Estela-Uribe (1999)	68	–	170 – 400	0.1 – 15.6	0.54	68	68	0.026	0.065	0.006	−0.043	0.041	0.152	0.113	−0.696
Trusler (2000)	107	107	220 – 400	0.2 – 30.3	0.10	106	106	0.010	0.044	0.004	0.033	0.014	0.059	0.045	0.266
Trusler (2000)	106	106	220 – 400	0.2 – 30.2	0.20	106	106	0.013	0.062	0.007	0.035	0.016	0.086	0.044	−0.390
Younglove *et al.* (1993)	76	76	250 – 350	0.4 – 10.7	0.05	76	76	0.015	0.040	0.013	0.040	0.019	0.048	0.044	0.105
Younglove *et al.* (1993)	70	70	275 – 350	0.3 – 10.5	0.15	70	70	0.014	0.035	0.004	0.034	0.017	0.043	0.042	0.098
Younglove *et al.* (1993)	97	97	250 – 350	0.1 – 10.5	0.29	97	97	0.020	0.032	−0.006	0.025	0.025	0.041	0.082	0.112
Zhang & Schouten (1992a)	63	–	173 – 298	200 – 750	0.50	63	63	1.313	1.301	−1.307	−1.025	1.455	1.625	−2.514	−3.435
Isobaric heat capacity						**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA
Trappehl (1987)	76	–	160 – 260	3.0 – 10.0	0.70	73	73	0.966	0.927	0.227	0.084	1.269	1.165	−4.469	3.563
van Kasteren & Zeldenrust (1979)	35	–	110 – 275	3.0 – 5.1	0.47	35	–	2.594		−2.594		2.916		−5.561	
Enthalpy differences						**EqG**	EqA	**EqG**[u]	EqA[u]	**EqG**[u]	EqA[u]	**EqG**[u]	EqA[u]	**EqG**[u]	EqA[u]
Dawe & Snowdon (1975)[p]	15	–	248 – 367	0.1 – 10.0	0.10	14	14	0.104	0.119	−0.100	−0.117	0.135	0.144	−0.338	−0.337
Dawe & Snowdon (1975)[p]	15	–	248 – 367	0.1 – 10.0	0.50	15	15	0.074	0.101	−0.064	−0.101	0.104	0.123	−0.264	−0.307
Dawe & Snowdon (1975)[p]	16	–	248 – 367	0.1 – 10.0	0.75	16	16	0.038	0.087	0.004	−0.087	0.045	0.107	0.087	−0.254
Grini *et al.* (1998)[h]	25	–	163 – 258	0.2 – 7.1	0.50	24	24	*2.063*	*2.781*	*0.568*	*0.969*	*3.406*	*4.183*	*11.349*	*13.034*
Grini *et al.* (1998)[p]	25	–	169 – 258	0.9 – 7.1	0.50	24	24	1.206	1.910	1.206	1.910	2.045	2.841	8.722	8.875
Trappehl (1987)[h]	76	–	107 – 260	0.3 – 10.0	0.70	74	69	*7.077*	*10.811*	*6.416*	*10.556*	*8.410*	*12.232*	*24.006*	*26.252*
Trappehl (1987)[p]	36	–	160 – 255	3.0 – 10.0	0.70	36	36	1.248	1.291	0.273	0.155	1.798	1.930	7.269	7.608
van Kasteren & Zeldenrust (1979)[p]	39	–	110 – 275	3.0 – 5.1	0.47	38	–	3.673		−3.673		3.805		−5.763	

Table A2.1 (continued)

Authors	Number of data points total[a]	used[b]	Covered ranges Temp. T/K	Pressure p/MPa	Compos.[c,d] x	N_1	N_2	Statistical analysis[n] AAD_1 %	AAD_2 %	$Bias_1$ %	$Bias_2$ %	RMS_1 %	RMS_2 %	$MaxD_1$ %	$MaxD_2$ %
$(1-x)$ CH_4 + x N_2 (continued)															
Saturated liquid density[g]						**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP
Fontaine (1989)	176	–	112 – 183	0.2 – 4.9	0.00 – 1.00	176	176	1.346	5.270	1.118	−2.470	1.766	6.387	5.380	13.777
Hiza *et al.* (1977)	8	8	105 – 140	0.1 – 0.9	0.05	8	8	0.106	11.713	0.106	−11.713	0.114	11.746	0.156	−12.804
Hiza *et al.* (1977)	5	5	100 – 120	0.3 – 1.0	0.30	5	5	0.093	12.850	0.093	−12.850	0.096	12.858	0.133	−13.425
Hiza *et al.* (1977)	8	8	95.0 – 130	0.3 – 2.1	0.49	8	8	0.069	11.896	0.069	−11.896	0.079	11.993	0.143	−13.613
VLE data						**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP
Bloomer & Parent (1953)[x,y]	240	–	91.2 – 190	0.06 – 5.1	0.01 – 0.95	179	165	0.983	1.040	0.595	0.351	1.377	1.401	4.515	4.704
Brandt & Stroud (1958)	9	–	137 – 175	3.4	0.05 – 0.71	9	9	2.265	2.343	1.731	1.660	2.529	2.588	4.007	4.091
Chang & Lu (1967)	27	–	122 – 171	0.3 – 5.0	0.02 – 0.99	25	25	3.601	3.668	3.470	3.611	4.077	4.121	8.343	8.868
Cheung & Wang (1964)	20	–	91.6 – 124	0.02 – 0.6	0.01 – 0.15	20	20	3.278	2.787	−3.189	−0.650	4.333	3.824	−12.499	−11.938
Cines *et al.* (1953)[e,f]	143	110	99.8 – 172	0.1 – 4.5	0.01 – 0.99	135	138	1.072	1.564	−0.002	0.048	1.449	1.917	−4.790	4.946
Ellington *et al.* (1959)[x,y]	196	–	78.4 – 186	0.1 – 4.8	0.06 – 0.95	176	172	0.985	0.926	0.374	0.094	1.371	1.207	4.745	4.169
Fastovskii & Petrovskii (1957a)	37	–	81.8 – 150	0.1 – 1.6	0.07 – 0.83	37	37	2.520	2.584	1.203	1.223	3.186	3.411	6.860	8.182
Fontaine (1989)	176	174	112 – 183	0.2 – 4.9	0.00 – 1.00	172	165	0.825	0.866	0.658	0.620	1.061	1.165	2.936	3.284
Fuks & Bellemans (1967)[x]	20	–	84.2 – 90.8	0.1 – 0.2	0.14 – 0.67	20	20	2.680	0.841	−0.773	0.500	3.413	0.961	−6.420	1.909
Janisch (2000a)[e,f]	68	–	130 – 180	0.6 – 5.1	0.03 – 0.83	59	58	1.733	1.578	1.711	1.518	1.879	1.729	4.026	3.534
Janisch (2000b)	32	–	130 – 180	0.7 – 5.1	0.01 – 0.83	28	28	1.544	1.476	1.544	1.433	1.763	1.719	4.157	3.941
Janisch (2000c)	41	–	130 – 180	0.7 – 5.1	0.01 – 0.83	36	36	1.474	1.388	1.441	1.339	1.666	1.616	4.157	3.941
Jin *et al.* (1993)	10	–	123	0.4 – 2.6	0.05 – 0.91	10	10	1.289	1.397	1.079	0.897	1.469	1.570	2.560	2.590
McClure *et al.* (1976)	8	8	90.7	0.1 – 0.3	0.19 – 0.88	8	8	0.294	1.058	0.284	0.615	0.379	1.510	0.693	3.683
McTaggart & Edwards (1919)	7	–	84.5 – 107	0.1	0.05 – 0.67	–	–								
Miller *et al.* (1973)[f]	22	–	112	0.2 – 1.3	0.03 – 0.78	21	21	6.782	6.701	5.278	5.704	10.248	10.475	25.006	25.118
Parrish & Hiza (1973)	48	48	95.0 – 120	0.2 – 2.0	0.10 – 0.90	48	48	0.660	0.602	0.542	0.452	0.823	0.854	2.268	3.438
Skripka *et al.* (1970)[x,y]	12	–	113	0.1 – 1.7	0.05 – 0.95	12	12	3.006	3.184	2.838	2.951	4.125	4.434	7.674	9.677
Stryjek *et al.* (1974a)[e,f]	107	99	114 – 183	0.2 – 5.0	0.00 – 1.00	100	91	0.702	0.791	0.444	0.391	0.841	1.043	2.420	3.302
Wilson (1975)	14	–	111	0.2 – 1.3	0.06 – 0.86	14	14	1.512	1.323	1.192	1.323	1.631	1.339	2.076	1.580

Table A2.1 (continued)

Authors	Number of data points total[a]	used[b]	Temp. T/K	Covered ranges Pressure p/MPa	Compos.[c,d] x	N_1	N_2	Statistical analysis[n] AAD$_1$ %	AAD$_2$ %	Bias$_1$ %	Bias$_2$ %	RMS$_1$ %	RMS$_2$ %	MaxD$_1$ %	MaxD$_2$ %
(1 − x) CH_4 + x CO_2															
***pρT* data**						**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA
Arai *et al.* (1971)	2	–	253	6.9 – 7.6	0.45	2	–	0.275		0.196		0.338		0.471	
Arai *et al.* (1971)	10	–	273	2.4 – 14.5	0.49	10	–	1.946		−1.946		2.326		−4.154	
Arai *et al.* (1971)	2	–	253	5.3 – 8.3	0.50	2	–	3.199		−2.251		3.912		−5.450	
Arai *et al.* (1971)	2	–	253	4.4 – 8.3	0.56	2	–	2.632		0.890		2.778		3.521	
Arai *et al.* (1971)	10	–	273	3.0 – 14.5	0.59	10	–	1.270		−1.270		1.546		−2.878	
Arai *et al.* (1971)	9	–	273	2.6 – 8.3	0.65	9	–	1.632		−1.591		2.189		−5.090	
Arai *et al.* (1971)	9	–	273	7.0 – 14.5	0.68	5	–	6.134		−6.134		6.383		−8.258	
Arai *et al.* (1971)	9	–	273	6.5 – 14.5	0.68	9	–	3.595		−3.595		4.524		−7.930	
Arai *et al.* (1971)	6	–	273	2.4 – 6.1	0.70	6	–	0.996		−0.996		1.223		−2.288	
Arai *et al.* (1971)	10	–	288	2.7 – 14.5	0.70	10	–	1.181		1.181		1.398		3.309	
Arai *et al.* (1971)	2	–	253	3.1 – 7.4	0.70	2	–	1.485		1.485		1.636		2.171	
Arai *et al.* (1971)	8	–	273	5.7 – 14.5	0.72	8	–	2.601		−2.601		3.595		−7.316	
Arai *et al.* (1971)	12	–	288	2.6 – 14.5	0.75	12	–	1.225		1.127		1.647		4.083	
Arai *et al.* (1971)	8	–	273	5.0 – 14.5	0.78	8	–	1.212		−0.954		1.595		−2.936	
Arai *et al.* (1971)	5	–	273	2.4 – 4.5	0.79	5	–	0.682		0.682		0.765		1.157	
Arai *et al.* (1971)	2	–	253	2.6 – 6.2	0.80	2	–	2.916		2.916		2.919		3.039	
Arai *et al.* (1971)	7	–	288	7.4 – 14.5	0.82	7	–	1.486		0.673		1.615		2.168	
Arai *et al.* (1971)	6	–	288	2.4 – 7.0	0.82	6	–	0.708		0.708		0.738		1.114	
Arai *et al.* (1971)	7	–	288	7.1 – 14.5	0.83	7	–	2.015		−0.278		2.423		−4.293	
Arai *et al.* (1971)	6	–	288	6.7 – 14.5	0.85	6	–	2.939		−2.939		3.686		−7.524	
Arai *et al.* (1971)	6	–	288	2.4 – 6.1	0.86	6	–	0.306		0.106		0.312		0.385	
Arai *et al.* (1971)	8	–	273	4.2 – 14.5	0.87	8	–	1.491		1.454		1.612		2.206	
Arai *et al.* (1971)	7	–	288	6.3 – 14.5	0.88	7	–	0.945		−0.038		1.153		−2.334	
Arai *et al.* (1971)	6	–	288	2.4 – 5.7	0.90	6	–	0.994		0.994		1.001		1.161	
Arai *et al.* (1971)	7	–	288	5.9 – 14.5	0.91	7	–	1.655		1.655		1.827		2.491	
Arai *et al.* (1971)	6	–	288	2.4 – 5.3	0.94	6	–	0.581		0.581		0.605		0.761	

Table A2.1 (continued)

Authors	Number of data points		Covered ranges			Statistical analysis[n]									
	total[a]	used[b]	Temp. T/K	Pressure p/MPa	Compos.[c,d] x	N_1	N_2	AAD_1 %	AAD_2 %	Bias_1 %	Bias_2 %	RMS_1 %	RMS_2 %	MaxD_1 %	MaxD_2 %
$(1-x)$ $CH_4 + x$ CO_2 (continued)															
pρT **data (continued)**						**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA
Arai *et al.* (1971)	7	–	288	5.5 – 14.5	0.96	7	–	1.981		1.981		2.187		2.755	
Beer (1969)	7	–	293 – 453	4.1 – 19.3	0.20	7	7	0.695	0.706	0.316	0.299	0.759	0.773	1.238	1.243
Beer (1969)	7	–	293 – 453	4.1 – 19.3	0.40	7	7	0.988	1.017	−0.067	0.002	1.314	1.316	−2.797	−2.743
Beer (1969)	7	–	293 – 453	4.1 – 19.3	0.60	7	7	0.953	0.910	−0.319	−0.118	1.462	1.365	−3.576	−3.244
Beer (1969)	7	–	293 – 453	4.1 – 19.3	0.80	6	6	0.429	0.535	0.265	0.490	0.435	0.582	0.520	0.853
Brugge *et al.* (1989b)	35	35	300 – 320	0.2 – 9.2	0.10	35	35	0.012	0.011	0.008	−0.005	0.022	0.015	0.089	−0.034
Brugge *et al.* (1989b)	40	40	300 – 320	0.2 – 9.8	0.30	40	40	0.007	0.013	0.001	−0.007	0.013	0.017	0.057	0.063
Brugge *et al.* (1989b)	40	40	300 – 320	0.2 – 8.0	0.68	40	40	0.057	0.023	−0.057	0.017	0.085	0.055	−0.208	0.256
Brugge *et al.* (1989b)	40	40	300 – 320	0.2 – 6.8	0.90	40	40	0.054	0.019	−0.054	0.011	0.088	0.039	−0.235	0.197
Esper (1987)	118	–	220 – 320	0.1 – 48.3	0.48	118	–	0.388		−0.257		0.862		−3.073	
Gasunie (1990)	52	52	279 – 300	3.7 – 6.4	0.10	52	52	0.019	0.052	−0.014	−0.052	0.021	0.054	−0.039	−0.080
Gasunie (1990)	32	32	280 – 308	3.8 – 6.3	0.19	32	32	0.052	0.023	0.052	0.007	0.057	0.027	0.101	0.048
Gasunie (1990)	33	33	293 – 308	3.8 – 6.3	0.25	33	33	0.018	0.021	0.017	−0.021	0.021	0.023	0.045	−0.041
Gasunie (1990)	32	32	280 – 308	3.7 – 6.1	0.30	32	32	0.026	0.018	0.025	−0.012	0.030	0.025	0.056	−0.067
Glos *et al.* (2000)	8	8	273	2.0 – 9.0	0.06	8	8	0.004	0.041	−0.003	−0.041	0.005	0.044	−0.010	−0.067
Glos *et al.* (2000)	9	9	273 – 290	2.0 – 9.5	0.15	9	9	0.014	0.047	0.014	−0.047	0.014	0.051	0.021	−0.073
Hwang *et al.* (1997a)	66	29	225 – 350	1.8 – 69.5	0.10	65	58	0.089	0.186	0.034	−0.123	0.132	0.224	0.464	−0.486
Hwang *et al.* (1997a)	41	7	225 – 350	3.3 – 34.5	0.29	41	–	0.233		0.002		0.315		−0.826	
Hwang *et al.* (1997a)	13	9	300	3.3 – 40.7	0.30	13	13	0.205	0.427	−0.205	−0.427	0.212	0.505	−0.263	−0.803
Hwang *et al.* (1997a)	49	–	225 – 350	2.1 – 34.4	0.67	46	–	0.440		−0.437		0.569		−1.700	
Hwang *et al.* (1997a)	59	25	225 – 350	3.2 – 44.9	0.90	58	–	0.202		−0.147		0.347		−1.834	
Lemming (1989)	28	–	289	0.03 – 6.7	0.10	28	28	0.006	0.006	0.006	−0.006	0.010	0.009	0.027	−0.025
Magee & Ely (1988)	91	–	225 – 400	2.1 – 35.8	0.98	88	–	0.138		−0.011		0.172		0.480	
Reamer *et al.* (1944)	116	42	311 – 478	1.4 – 68.9	0.15	116	116	0.208	0.190	0.169	0.097	0.261	0.252	0.569	−0.775
Reamer *et al.* (1944)	120	42	311 – 478	1.4 – 68.9	0.39	120	120	0.143	0.213	−0.109	−0.129	0.206	0.364	−0.692	−1.351
Reamer *et al.* (1944)	120	42	311 – 478	1.4 – 68.9	0.59	120	120	0.342	0.303	−0.342	−0.288	0.372	0.424	−0.959	−1.730

Table A2.1 (continued)

Authors	Number of data points			Covered ranges				Statistical analysis[n]								
	total[a]	used[b]	Temp. T/K	Pressure p/MPa	Compos.[c,d] x	N_1	N_2	AAD$_1$ %	AAD$_2$ %	Bias$_1$ %	Bias$_2$ %	RMS$_1$ %	RMS$_2$ %	MaxD$_1$ %	MaxD$_2$ %
(1 − x) CH_4 + x CO_2 (continued)															
***pρT* data (continued)**						**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA
Reamer *et al.* (1944)	120	42	311 – 478	1.4 – 68.9	0.80	120	120	0.391	0.297	−0.369	−0.285	0.474	0.375	−1.469	−1.314
Ruhrgas (1990), Bu	46	46	330	0.4 – 26.3	0.31	46	46	0.012	0.021	0.009	0.013	0.019	0.037	0.056	−0.104
Ruhrgas (1990), Op	252	252	270 – 350	0.2 – 28.4	0.31	252	252	0.049	0.048	−0.001	−0.012	0.067	0.062	0.259	−0.176
Seitz & Blencoe (1996)	2	–	673	79.9 – 99.9	0.10	2	2	0.202	0.278	0.202	0.278	0.207	0.283	0.248	0.328
Seitz & Blencoe (1996)	6	–	673	19.9 – 99.9	0.20	6	6	0.202	0.258	0.063	0.158	0.254	0.294	−0.401	0.500
Seitz & Blencoe (1996)	6	–	673	19.9 – 99.9	0.30	6	6	0.183	0.173	−0.058	0.104	0.212	0.205	−0.359	0.388
Seitz & Blencoe (1996)	5	–	673	19.9 – 79.9	0.40	5	5	0.167	0.148	−0.112	0.148	0.192	0.185	−0.294	0.311
Seitz & Blencoe (1996)	6	–	673	19.9 – 99.9	0.50	6	6	0.137	0.179	−0.132	0.179	0.174	0.193	−0.306	0.304
Seitz & Blencoe (1996)	6	–	673	19.9 – 99.9	0.60	6	6	0.189	0.190	−0.189	0.190	0.216	0.207	−0.329	0.270
Seitz & Blencoe (1996)	6	–	673	19.9 – 99.9	0.70	6	6	0.230	0.203	−0.230	0.203	0.275	0.232	−0.434	0.352
Seitz & Blencoe (1996)	6	–	673	19.9 – 99.9	0.80	6	6	0.202	0.271	−0.202	0.260	0.241	0.302	−0.333	0.402
Seitz & Blencoe (1996)	1	–	673	99.9	0.90	1	1	0.149	0.102	−0.149	−0.102	0.149	0.102	−0.149	−0.102
Seitz *et al.* (1996a)	15	–	323 – 573	19.9 – 99.9	0.10	15	15	0.866	0.774	0.866	0.774	0.999	0.953	1.848	1.826
Seitz *et al.* (1996a)	22	–	323 – 573	9.9 – 99.9	0.20	22	22	0.884	0.801	0.850	0.757	1.161	1.152	2.849	2.879
Seitz *et al.* (1996a)	23	–	323 – 573	9.9 – 99.9	0.30	23	23	0.576	0.566	0.569	0.468	0.833	0.864	2.308	2.387
Seitz *et al.* (1996a)	24	–	323 – 573	9.9 – 99.9	0.40	24	24	0.460	0.579	0.386	0.338	0.659	0.758	1.672	1.808
Seitz *et al.* (1996a)	25	–	323 – 573	9.9 – 99.9	0.50	25	25	0.347	0.559	0.232	0.193	0.523	0.695	1.670	1.861
Seitz *et al.* (1996a)	22	–	323 – 573	9.9 – 99.9	0.60	22	22	0.313	0.551	0.124	0.110	0.556	0.751	1.872	2.230
Seitz *et al.* (1996a)	25	–	323 – 573	9.9 – 99.9	0.70	24	24	0.209	0.427	−0.135	−0.150	0.291	0.505	−0.848	−0.977
Seitz *et al.* (1996a)	22	–	323 – 573	9.9 – 99.9	0.80	21	21	0.297	0.372	−0.278	−0.251	0.367	0.474	−0.747	−1.079
Seitz *et al.* (1996a)	16	–	323 – 573	19.9 – 99.9	0.90	16	16	0.248	0.318	−0.217	−0.224	0.298	0.393	−0.578	−0.828
Simon *et al.* (1977)	63	–	283 – 322	4.7 – 20.7	0.91	62	–	3.124		−2.648		3.327		−5.013	
Wöll & El Hawary (2003)	151	113	233 – 373	0.2 – 18.3	0.08	132	105	0.050	0.067	0.036	−0.024	0.065	0.089	0.192	−0.199
Wöll & El Hawary (2003)	173	137	233 – 373	1.8 – 18.2	0.15	173	159	0.040	0.113	0.031	−0.062	0.070	0.149	0.279	−0.482
Speed of sound						**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA
Estela-Uribe (1999)	83	83	200 – 450	0.08 – 17.3	0.20	82	82	0.007	0.029	−0.003	−0.024	0.010	0.051	−0.033	−0.221

Table A2.1 (continued)

Authors	Number of data points		Covered ranges			Statistical analysis[n]									
	total[a]	used[b]	Temp. T/K	Pressure p/MPa	Compos.[c,d] x	N_1	N_2	AAD_1 %	AAD_2 %	Bias_1 %	Bias_2 %	RMS_1 %	RMS_2 %	MaxD_1 %	MaxD_2 %
$(1-x)$ CH_4 + x CO_2 (continued)															
Speed of sound (continued)						**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA
Younglove *et al.* (1993)	80	80	250 – 350	0.4 – 10.6	0.05	80	80	0.023	0.054	0.022	0.054	0.027	0.066	0.071	0.217
Younglove *et al.* (1993)	71	71	250 – 350	0.5 – 10.8	0.15	71	71	0.030	0.045	0.023	0.043	0.032	0.058	0.056	0.240
Younglove *et al.* (1993)	90	90	250 – 350	0.6 – 10.7	0.30	90	90	0.109	0.102	0.012	0.012	0.201	0.184	−0.975	−0.759
Isobaric heat capacity						**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA
Bishnoi & Robinson (1971)	110	–	313 – 363	0.2 – 15.5	0.58	109	109	0.611	0.599	0.611	0.599	0.717	0.691	1.651	1.449
Bishnoi & Robinson (1971)	139	–	313 – 424	0.2 – 15.2	0.86	136	136	0.437	0.730	0.040	0.197	0.543	0.974	−1.435	−3.077
VLE data						**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP
Al-Sahhaf *et al.* (1983)[f]	29	17	219 – 270	0.9 – 8.5	0.45 – 0.98	27	27	2.534	2.838	−2.432	2.029	3.255	3.748	−7.233	8.680
Arai *et al.* (1971)[e,f]	32	–	253 – 288	2.6 – 8.5	0.56 – 0.96	8	9	1.994	3.071	−0.080	3.071	2.850	3.859	−6.844	8.233
Bian *et al.* (1993)	6	5	301	7.0 – 7.7	0.97 – 0.99	5	2	1.114	1.916	1.114	1.916	1.186	1.928	1.516	2.127
Davalos *et al.* (1976)	33	–	230 – 270	1.5 – 8.5	0.42 – 0.99	33	32	2.819	1.393	−2.672	0.373	3.446	1.759	−6.557	4.594
DeVaney *et al.* (1978)	3	–	222	6.9	0.77	–	–								
Donnelly & Katz (1954)[e,f]	78	–	200 – 271	1.1 – 8.1	0.08 – 0.97	65	66	3.503	3.492	−1.151	1.674	4.944	4.287	−14.095	11.148
Hwang *et al.* (1976)[y]	126	–	153 – 219	1.2 – 6.5	0.00 – 0.23	86	39	2.463	5.191	0.429	4.178	4.332	8.261	15.159	18.418
Joffe (1976)	12	–	209 – 271	3.4 – 7.3	0.36 – 0.90	12	12	3.410	3.020	−0.400	2.807	4.081	3.449	−8.419	6.141
Kaminishi *et al.* (1968)[e,f]	18	13	233 – 283	3.7 – 8.2	0.48 – 0.93	16	17	2.148	1.536	−2.075	0.392	3.034	2.172	−9.372	−6.542
Mraw *et al.* (1978)[e,f]	59	5	153 – 219	0.9 – 6.5	0.00 – 0.90	51	52	1.255	1.388	−0.736	1.136	2.165	2.078	−6.389	7.753
Neumann & Walch (1968)	57	8	173 – 220	2.7 – 6.2	0.00 – 0.75	54	54	3.025	2.630	2.173	2.475	3.376	3.032	−7.591	6.381
Somait & Kidnay (1978)[f]	12	–	270	3.8 – 8.4	0.69 – 0.98	10	9	2.804	2.540	−2.703	0.988	5.863	3.056	−16.861	−6.986
Tsiklis (1946)	7	–	255	3.9 – 6.9	0.80 – 0.95	7	7	5.664	8.857	5.664	8.857	6.358	9.261	10.782	13.844
Vrabec & Fischer (1996)[z]	19	–	230 – 270	1.3 – 7.8	0.70 – 0.98	19	19	4.344	3.318	−2.426	2.116	5.482	4.021	−15.382	−7.338
Webster & Kidnay (2001)[e,f]	40	36	230 – 270	1.2 – 8.4	0.41 – 0.98	38	37	1.832	1.710	−1.747	1.127	2.294	2.265	−4.947	5.656
Wei *et al.* (1995)	57	53	230 – 270	1.1 – 8.4	0.42 – 0.99	55	46	2.061	1.716	−1.874	1.367	2.473	2.193	4.610	4.365
Xu *et al.* (1992)	21	19	288 – 293	5.6 – 8.2	0.83 – 0.99	19	17	1.293	0.857	−1.151	0.622	1.451	1.004	−2.754	1.659
Yorizane *et al.* (1968a)	7	–	143	1.5 – 3.9	0.19 – 0.80	–	–								

Table A2.1 (continued)

Authors	Number of data points		Covered ranges			Statistical analysis[n]									
	total[a]	used[b]	Temp. T/K	Pressure p/MPa	Compos.[c,d] x	N_1	N_2	AAD_1 %	AAD_2 %	Bias_1 %	Bias_2 %	RMS_1 %	RMS_2 %	MaxD_1 %	MaxD_2 %
$(1-x)$ CH_4 + x C_2H_6															
***pρT* data**						**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA
Blanke & Weiss (1995)	44	–	274 – 333	2.0 – 7.0	0.05	44	44	0.109	0.112	−0.098	−0.102	0.128	0.132	−0.262	−0.268
Blanke & Weiss (1995)	42	–	274 – 333	2.1 – 7.1	0.15	42	42	0.059	0.066	−0.058	−0.065	0.072	0.078	−0.157	−0.161
Blanke & Weiss (1995)	43	–	274 – 333	2.1 – 7.0	0.25	43	43	0.030	0.037	−0.019	−0.029	0.036	0.043	0.091	−0.087
Bloomer *et al.* (1953)	50	–	217 – 305	2.2 – 26.3	0.15	50	–	0.619		0.619		0.671		1.301	
Bloomer *et al.* (1953)	26	–	239 – 305	5.4 – 27.7	0.30	26	–	1.455		1.455		1.492		2.430	
Bloomer *et al.* (1953)	34	–	244 – 305	1.6 – 27.4	0.50	34	–	0.848		0.848		1.067		2.396	
Bloomer *et al.* (1953)	32	–	250 – 316	3.2 – 31.2	0.70	32	–	1.649		1.649		2.072		5.026	
Gasunie (1990)	33	–	280 – 308	3.8 – 6.3	0.05	33	33	0.018	0.016	0.004	−0.001	0.020	0.019	−0.038	−0.044
Gasunie (1990)	49	–	279 – 300	3.7 – 6.4	0.09	49	49	0.096	0.091	0.096	0.091	0.105	0.101	0.178	0.178
Gasunie (1990)	30	–	280 – 308	3.7 – 6.3	0.20	30	30	0.021	0.018	0.020	0.016	0.023	0.020	0.037	0.035
Haynes *et al.* (1985)	144	17	105 – 320	1.7 – 34.8	0.31	144	–	0.173		0.162		0.251		0.887	
Haynes *et al.* (1985)	164	27	108 – 320	1.7 – 34.4	0.50	159	–	0.520		0.507		0.784		1.989	
Haynes *et al.* (1985)	106	13	100 – 320	1.7 – 35.9	0.65	106	–	0.942		0.860		1.429		3.767	
Hiza & Haynes (1978)	1	1	135	0.4	0.26	1	–	0.148		0.148		0.148		0.148	
Hiza & Haynes (1978)	1	1	135	0.3	0.41	1	–	0.086		0.086		0.086		0.086	
Hiza & Haynes (1978)	1	1	125	0.2	0.50	1	–	0.058		0.058		0.058		0.058	
Hiza & Haynes (1978)	1	1	135	0.3	0.56	1	–	0.044		0.044		0.044		0.044	
Hiza & Haynes (1978)	1	1	135	0.2	0.64	1	–	0.024		−0.024		0.024		−0.024	
Hiza *et al.* (1977)	6	6	105 – 130	0.04 – 0.3	0.32	6	–	0.062		0.062		0.071		0.130	
Hiza *et al.* (1977)	8	8	105 – 140	0.03 – 0.4	0.51	8	–	0.023		0.012		0.026		0.037	
Hiza *et al.* (1977)	6	6	105 – 130	0.03 – 0.2	0.65	6	–	0.093		−0.093		0.103		−0.150	
Hoover (1965)	42	–	215 – 273	0.3 – 2.6	0.32	42	42	0.223	0.232	0.223	0.232	0.292	0.319	0.733	0.843
Hoover (1965)	43	–	215 – 273	0.2 – 2.7	0.49	43	43	0.099	0.114	0.076	0.097	0.115	0.144	0.268	0.370
Hoover (1965)	34	–	215 – 273	0.2 – 2.7	0.65	33	33	0.141	0.178	0.099	0.154	0.208	0.255	0.714	0.800
Hoover (1965)	11	–	273	0.2 – 2.0	0.80	11	11	0.026	0.028	0.011	0.028	0.032	0.044	−0.077	0.124
Hou *et al.* (1996)	44	44	300 – 320	0.1 – 7.2	0.30	44	44	0.010	0.018	−0.005	−0.018	0.016	0.024	−0.040	−0.061

Table A2.1 (continued)

Authors	Number of data points total[a]	used[b]	Temp. T/K	Covered ranges Pressure p/MPa	Compos.[c,d] x	N_1	N_2	Statistical analysis[n] AAD$_1$ %	AAD$_2$ %	Bias$_1$ %	Bias$_2$ %	RMS$_1$ %	RMS$_2$ %	MaxD$_1$ %	MaxD$_2$ %
$(1-x)$ CH$_4$ + x C$_2$H$_6$ (continued)															
***pρT* data (continued)**						**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA
Hou *et al.* (1996)	45	45	300 – 320	0.1 – 7.4	0.50	45	45	0.033	0.037	−0.027	−0.037	0.057	0.060	−0.162	−0.206
Hou *et al.* (1996)	46	44	300 – 320	0.1 – 7.6	0.69	46	46	0.078	0.070	−0.074	−0.070	0.137	0.135	−0.442	−0.566
Michels & Nederbragt (1939)	18	–	273 – 323	1.0 – 6.1	0.20	18	18	0.055	0.049	0.046	0.037	0.064	0.060	0.122	0.116
Michels & Nederbragt (1939)	32	–	273 – 323	2.0 – 8.2	0.60	19	–	0.256		0.198		0.537		1.733	
Michels & Nederbragt (1939)	29	–	273 – 323	2.0 – 6.1	0.80	20	–	0.475		0.191		0.646		1.932	
Pan *et al.* (1975)	4	–	91.0 – 115	0.003 – 0.01	0.30	4	–	0.017		0.016		0.023		0.040	
Pan *et al.* (1975)	4	–	91.0 – 115	0.002 – 0.01	0.49	4	–	0.048		−0.038		0.058		−0.083	
Rodosevich & Miller (1973)	4	4	91.1 – 116	0.03 – 0.1	0.05	4	–	0.054		0.054		0.055		0.066	
Rodosevich & Miller (1973)	4	4	91.0 – 115	0.04 – 0.9	0.15	4	–	0.050		0.020		0.062		0.105	
Rodosevich & Miller (1973)	3	3	91.1 – 108	0.03 – 0.1	0.25	3	–	0.042		0.042		0.044		0.063	
Rodosevich & Miller (1973)	3	3	91.0 – 115	0.03 – 0.1	0.30	3	–	0.010		−0.010		0.013		−0.021	
Rodosevich & Miller (1973)	5	5	91.0 – 115	0.02 – 0.1	0.31	5	–	0.016		0.014		0.020		0.037	
Ruhrgas (1990), Bu	32	32	330	0.4 – 25.8	0.04	32	32	0.007	0.004	0.007	0.001	0.010	0.006	0.018	0.020
Ruhrgas (1990), Bu	59	59	290 – 330	0.3 – 26.0	0.08	59	59	0.006	0.006	0.004	0.000	0.007	0.007	0.015	0.018
Ruhrgas (1990), Bu	83	82	290 – 330	0.2 – 26.0	0.12	83	83	0.008	0.005	0.006	0.000	0.012	0.011	0.081	0.077
Ruhrgas (1990), Bu	81	81	290 – 330	0.4 – 26.1	0.16	81	81	0.007	0.008	0.004	−0.005	0.009	0.010	−0.024	−0.030
Ruhrgas (1990), Bu	30	30	330	0.6 – 26.1	0.30	30	30	0.008	0.043	−0.002	−0.043	0.010	0.064	0.017	−0.144
Ruhrgas (1990), Op	343	343	270 – 350	0.5 – 28.9	0.04	343	343	0.013	0.010	0.011	0.006	0.017	0.015	0.060	0.059
Ruhrgas (1990), Op	285	285	270 – 350	0.4 – 28.9	0.08	285	285	0.016	0.014	0.009	0.009	0.021	0.020	−0.084	−0.071
Ruhrgas (1990), Op	139	139	270 – 350	0.3 – 13.5	0.12	139	139	0.010	0.011	0.004	−0.002	0.013	0.017	−0.056	−0.080
Ruhrgas (1990), Op	306	306	270 – 350	0.4 – 28.4	0.16	306	306	0.014	0.025	0.002	−0.015	0.018	0.031	0.051	−0.087
Ruhrgas (1990), Op	207	207	270 – 350	0.2 – 28.4	0.30	207	207	0.015	0.075	−0.003	−0.075	0.021	0.096	−0.077	−0.300
Sage & Lacey (1939)	146	–	294 – 394	0.1 – 27.6	0.08	146	146	1.177	1.167	1.177	1.167	1.553	1.542	3.555	3.564
Sage & Lacey (1939)	167	–	294 – 394	0.1 – 31.0	0.20	166	166	1.647	1.625	1.647	1.625	2.026	1.999	3.733	3.722
Sage & Lacey (1939)	161	–	294 – 394	0.1 – 24.1	0.49	161	161	0.768	0.665	0.575	0.389	1.121	1.029	−3.226	−4.927
Sage & Lacey (1939)	170	–	294 – 394	0.1 – 31.0	0.61	170	170	0.266	0.315	−0.029	−0.305	0.362	0.570	−1.285	−4.386

Table A2.1 (continued)

Authors	Number of data points total[a]	used[b]	Covered ranges Temp. T/K	Pressure p/MPa	Compos.[c,d] x	Statistical analysis[n] N_1	N_2	AAD$_1$ %	AAD$_2$ %	Bias$_1$ %	Bias$_2$ %	RMS$_1$ %	RMS$_2$ %	MaxD$_1$ %	MaxD$_2$ %
(1 − x) CH_4 + x C_2H_6 (continued)															
***pρT* data (continued)**						**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA
Sage & Lacey (1939)	97	–	294 – 394	0.1 – 10.3	0.68	86	87	0.305	0.327	0.036	0.052	0.476	0.502	1.738	1.768
Shana'a & Canfield (1968)	1	–	108	0.07	0.13	1	–	0.079		0.079		0.079		0.079	
Shana'a & Canfield (1968)	1	–	108	0.05	0.32	1	–	0.144		0.144		0.144		0.144	
Shana'a & Canfield (1968)	1	–	108	0.04	0.45	1	–	0.031		−0.031		0.031		−0.031	
Shana'a & Canfield (1968)	1	–	108	0.03	0.66	1	–	0.173		−0.173		0.173		−0.173	
Shana'a & Canfield (1968)	1	–	108	0.02	0.81	1	–	0.170		−0.170		0.170		−0.170	
Wöll & El Hawary (2003)	82	56	233 – 373	0.2 – 18.4	0.08	70	71	0.046	0.050	0.036	0.041	0.065	0.070	0.183	0.193
Wöll & El Hawary (2003)	173	147	233 – 373	1.7 – 19.6	0.15	161	125	0.055	0.076	−0.004	−0.027	0.070	0.093	0.188	0.180
Isochoric heat capacity						**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA
Anisimov *et al.* (1988)	36	–	206 – 256	149^{ρ} – 211^{ρ}	0.10	27	29	7.841	8.567	7.479	8.340	10.009	10.406	19.336	19.989
Anisimov *et al.* (1988)	74	–	243 – 296	130^{ρ} – 264^{ρ}	0.40	44	46	5.789	6.505	5.173	6.400	8.067	8.565	19.306	18.767
Anisimov *et al.* (1988)	49	–	288 – 335	140^{ρ} – 278^{ρ}	0.84	40	41	6.003	5.473	3.701	2.870	8.006	7.321	19.039	19.625
Mayrath & Magee (1989)	270	270	107 – 328	70.6^{ρ} – 518^{ρ}	0.31	270	–	0.540		−0.104		0.789		4.257	
Mayrath & Magee (1989)	101	100	107 – 320	84.7^{ρ} – 553^{ρ}	0.50	100	–	1.165		0.821		1.753		5.596	
Mayrath & Magee (1989)	255	255	101 – 327	67.1^{ρ} – 588^{ρ}	0.65	255	–	0.607		0.161		0.877		3.915	
Speed of sound						**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA
Beckermann (1993)	103	–	250 – 350	0.05 – 10.0	0.14	103	103	0.088	0.131	0.024	0.009	0.100	0.159	0.203	−0.375
Boyes (1992)	172	–	225 – 350	0.05 – 10.2	0.15	172	172	0.067	0.080	−0.062	−0.073	0.079	0.123	−0.215	−0.638
Costa Gomes & Trusler (1998)	40	40	250 – 350	0.00 – 20.1	0.15	39	39	0.022	0.121	0.001	−0.075	0.029	0.248	−0.057	−0.851
Le Noë & Desentfant (1996)	46	–	225 – 350	2.5 – 20.0	0.15	45	45	0.090	0.502	−0.010	−0.401	0.127	1.126	−0.432	−3.738
Trusler (1994)	57	55	200 – 375	0.03 – 13.1	0.20	57	57	0.025	0.113	0.004	−0.055	0.043	0.206	−0.175	−0.787
Younglove *et al.* (1993)	80	80	250 – 350	0.5 – 10.6	0.05	80	80	0.011	0.030	0.007	0.028	0.014	0.038	0.033	0.090
Younglove *et al.* (1993)	67	67	250 – 350	0.5 – 11.1	0.15	67	67	0.018	0.070	0.004	−0.014	0.023	0.132	−0.053	−0.508
Younglove *et al.* (1993)	95	84	250 – 350	0.3 – 10.7	0.31	95	95	0.185	0.411	−0.100	−0.303	0.622	1.135	−3.167	−4.429
Younglove *et al.* (1993)	78	53	250 – 350	0.5 – 10.4	0.50	78	78	0.206	0.351	0.043	−0.101	0.336	0.803	−1.196	−3.999

Table A2.1 (continued)

Authors	Number of data points total^a	used^b	Temp. T/K	Covered ranges Pressure p/MPa	Compos.^{c,d} x	N_1	N_2	Statistical analysis^n AAD$_1$ %	AAD$_2$ %	Bias$_1$ %	Bias$_2$ %	RMS$_1$ %	RMS$_2$ %	MaxD$_1$ %	MaxD$_2$ %
(1 − x) CH_4 + x C_2H_6 (continued)															
Speed of sound (continued)						**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA
Younglove *et al.* (1993)	72	32	250 – 350	0.3 – 10.6	0.65	72	72	0.034	0.088	0.012	0.012	0.043	0.125	−0.125	−0.408
Isobaric heat capacity						**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA
van Kasteren & Zeldenrust (1979)	42	16	110 – 270	3.0 – 5.1	0.29	20	–	0.941		0.730		1.557		6.081	
Wirbser *et al.* (1996)	56	56	250 – 350	0.6 – 30.0	0.15	56	56	0.588	0.574	−0.087	−0.180	0.794	0.780	2.373	2.097
Enthalpy differences						**EqG**	EqA	**EqG^u**	EqA^u	**EqG^u**	EqA^u	**EqG^u**	EqA^u	**EqG^u**	EqA^u
Day *et al.* (1997)^{h,p}	49	–	356 – 525	0.2 – 7.0	0.11	21	21	1.838	1.778	1.838	1.778	1.940	1.887	3.593	3.557
						28	28	*2.979*	*3.081*	*2.396*	*−0.953*	*3.440*	*3.715*	*6.113*	*−9.206*
Day *et al.* (1997)^{h,p}	44	–	352 – 489	0.2 – 7.0	0.25	20	20	1.538	1.476	1.538	1.476	1.573	1.514	2.481	2.426
						24	24	*7.060*	*6.333*	*7.060*	*5.998*	*7.942*	*7.611*	*13.945*	*14.793*
Grini *et al.* (1998)^h	67	–	158 – 349	0.2 – 14.1	0.50	62	–	*7.832*		*3.211*		*10.601*		*29.115*	
Grini *et al.* (1998)^h	73	–	211 – 347	0.2 – 14.0	0.75	60	43	*6.625*	*7.954*	*−0.138*	*0.372*	*9.831*	*12.029*	*−28.735*	*−28.144*
Grini *et al.* (1998)^p	67	–	150 – 349	1.0 – 14.1	0.50	67	–	0.638		0.138		0.924		−2.824	
Grini *et al.* (1998)^p	73	–	204 – 347	0.5 – 14.0	0.75	73	68	0.414	2.932	0.237	−2.561	0.801	4.471	4.757	−15.830
Owren *et al.* (1996)^h	29	–	235 – 349	0.9 – 16.5	0.15	29	29	*1.273*	*2.270*	*0.500*	*−0.059*	*1.487*	*3.021*	*−2.800*	*−8.794*
Owren *et al.* (1996)^p	29	22	242 – 349	2.5 – 16.5	0.15	29	29	0.130	0.123	0.004	−0.011	0.161	0.172	−0.291	0.512
Powers *et al.* (1979)^p	154	–	122 – 422	1.7 – 13.8	0.06	143	–	2.106		−1.172		2.929		−9.631	
Powers *et al.* (1979)^p	140	–	111 – 433	1.7 – 13.8	0.22	132	–	0.850		0.760		0.932		1.651	
Powers *et al.* (1979)^p	139	–	116 – 428	1.7 – 13.8	0.52	112	–	1.377		0.564		1.972		−9.959	
van Kasteren & Zeldenrust (1979)^p	32	–	110 – 270	5.1	0.29	18	–	1.107		0.668		2.275		9.077	
Second acoustic virial coefficient															
Trusler (1994)	9	–	200 – 375		0.20										
Saturated liquid density^g						**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP
Hiza *et al.* (1977)	6	6	105 – 130	0.04 – 0.3	0.32	6	6	0.059	10.584	0.059	−10.584	0.068	10.585	0.126	−10.717
Hiza *et al.* (1977)	8	8	105 – 140	0.03 – 0.4	0.51	8	8	0.021	9.591	0.009	−9.591	0.024	9.595	−0.038	−9.884

Table A2.1 (continued)

Authors	Number of data points total[a]	used[b]	Covered ranges Temp. T/K	Pressure p/MPa	Compos.[c,d] x	N_1	N_2	Statistical analysis[n] AAD_1 %	AAD_2 %	$Bias_1$ %	$Bias_2$ %	RMS_1 %	RMS_2 %	$MaxD_1$ %	$MaxD_2$ %
(1 − x) CH_4 + x C_2H_6 (continued)															
Saturated liquid density[g] (continued)						**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP
Hiza *et al.* (1977)	6	6	105 – 130	0.03 – 0.2	0.65	6	6	0.097	8.825	−0.097	−8.825	0.106	8.829	−0.153	−9.173
Vrabec & Fischer (1996)[z]	25	–	160 – 250	0.2 – 6.3	0.10 – 0.95	25	25	0.847	6.702	0.617	−5.937	1.726	7.360	5.549	−10.070
VLE data						**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP
Bloomer *et al.* (1953)[x,y]	224	–	139 – 302	0.3 – 6.8	0.03 – 0.95	180	172	1.763	1.498	−0.769	0.571	2.498	2.214	9.559	9.674
Chang & Lu (1967)	15	–	122 – 171	0.1 – 2.1	0.14 – 0.88	15	15	6.594	6.614	1.103	3.182	8.589	8.577	−18.162	18.506
Davalos *et al.* (1976)	7	7	250	1.5 – 6.7	0.45 – 0.98	7	7	0.599	2.131	−0.457	2.073	0.709	2.315	−1.293	3.208
Ellington *et al.* (1959)[x,y]	248	–	142 – 300	0.7 – 6.6	0.03 – 0.95	223	226	1.528	1.351	−0.739	0.511	2.171	1.878	−8.457	9.046
Janisch (2000a)[e,f]	34	–	180 – 270	0.5 – 6.6	0.06 – 0.95	34	34	1.257	2.918	0.366	2.684	1.673	3.474	−4.382	9.991
Janisch (2000b)	20	–	180 – 270	0.5 – 6.6	0.05 – 0.95	20	19	1.064	2.949	0.798	2.939	1.442	3.722	4.285	10.160
Janisch (2000c)	30	–	140 – 270	0.4 – 6.6	0.05 – 0.95	30	29	1.239	3.054	0.942	3.046	1.598	3.669	4.285	10.160
Levitskaja (1941)	3	–	178 – 188	3.0 – 4.1	0.11 – 0.28	3	3	12.050	11.478	12.050	11.478	12.334	11.789	14.114	13.700
Miller & Staveley (1976)[x]	9	–	116	0.01 – 0.1	0.13 – 0.93	9	9	0.816	5.243	−0.713	5.136	1.151	6.802	−2.396	13.050
Miller *et al.* (1977)[e]	21	–	160 – 180	0.1 – 2.8	0.10 – 0.97	21	21	2.215	2.407	−1.843	2.226	3.652	3.040	−9.649	5.178
Price & Kobayashi (1959)	18	15	144 – 283	0.7 – 6.9	0.17 – 0.99	17	17	2.134	1.450	−1.073	1.244	2.612	2.220	4.546	6.467
Raabe *et al.* (2001)	10	–	240 – 270	1.5 – 6.6	0.38 – 0.95	10	9	0.640	2.653	0.106	2.653	0.823	2.795	1.672	4.106
Skripka *et al.* (1970)[x,y]	25	–	123 – 153	0.01 – 1.1	0.05 – 0.95	23	24	4.725	3.863	−3.259	−0.237	6.830	5.386	−17.949	−18.604
Vrabec & Fischer (1996)[z]	25	–	160 – 250	0.2 – 6.3	0.10 – 0.95	25	25	6.460	4.264	−6.322	−3.683	7.793	5.308	−18.028	−12.097
Wei *et al.* (1995)	57	55	210 – 270	0.8 – 6.5	0.14 – 0.99	57	57	0.847	1.389	−0.733	1.350	1.145	1.604	−4.160	3.526
Wichterle & Kobayashi (1972a)	118	106	130 – 200	0.2 – 5.2	0.00 – 0.98	110	110	1.537	1.404	−0.680	0.936	2.517	2.086	−8.327	8.292
Wichterle *et al.* (1971)	23	–	191 – 197	4.5 – 5.0	0.01 – 0.08	20	17	1.037	1.214	1.037	1.214	1.403	1.246	3.858	1.738
Wilson (1975)[x]	14	–	111	0.02 – 0.09	0.07 – 0.88	14	14	1.590	3.865	−1.374	3.570	2.077	5.465	−3.750	14.172
(1 − x) CH_4 + x C_3H_8															
***pρT* data**						**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA
Arai & Kobayashi (1980)	426	418	152 – 327	1.9 – 65.4	0.05	417	–	0.352		0.094		0.463		−1.962	
Blanke *et al.* (1996)	30	–	273 – 323	2.1 – 6.3	0.01	30	30	0.039	0.039	0.014	0.008	0.051	0.050	0.131	0.127

Table A2.1 (continued)

Authors	Number of data points		Covered ranges					Statistical analysis[n]							
	total[a]	used[b]	Temp. T/K	Pressure p/MPa	Compos.[c,d] x	N_1	N_2	AAD$_1$ %	AAD$_2$ %	Bias$_1$ %	Bias$_2$ %	RMS$_1$ %	RMS$_2$ %	MaxD$_1$ %	MaxD$_2$ %
(1 − x) CH_4 + x C_3H_8 (continued)															
***pρT* data (continued)**						**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA
Blanke *et al.* (1996)	30	–	274 – 323	2.0 – 6.3	0.03	30	30	0.051	0.055	−0.032	−0.043	0.055	0.062	−0.092	−0.107
Blanke *et al.* (1996)	30	–	273 – 323	2.0 – 6.2	0.05	30	30	0.052	0.041	0.049	0.035	0.059	0.047	0.098	0.084
Gasunie (1990)	54	54	279 – 300	3.7 – 6.4	0.04	54	54	0.031	0.024	0.030	0.017	0.036	0.028	0.070	0.059
Gasunie (1990)	44	44	280 – 308	3.7 – 6.4	0.05	44	44	0.027	0.016	0.026	0.013	0.030	0.018	0.044	0.028
Hiza *et al.* (1977)	6	6	105 – 130	0.05 – 0.3	0.14	6	–	0.052		0.045		0.064		0.103	
Hiza *et al.* (1977)	6	6	105 – 130	0.05 – 0.3	0.25	6	–	0.045		−0.045		0.046		−0.059	
Hiza *et al.* (1977)	6	6	105 – 130	0.04 – 0.2	0.50	6	–	0.031		−0.028		0.034		−0.050	
Hiza *et al.* (1977)	2	2	105 – 110	0.03 – 0.04	0.70	2	–	0.025		0.018		0.031		0.044	
Huang *et al.* (1967)	53	53	123 – 311	3.4 – 34.5	0.25	52	–	0.625		0.339		0.718		−1.242	
Huang *et al.* (1967)	41	35	153 – 311	3.4 – 34.5	0.50	33	–	0.998		−0.932		1.099		−1.910	
Huang *et al.* (1967)	46	46	153 – 311	3.4 – 34.5	0.78	46	–	0.521		−0.337		0.654		−1.797	
May *et al.* (2001)	15	15	290 – 313	0.9 – 7.9	0.07	15	15	0.019	0.027	0.010	−0.007	0.043	0.044	0.160	0.151
May *et al.* (2001)	23	22	273 – 313	2.1 – 9.5	0.16	23	23	0.151	0.154	−0.057	−0.132	0.207	0.172	0.768	−0.268
May *et al.* (2001)	21	21	285 – 293	1.9 – 10.0	0.21	21	21	0.222	0.444	−0.149	−0.444	0.261	0.591	−0.502	−1.378
May *et al.* (2002)	14	14	297 – 313	2.1 – 9.5	0.16	14	14	0.152	0.183	−0.152	−0.183	0.158	0.187	−0.219	−0.250
Pan *et al.* (1975)	4	–	91.0 – 115	0.03 – 0.1	0.10	4	–	0.030		0.025		0.042		0.079	
Pan *et al.* (1975)	4	–	91.0 – 115	0.03 – 0.1	0.17	4	–	0.035		−0.024		0.052		−0.102	
Reamer *et al.* (1950)	154	70	311 – 511	1.4 – 68.9	0.10	154	154	0.291	0.283	0.267	0.279	0.352	0.342	1.210	1.109
Reamer *et al.* (1950)	176	80	278 – 511	1.4 – 68.9	0.20	172	–	0.325		0.305		0.400		1.661	
Reamer *et al.* (1950)	175	–	278 – 511	1.4 – 68.9	0.30	169	–	0.293		0.185		0.382		1.313	
Reamer *et al.* (1950)	173	80	278 – 511	1.4 – 68.9	0.40	166	–	0.285		0.142		0.367		−1.054	
Reamer *et al.* (1950)	172	80	278 – 511	1.4 – 68.9	0.50	165	–	0.317		0.217		0.415		1.404	
Reamer *et al.* (1950)	172	80	278 – 511	1.4 – 68.9	0.60	165	–	0.401		0.324		0.527		1.750	
Reamer *et al.* (1950)	171	80	278 – 511	1.4 – 68.9	0.70	164	–	0.436		0.380		0.561		1.822	
Reamer *et al.* (1950)	172	80	278 – 511	1.4 – 68.9	0.80	165	–	0.408		0.330		0.528		1.836	
Reamer *et al.* (1950)	151	70	311 – 511	1.4 – 68.9	0.90	145	–	0.375		0.239		0.468		−1.810	

Table A2.1 (continued)

Authors	Number of data points total[a]	used[b]	Covered ranges Temp. T/K	Pressure p/MPa	Compos.[c,d] x	Statistical analysis[n] N_1	N_2	AAD$_1$ %	AAD$_2$ %	Bias$_1$ %	Bias$_2$ %	RMS$_1$ %	RMS$_2$ %	MaxD$_1$ %	MaxD$_2$ %
$(1-x)$ CH$_4$ + x C$_3$H$_8$ (continued)															
***pρT* data (continued)**						**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA
Rodosevich & Miller (1973)	4	4	91.0 – 115	0.04 – 0.1	0.03	4	–	0.056		0.056		0.061		0.084	
Rodosevich & Miller (1973)	4	4	91.0 – 115	0.03 – 0.1	0.07	4	–	0.075		0.075		0.079		0.108	
Rodosevich & Miller (1973)	4	4	91.0 – 115	0.03 – 0.1	0.10	4	–	0.047		0.047		0.057		0.089	
Ruhrgas (1990), Bu	30	30	313 – 353	0.4 – 18.2	0.07	30	30	0.010	0.011	0.010	−0.011	0.012	0.013	0.021	−0.034
Ruhrgas (1999), Bu	38	36	313	0.2 – 30.2	0.15	38	38	0.020	0.063	0.009	−0.046	0.029	0.104	0.102	−0.289
Ruhrgas (1990), Op	188	188	280 – 353	0.3 – 28.4	0.07	188	188	0.018	0.015	0.013	−0.008	0.021	0.019	0.046	−0.044
Ruhrgas (1999), Op	257	257	290 – 350	0.5 – 29.3	0.15	257	257	0.015	0.150	−0.005	−0.149	0.021	0.225	−0.060	−0.721
Shana'a & Canfield (1968)	1	1	108	0.07	0.15	1	–	0.004		0.004		0.004		0.004	
Shana'a & Canfield (1968)	1	1	108	0.06	0.31	1	–	0.113		−0.113		0.113		−0.113	
Shana'a & Canfield (1968)	1	–	108	0.05	0.45	1	–	0.104		−0.104		0.104		−0.104	
Shana'a & Canfield (1968)	1	1	108	0.04	0.59	1	–	0.075		−0.075		0.075		−0.075	
Shana'a & Canfield (1968)	1	1	108	0.03	0.74	1	–	0.063		−0.063		0.063		−0.063	
Speed of sound						**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA
Ingrain *et al.* (1993)	51	50	213 – 346	0.2 – 17.0	0.10	51	48	0.306	0.494	0.060	−0.227	0.585	1.035	−3.016	−4.028
Trusler *et al.* (1993)	30	29	280 – 375	0.2 – 12.9	0.15	30	30	0.027	0.086	0.007	0.025	0.042	0.119	−0.110	−0.367
Trusler *et al.* (1996)	68	67	225 – 375	0.05 – 1.4	0.15	68	68	0.009	0.031	0.006	−0.007	0.012	0.046	−0.069	−0.156
Younglove *et al.* (1993)	76	76	250 – 350	0.5 – 10.4	0.10	76	76	0.072	0.237	−0.023	−0.142	0.210	0.728	−1.297	−3.995
Isobaric heat capacity						**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA
van Kasteren & Zeldenrust (1979)	26	18	110 – 270	3.0 – 5.1	0.09	21	–	1.441		−1.297		1.743		−4.041	
Yesavage *et al.* (1969)	254	197	100 – 422	1.7 – 13.8	0.77	243	–	1.082		0.338		1.486		−4.969	
Enthalpy differences						**EqG**	EqA	**EqG**[u]	EqA[u]	**EqG**[u]	EqA[u]	**EqG**[u]	EqA[u]	**EqG**[u]	EqA[u]
Dillard *et al.* (1968)[T]	20	–	305 – 366	0.001 – 13.8	0.05	13	13	4.327	4.207	−4.244	−4.109	5.107	4.981	−8.252	−8.130
Dillard *et al.* (1968)[T]	12	12	305 – 366	0.001 – 13.8	0.13	12	12	2.183	2.170	−1.868	−1.832	2.601	2.528	−4.611	−4.476
Grini *et al.* (1994)[h]	77	–	150 – 341	0.2 – 14.0	0.32	66	–	*7.624*		*2.372*		*10.907*		*28.225*	

Table A2.1 (continued)

Authors	Number of data points total^a	used^b	Covered ranges Temp. T/K	Pressure p/MPa	Compos.^{c,d} x	N_1	N_2	Statistical analysis^n AAD$_1$ %	AAD$_2$ %	Bias$_1$ %	Bias$_2$ %	RMS$_1$ %	RMS$_2$ %	MaxD$_1$ %	MaxD$_2$ %
$(1-x)$ CH_4 + x C_3H_8 (continued)															
Enthalpy differences (continued)						**EqG**	EqA	**EqG^u**	EqA^u	**EqG^u**	EqA^u	**EqG^u**	EqA^u	**EqG^u**	EqA^u
Grini *et al.* (1995)^p	77	75	143 – 341	0.5 – 14.0	0.32	77	–	1.369		−0.962		1.901		−6.913	
Mather *et al.* (1969)^T	12	12	240 – 366	0.00 – 13.8	0.05	12	12	0.727	0.773	−0.597	−0.438	0.810	0.837	−1.169	−1.185
van Kasteren & Zeldenrust (1979)^p	40	–	110 – 270	3.0 – 5.1	0.09	21	–	1.152		−1.152		1.485		−3.785	
Second acoustic virial coefficient															
Trusler *et al.* (1993)	5	–	280 – 375		0.15										
Trusler *et al.* (1996)	7	–	225 – 375		0.15										
Saturated liquid density^g						**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP
Hiza *et al.* (1977)	6	6	105 – 130	0.05 – 0.3	0.14	6	6	0.051	10.416	0.042	−10.416	0.062	10.417	0.099	−10.510
Hiza *et al.* (1977)	6	6	105 – 130	0.05 – 0.3	0.25	6	6	0.048	9.152	−0.048	−9.152	0.049	9.154	−0.062	−9.361
Hiza *et al.* (1977)	6	6	105 – 130	0.04 – 0.2	0.50	6	6	0.033	6.605	−0.032	−6.605	0.037	6.613	−0.053	−7.060
Hiza *et al.* (1977)	2	2	105 – 110	0.03 – 0.04	0.70	2	2	0.025	4.733	0.015	−4.733	0.029	4.735	0.040	−4.869
VLE data						**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP
Akers *et al.* (1954a)	80	–	158 – 273	0.3 – 10.0	0.00 – 0.99	73	72	3.152	3.447	−0.030	−0.181	4.236	4.379	−10.937	11.123
Calado *et al.* (1974)^x	16	–	116 – 135	0.02 – 0.4	0.09 – 0.90	16	16	2.254	2.893	−2.223	2.688	2.732	4.001	−4.762	10.336
Cheung & Wang (1964)^x	10	–	91.7 – 128	0.001 – 0.2	0.53 – 0.97	10	8	5.545	7.066	−5.545	6.161	6.280	8.778	−12.571	16.796
Joffe (1976)	13	–	228 – 344	3.4 – 9.0	0.26 – 0.96	12	13	0.886	1.668	−0.127	0.447	1.104	1.830	−2.099	2.822
Kandil *et al.* (2005)^y	10	–	316 – 340	2.9 – 6.8	0.60	2	5	6.265	0.370	−6.265	−0.370	6.323	0.418	−7.117	−0.613
Poon & Lu (1974)	22	–	114 – 122	0.04 – 0.2	0.10 – 0.89	22	22	5.034	10.471	4.698	10.427	6.911	12.977	16.446	24.983
Price & Kobayashi (1959)	30	–	144 – 283	0.7 – 9.0	0.20 – 1.00	30	30	2.385	2.635	−0.025	0.091	3.512	3.719	−11.710	−11.255
Reamer *et al.* (1950)	122	92	278 – 361	0.7 – 10.2	0.25 – 1.00	110	112	0.972	1.989	−0.082	1.897	1.313	2.336	−4.056	4.843
Sage *et al.* (1934)^f	55	31	293 – 363	1.0 – 9.6	0.42 – 1.00	48	52	3.238	4.665	1.991	4.379	4.390	5.499	−12.142	12.365
Skripka *et al.* (1970)^x	24	–	123 – 153	0.02 – 1.1	0.05 – 0.95	24	24	6.202	3.376	−4.857	−0.921	8.797	4.892	−24.467	12.451
Webster & Kidnay (2001)^{e,f}	72	65	230 – 270	0.7 – 9.3	0.16 – 0.98	72	72	1.860	2.019	−1.733	−1.791	2.250	2.515	−5.530	−6.593
Wichterle & Kobayashi (1972b)	90	78	130 – 214	0.2 – 6.5	0.00 – 0.98	84	82	1.020	1.490	0.132	−0.065	1.309	1.832	4.872	−4.584

Table A2.1 (continued)

Authors	Number of data points total[a]	used[b]	Covered ranges Temp. T/K	Pressure p/MPa	Compos.[c,d] x	N_1	N_2	Statistical analysis[n] AAD_1 %	AAD_2 %	Bias_1 %	Bias_2 %	RMS_1 %	RMS_2 %	MaxD_1 %	MaxD_2 %
(1 − x) CH_4 + x C_3H_8 (continued)															
VLE data (continued)						**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP
Wilson (1975)[x]	14	–	111	0.02 – 0.09	0.06 – 0.86	14	14	3.276	2.800	−2.847	2.800	4.293	3.607	−10.875	6.494
(1 − x) CH_4 + x n-C_4H_{10}															
***pρT* data**						**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA
Beattie *et al.* (1941)	125	–	348 – 573	3.2 – 35.7	0.25	115	111	0.538	0.802	0.538	0.621	0.547	0.863	0.770	−1.758
Beattie *et al.* (1941)	94	–	373 – 573	3.2 – 35.7	0.50	87	81	0.262	1.017	−0.024	0.766	0.356	1.105	1.235	−1.787
Beattie *et al.* (1941)	83	–	398 – 573	3.0 – 33.7	0.75	75	21	0.542	1.303	0.463	1.144	0.703	1.465	1.844	1.989
Ellington (1986)	27	–	278 – 300	0.8 – 6.3	0.04	27	27	0.059	0.020	0.057	0.000	0.069	0.025	0.126	−0.063
Fenghour *et al.* (1999)	12	12	340 – 478	11.5 – 38.6	0.47	10	–	0.284		0.147		0.321		0.476	
Fenghour *et al.* (1999)	9	9	316 – 404	12.0 – 40.9	0.50	9	–	0.225		0.225		0.254		0.389	
Fenghour *et al.* (1999)	16	16	337 – 479	10.1 – 48.1	0.56	15	–	0.192		−0.118		0.246		−0.580	
Fenghour *et al.* (1999)	11	11	381 – 478	8.8 – 20.9	0.63	11	–	1.035		1.035		1.069		1.403	
Fenghour *et al.* (1999)	15	15	366 – 477	8.8 – 31.0	0.65	14	–	0.351		0.333		0.414		0.626	
Fenghour *et al.* (1999)	8	8	363 – 415	8.8 – 19.5	0.65	7	–	0.311		0.301		0.338		0.439	
Gasunie (1990)	72	–	280 – 300	3.8 – 6.5	0.01	72	72	0.028	0.062	−0.015	−0.062	0.041	0.076	−0.112	−0.191
Hiza *et al.* (1977)	4	4	120 – 130	0.2 – 0.3	0.41	4	–	0.262		−0.262		0.269		−0.350	
Pan *et al.* (1975)	2	2	108 – 115	0.1 – 0.2	0.05	2	–	0.380		0.380		0.380		0.399	
Reamer *et al.* (1947)	135	119	311 – 511	1.4 – 68.9	0.20	126	–	0.268		0.166		0.339		−1.917	
Reamer *et al.* (1947)	126	59	311 – 511	1.4 – 68.9	0.40	119	–	0.363		−0.120		0.501		−1.860	
Reamer *et al.* (1947)	131	–	311 – 511	1.4 – 68.9	0.60	85	–	0.666		−0.340		0.780		−1.900	
Reamer *et al.* (1947)	120	84	311 – 511	1.4 – 68.9	0.81	115	–	0.682		−0.404		0.764		−1.937	
Ruhrgas (1990), Bu	29	29	313 – 353	0.4 – 18.3	0.02	29	29	0.013	0.009	0.012	0.002	0.017	0.013	0.037	−0.048
Ruhrgas (1999), Bu	13	–	310	1.2 – 27.8	0.05	13	13	0.057	0.212	−0.050	−0.212	0.065	0.269	−0.101	−0.539
Ruhrgas (1990), Op	239	239	270 – 353	0.3 – 28.1	0.02	239	239	0.016	0.028	0.014	−0.020	0.019	0.043	0.032	−0.162
Ruhrgas (1999), Op	272	272	280 – 350	0.5 – 27.5	0.05	272	272	0.029	0.372	0.000	−0.369	0.036	0.532	−0.102	−1.315
Sage *et al.* (1940a)	138	–	294 – 394	0.3 – 10.3	0.08 – 1.00	121	–	1.595		1.135		2.067		4.991	

Table A2.1 (continued)

Authors	Number of data points total[a]	used[b]	Temp. T/K	Covered ranges Pressure p/MPa	Compos.[c,d] x	N_1	N_2	Statistical analysis[n] AAD_1 %	AAD_2 %	Bias_1 %	Bias_2 %	RMS_1 %	RMS_2 %	MaxD_1 %	MaxD_2 %
$(1-x)$ CH_4 + x n-C_4H_{10} (continued)															
Speed of sound						**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA
Plantier *et al.* (2005)	23	–	311	2.1 – 17.2	0.11	23	23	1.137	1.205	−1.137	−1.205	1.168	1.286	−1.464	−2.103
Plantier *et al.* (2005)	11	–	311	13.1 – 17.2	0.28	6	–	3.281		−2.987		4.579		−9.360	
Plantier *et al.* (2005)	9	–	311	3.9 – 13.8	0.84	9	–	1.051		0.659		1.223		2.053	
Saturated liquid density[g]						**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP
Haynes (1983)	3	3	115 – 125	0.1 – 0.3	0.07	3	3	0.523	10.602	0.523	−10.602	0.524	10.603	0.551	−10.692
Haynes (1983)	5	5	120 – 140	0.2 – 0.6	0.07	5	5	0.490	10.390	0.490	−10.390	0.491	10.393	0.536	−10.671
Haynes (1983)	6	6	115 – 140	0.1 – 0.6	0.22	6	6	0.376	7.981	0.376	−7.981	0.379	7.984	0.440	−8.228
Haynes (1983)	5	5	120 – 140	0.2 – 0.6	0.22	5	5	0.427	8.014	0.427	−8.014	0.427	8.015	0.458	−8.147
Hiza *et al.* (1977)	8	8	105 – 140	0.05 – 0.6	0.08	8	8	0.718	10.072	0.718	−10.072	0.720	10.075	0.826	−10.289
Hiza *et al.* (1977)	4	4	120 – 130	0.2 – 0.3	0.41	4	4	0.264	5.414	−0.264	−5.414	0.271	5.416	−0.352	−5.637
VLE data						**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP
Benedict *et al.* (1942)	10	–	294 – 394	2.8 – 11.0	0.46 – 0.91	10	10	2.322	4.737	0.361	4.737	3.523	5.359	9.302	11.125
Chen *et al.* (1974a)[y]	171	–	144 – 278	0.1 – 12.9	0.00 – 0.41	111	120	11.287	7.419	6.318	2.954	13.308	9.916	28.998	29.352
Elliot *et al.* (1974)	105	–	144 – 278	0.1 – 12.6	0.02 – 0.97	96	94	7.770	3.540	−7.743	−2.250	8.639	4.594	−14.740	−12.393
Fenghour *et al.* (1999)[x]	5	–	337 – 381	8.8 – 11.5	0.47 – 0.65	5	5	1.671	2.786	−1.665	2.738	2.331	3.252	−4.071	4.920
Kahre (1974)	70	–	166 – 283	0.1 – 11.0	0.03 – 0.99	70	69	6.421	3.806	−1.877	1.099	7.978	4.924	−16.416	12.360
Nederbragt (1938)	9	–	252 – 316	1.0 – 3.0	0.80 – 0.97	9	9	6.361	6.868	6.361	6.868	7.239	7.824	13.120	12.518
Rigas *et al.* (1958)	7	–	311	6.6 – 12.8	0.32 – 0.69	7	7	5.919	1.840	−5.919	−1.260	6.056	2.517	−7.472	−4.526
Roberts *et al.* (1962)	76	–	211 – 411	0.2 – 13.2	0.08 – 0.99	69	65	6.528	8.088	0.413	4.857	9.265	9.533	−29.789	−25.818
Sage *et al.* (1940b)	117	108	294 – 394	0.3 – 13.3	0.23 – 1.00	106	108	2.245	3.847	0.416	3.607	2.986	4.434	9.484	11.119
Wang & McKetta (1964)	8	–	178	0.5 – 2.9	0.09 – 0.84	8	8	17.139	6.902	−15.158	−4.988	19.763	8.148	−29.404	−13.079
Wiese *et al.* (1970)	25	9	278 – 378	1.4 – 13.3	0.20 – 0.97	16	16	1.105	5.159	1.052	5.126	1.565	5.552	3.892	8.502

Table A2.1 (continued)

Authors	Number of data points		Covered ranges			Statistical analysis[n]									
	total[a]	used[b]	Temp. T/K	Pressure p/MPa	Compos.[c,d] x	N_1	N_2	AAD$_1$ %	AAD$_2$ %	Bias$_1$ %	Bias$_2$ %	RMS$_1$ %	RMS$_2$ %	MaxD$_1$ %	MaxD$_2$ %
(1 − x) CH_4 + x i-C_4H_{10}															
***pρT* data**						**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA
Ellington (1986)	27	27	278 – 300	0.8 – 6.3	0.04	27	27	0.161	0.089	0.160	−0.088	0.184	0.111	0.317	−0.245
Hiza *et al.* (1977)	4	4	110 – 125	0.06 – 0.2	0.51	4	–	0.213		0.213		0.254		0.420	
Olds *et al.* (1942)	140	139	311 – 511	1.4 – 34.5	0.29	139	–	0.400		−0.339		0.486		−1.712	
Olds *et al.* (1942)	136	136	311 – 511	1.4 – 34.5	0.53	136	–	0.174		0.115		0.242		−1.171	
Olds *et al.* (1942)	137	135	311 – 511	1.4 – 34.5	0.72	135	–	0.331		−0.016		0.418		1.172	
Olds *et al.* (1942)	142	141	311 – 511	1.4 – 34.5	0.84	141	–	0.595		−0.580		0.672		−1.479	
Rodosevich & Miller (1973)	3	–	100 – 115	0.05 – 0.1	0.05	3	–	0.017		−0.002		0.017		0.023	
Rodosevich & Miller (1973)	4	–	95.0 – 115	0.04 – 0.1	0.08	4	–	0.027		0.027		0.030		0.042	
Saturated liquid density[g]						**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP
Haynes (1983)	6	6	115 – 140	0.1 – 0.6	0.08	6	6	0.071	10.203	0.071	−10.203	0.075	10.208	0.105	−10.550
Haynes (1983)	7	7	110 – 140	0.08 – 0.5	0.22	7	7	0.030	8.313	−0.023	−8.313	0.035	8.314	−0.055	−8.424
Hiza *et al.* (1977)	4	4	110 – 125	0.06 – 0.2	0.51	4	4	0.211	5.011	0.211	−5.011	0.252	5.018	0.419	−5.358
VLE data						**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP
Barsuk *et al.* (1970)[e]	96	72	198 – 378	0.5 – 11.8	0.02 – 1.00	84	82	2.076	4.943	−1.022	−4.610	2.974	5.691	−9.501	−9.795
Olds *et al.* (1942)[f]	75	38	311 – 378	0.6 – 11.5	0.31 – 1.00	61	60	2.659	2.308	0.453	0.771	3.107	2.916	−7.768	−7.048
(1 − x) CH_4 + x n-C_5H_{12}															
***pρT* data**						**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA
Jaeschke *et al.* (1997)	21	21	293 – 308	3.7 – 6.3	0.003	21	21	0.030	0.043	−0.030	−0.043	0.031	0.044	−0.052	−0.067
Sage *et al.* (1936)	28	–	311 – 378	5.5 – 20.7	0.37	9	–	2.185		1.561		2.497		4.285	
Sage *et al.* (1936)	31	–	311 – 378	4.1 – 20.7	0.47	11	–	2.591		2.562		3.240		4.825	
Sage *et al.* (1936)	39	–	311 – 378	2.8 – 20.7	0.74	32	–	1.194		0.884		1.373		−3.085	
Sage *et al.* (1942)	147	140	311 – 511	1.4 – 34.5	0.02	147	–	0.221		−0.186		0.282		0.795	
Sage *et al.* (1942)	122	–	311 – 444	0.1 – 16.9	0.05 – 1.00	113	–	0.982		−0.055		1.453		−4.971	
Sage *et al.* (1942)	147	147	311 – 511	1.4 – 34.5	0.06	147	–	0.211		0.049		0.327		1.778	

Table A2.1 (continued)

Authors	Number of data points total[a]	used[b]	Covered ranges Temp. T/K	Pressure p/MPa	Compos.[c,d] x	Statistical analysis[n] N_1	N_2	AAD_1 %	AAD_2 %	Bias_1 %	Bias_2 %	RMS_1 %	RMS_2 %	MaxD_1 %	MaxD_2 %
(1 − x) CH_4 + x n-C_5H_{12} (continued)															
***pρT* data (continued)**						**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA
Sage *et al.* (1942)	145	84	311 – 511	1.4 – 34.5	0.26	129	–	0.841		−0.122		1.132		−4.037	
Sage *et al.* (1942)	146	102	311 – 511	1.4 – 34.5	0.54	133	–	1.374		0.469		1.657		−4.617	
Sage *et al.* (1942)	145	95	311 – 511	1.4 – 34.5	0.71	134	–	0.970		0.388		1.198		−4.257	
Sage *et al.* (1942)	135	110	311 – 511	1.4 – 34.5	0.87	131	–	0.302		−0.087		0.606		−3.861	
VLE data						**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP
Berry & Sage (1970)	499	–	278 – 461	0.1 – 17.1	0.13 – 1.00	451	451	2.948	1.702	−1.078	0.613	3.887	2.429	−9.983	−8.162
Chen *et al.* (1974b)[y]	118	–	173 – 273	0.1 – 15.2	0.00 – 0.18	71	58	8.662	5.634	3.421	1.011	11.093	8.428	26.876	28.860
Chu *et al.* (1976)[e]	70	–	176 – 273	0.1 – 15.2	0.05 – 0.97	54	63	7.961	6.692	−0.383	0.411	10.115	8.006	−29.627	−20.347
Kahre (1975)[f]	64	–	178 – 283	0.3 – 15.2	0.03 – 0.98	51	60	7.767	5.197	−5.337	1.788	10.533	6.515	−27.956	−16.275
Sage *et al.* (1942)	61	40	311 – 444	0.1 – 16.9	0.18 – 1.00	54	55	1.966	1.787	0.159	1.130	2.524	2.544	6.981	7.027
(1 − x) CH_4 + x i-C_5H_{12}															
***pρT* data**						**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA
Amick *et al.* (1952)	91	89	344 – 478	1.4 – 9.0	0.21	89	90	0.193	0.401	−0.088	−0.341	0.269	0.523	−1.017	−1.847
Amick *et al.* (1952)	12	–	325 – 371	1.4 – 9.0	0.21	12	12	0.332	1.155	−0.051	−1.030	0.449	1.473	0.995	−3.480
Amick *et al.* (1952)	78	77	361 – 478	1.4 – 10.3	0.38	78	78	0.268	0.780	−0.028	−0.418	0.397	1.334	−1.807	−5.645
Amick *et al.* (1952)	14	–	352 – 405	1.4 – 10.3	0.38	13	13	0.554	2.025	−0.043	−1.845	0.621	2.874	0.933	−6.586
Amick *et al.* (1952)	67	55	378 – 478	1.4 – 10.3	0.50	64	60	0.771	1.230	0.441	0.557	0.967	1.515	2.661	−4.710
Amick *et al.* (1952)	13	–	257 – 420	1.4 – 9.7	0.50	12	9	3.233	3.921	−0.556	−0.656	3.904	5.013	8.685	−9.683
Amick *et al.* (1952)	23	23	450 – 478	2.8 – 7.6	0.67	23	23	1.367	2.697	0.920	2.697	1.701	2.841	3.910	4.379
Amick *et al.* (1952)	14	–	311 – 438	2.1 – 9.1	0.67	12	9	3.291	3.031	0.363	−1.333	4.500	4.318	9.194	−9.039
Amick *et al.* (1952)	12	12	461 – 478	3.8 – 5.5	0.85	12	4	4.837	8.873	4.837	8.873	5.183	8.891	7.739	9.601
Amick *et al.* (1952)	8	–	339 – 452	3.4 – 4.8	0.85	8	1	7.163	4.054	7.163	−4.054	7.378	4.054	9.005	−4.054
VLE data						**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP
Amick *et al.* (1952)	29	13	344 – 450	2.8 – 6.9	0.70 – 1.00	29	29	11.504	11.120	7.474	8.252	14.529	14.469	26.936	27.315

Table A2.1 (continued)

Authors	Number of data points total[a]	used[b]	Covered ranges Temp. T/K	Pressure p/MPa	Compos.[c,d] x	Statistical analysis[n] N_1	N_2	AAD$_1$ %	AAD$_2$ %	Bias$_1$ %	Bias$_2$ %	RMS$_1$ %	RMS$_2$ %	MaxD$_1$ %	MaxD$_2$ %
(1 − x) CH_4 + x n-C_6H_{14}															
***pρT* data**						**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA
Cebola *et al.* (2000)	125	–	348 – 383	2.1 – 19.5	0.03 – 0.96	68	–	4.780		−1.836		5.383		9.981	
Sage *et al.* (1936)	28	6	311 – 378	5.5 – 20.7	0.44	16	–	1.805		−1.805		2.074		−4.466	
Sage *et al.* (1936)	33	12	311 – 378	4.1 – 20.7	0.57	28	–	1.503		−1.457		1.695		−3.348	
Sage *et al.* (1936)	39	27	311 – 378	2.8 – 20.7	0.81	37	–	1.916		−1.916		2.010		−4.142	
Schoch *et al.* (1941)	16	–	311	19.0 – 41.4	0.22	7	–	3.781		−3.781		3.806		−4.506	
Schoch *et al.* (1941)	16	–	344	19.1 – 41.4	0.23	7	–	1.919		−1.919		2.242		−3.869	
Schoch *et al.* (1941)	15	–	378	18.3 – 41.4	0.25	6	–	3.557		−3.557		3.677		−5.224	
Schoch *et al.* (1941)	16	–	311	18.5 – 41.4	0.26	9	–	1.662		−1.662		1.769		−2.640	
Schoch *et al.* (1941)	15	–	344	18.9 – 41.4	0.26	7	–	1.595		−1.595		1.921		−3.562	
Schoch *et al.* (1941)	16	–	311	17.8 – 41.4	0.30	9	–	2.329		−2.329		2.378		−3.089	
Schoch *et al.* (1941)	15	–	344	17.8 – 41.4	0.30	8	–	1.477		−1.477		1.740		−2.998	
Schoch *et al.* (1941)	15	–	378	17.5 – 41.4	0.32	7	–	2.025		−2.025		2.364		−4.467	
Schoch *et al.* (1941)	16	–	311	16.8 – 41.4	0.36	10	–	1.397		−1.397		1.426		−1.825	
Schoch *et al.* (1941)	15	–	344	17.1 – 41.4	0.36	9	–	1.342		−1.342		1.541		−2.520	
Schoch *et al.* (1941)	16	–	378	16.2 – 41.4	0.40	9	–	2.337		−2.337		2.549		−4.014	
Schoch *et al.* (1941)	17	–	311	15.0 – 41.4	0.42	11	–	1.687		−1.687		1.694		−1.933	
Schoch *et al.* (1941)	16	–	344	15.5 – 41.4	0.43	11	–	1.099		−1.099		1.191		−1.792	
Schoch *et al.* (1941)	17	–	311	13.5 – 41.4	0.48	12	–	1.624		−1.624		1.625		−1.732	
Schoch *et al.* (1941)	16	–	344	14.0 – 41.4	0.48	11	–	0.937		−0.937		0.992		−1.436	
Schoch *et al.* (1941)	16	–	378	14.4 – 41.4	0.49	11	–	1.851		−1.851		2.007		−3.040	
Schoch *et al.* (1941)	17	–	311	11.3 – 41.4	0.55	12	–	1.441		−1.441		1.442		−1.513	
Schoch *et al.* (1941)	17	–	344	11.9 – 41.4	0.55	13	–	0.954		−0.954		0.972		−1.200	
Schoch *et al.* (1941)	17	–	378	12.5 – 41.4	0.56	13	–	2.042		−2.042		2.105		−2.786	
Schoch *et al.* (1941)	19	–	311	9.1 – 41.4	0.63	14	–	1.379		−1.379		1.383		−1.522	
Schoch *et al.* (1941)	17	–	344	9.8 – 41.4	0.63	13	–	0.879		−0.879		0.882		−0.981	
Schoch *et al.* (1941)	18	–	378	10.1 – 41.4	0.63	14	–	2.088		−2.088		2.112		−2.553	

Table A2.1 (continued)

Authors	Number of			Covered ranges						Statistical analysis^n					
	data points		Temp.	Pressure	Compos.^{c,d}	N_1	N_2	AAD$_1$	AAD$_2$	Bias$_1$	Bias$_2$	RMS$_1$	RMS$_2$	MaxD$_1$	MaxD$_2$
	total^a	used^b	T/K	p/MPa	x			%	%	%	%	%	%	%	%
$(1-x)$ $CH_4 + x$ n-C_6H_{14} (continued)															
***pρT* data (continued)**						**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA
Schoch *et al.* (1941)	18	–	311	7.1 – 41.4	0.70	15	–	1.332		−1.332		1.343		−1.826	
Schoch *et al.* (1941)	18	–	344	7.9 – 41.4	0.70	15	–	0.926		−0.926		0.964		−1.935	
Schoch *et al.* (1941)	18	–	378	7.9 – 41.4	0.71	15	–	1.972		−1.972		1.991		−2.832	
Schoch *et al.* (1941)	19	–	311	5.1 – 41.4	0.78	15	–	1.351		−1.351		1.355		−1.531	
Schoch *et al.* (1941)	19	–	344	5.6 – 41.4	0.78	17	–	0.885		−0.885		0.959		−2.147	
Schoch *et al.* (1941)	19	–	311	4.2 – 41.4	0.82	17	–	1.252		−1.252		1.274		−2.041	
Schoch *et al.* (1941)	20	–	344	3.9 – 41.4	0.84	18	–	0.588		−0.588		0.636		−1.463	
Schoch *et al.* (1941)	19	–	378	4.5 – 41.4	0.84	19	–	1.492		−1.492		1.587		−3.123	
Shim & Kohn (1962)	141	102	183 – 423	0.5 – 19.6	0.01 – 0.99	131	–	1.240		−0.564		1.597		4.690	
Watson & Millington (1998)	51	51	315 – 353	7.9 – 17.6	0.005	51	51	0.008	0.062	−0.001	−0.049	0.011	0.070	−0.028	−0.121
Watson & Millington (1998)	46	46	314 – 353	7.8 – 17.6	0.010	46	46	0.123	0.233	−0.123	−0.232	0.125	0.245	−0.190	−0.374
VLE data						**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP
Chen *et al.* (1976)^y	114	–	191 – 273	0.1 – 18.4	0.00 – 0.07	43	45	10.555	9.823	3.400	−4.292	13.666	12.161	29.458	−29.746
Gunn *et al.* (1974)^y	16	–	311 – 411	0.3 – 1.7	0.03 – 0.48	16	16	4.051	4.751	2.170	−2.917	4.957	5.859	9.683	−14.412
Lin *et al.* (1977)^e	160	–	182 – 273	0.1 – 18.4	0.00 – 0.99	118	132	9.703	5.445	−9.454	−0.674	12.429	7.768	−29.500	−28.602
Poston & McKetta (1966a)	39	13	311 – 444	2.5 – 19.8	0.24 – 0.98	32	36	6.455	5.436	0.210	−2.288	8.601	6.759	26.977	−13.603
Shim & Kohn (1962)^e	110	39	183 – 423	0.5 – 19.6	0.25 – 0.99	105	109	5.055	3.912	−2.825	0.583	7.319	5.384	−26.391	−17.324
Srivastan *et al.* (1992)^x	33	–	311 – 378	1.1 – 8.5	0.68 – 0.95	33	33	2.451	1.766	1.271	−1.619	2.601	2.372	4.954	−4.375
$(1-x)$ $CH_4 + x$ n-C_7H_{16}															
***pρT* data**						**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA
Reamer *et al.* (1956)	192	–	278 – 511	1.4 – 24.9	0.00 – 0.99	186	–	1.390		0.441		1.811		−4.502	
Reamer *et al.* (1956)	246	37	278 – 511	2.3 – 69.0	0.25	162	–	2.170		0.342		2.490		4.952	
Reamer *et al.* (1956)	161	74	278 – 511	2.7 – 69.4	0.55	109	–	1.623		0.937		1.806		−4.857	
Reamer *et al.* (1956)	259	90	278 – 511	0.3 – 68.2	0.80	127	–	0.814		0.063		1.255		−4.507	
Reamer *et al.* (1956)	180	91	278 – 511	0.4 – 69.8	0.90	114	–	0.473		−0.047		0.971		−4.865	

Table A2.1 (continued)

Authors	Number of data points		Covered ranges					Statistical analysis[n]							
	total[a]	used[b]	Temp. T/K	Pressure p/MPa	Compos.[c,d] x	N_1	N_2	AAD_1 %	AAD_2 %	$Bias_1$ %	$Bias_2$ %	RMS_1 %	RMS_2 %	$MaxD_1$ %	$MaxD_2$ %
(1 − x) CH_4 + x n-C_7H_{16} (continued)															
VLE data						**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP
Chang *et al.* (1966)	69	–	200 – 255	0.007 – 5.5	0.10 – 0.96	–	30		7.138		6.980		8.592		16.076
Chen *et al.* (1976)[y]	53	–	233 – 278	0.1 – 22.6	0.00 – 0.07	24	23	9.702	6.769	0.072	−3.723	11.640	8.496	−26.173	−17.457
Reamer *et al.* (1956)	96	44	278 – 511	1.4 – 24.9	0.11 – 0.99	85	86	5.880	2.656	−1.235	0.220	7.594	3.242	−23.793	7.325
(1 − x) CH_4 + x n-C_8H_{18}															
$p\rho T$ data						**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA
Kohn & Bradish (1964)	68	68	298 – 423	1.0 – 7.1	0.00 – 0.97	68	–	0.506		0.126		0.671		−1.417	
Kohn & Bradish (1964)	21	21	223 – 273	1.0 – 7.1	0.53 – 0.95	21	–	0.292		−0.132		0.367		−0.667	
Speed of sound						**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA
Barreau *et al.* (1993)	144	71	293 – 373	25.0 – 100	0.02	141	142	0.893	1.323	−0.056	0.291	1.249	1.677	−4.724	−4.999
VLE data						**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP
Kohn & Bradish (1964)[e]	35	28	298 – 423	1.0 – 7.1	0.71 – 0.97	35	35	7.402	2.131	−2.901	0.189	9.852	2.574	−28.255	7.353
(1 − x) CH_4 + x H_2															
$p\rho T$ data						**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA
Jaeschke *et al.* (1997)	68	67	273 – 353	0.4 – 30.5	0.15	67	67	0.017	0.012	−0.011	0.002	0.023	0.019	−0.078	−0.087
Jaeschke *et al.* (1997)	166	166	273 – 353	0.5 – 28.1	0.15	166	166	0.015	0.023	−0.011	0.014	0.019	0.031	0.071	0.101
Jaeschke *et al.* (1997)	188	188	270 – 350	0.5 – 28.7	0.25	188	188	0.028	0.045	0.016	0.042	0.033	0.056	0.065	0.133
Jaeschke *et al.* (1997)	83	83	275 – 350	0.2 – 26.1	0.50	83	83	0.015	0.014	−0.011	−0.006	0.021	0.020	−0.078	−0.080
Jaeschke *et al.* (1997)	126	126	270 – 350	0.5 – 28.9	0.50	126	126	0.015	0.019	−0.004	0.006	0.022	0.026	−0.104	−0.106
Jaeschke *et al.* (1997)	83	83	275 – 350	0.3 – 26.1	0.75	83	83	0.014	0.024	−0.007	−0.024	0.022	0.050	−0.117	−0.263
Jaeschke *et al.* (1997)	185	185	270 – 350	0.5 – 29.1	0.75	185	185	0.016	0.049	0.006	−0.042	0.021	0.063	−0.051	−0.205
Jett *et al.* (1994)	115	–	154 – 273	2.2 – 68.2	0.05	110	–	0.430		0.023		0.867		−5.133	
Machado *et al.* (1988)	20	20	140	6.3 – 105	0.08	20	–	0.750		0.055		1.141		−3.757	
Machado *et al.* (1988)	8	8	130	5.3 – 29.3	0.09	5	–	2.621		−2.621		2.794		−4.285	

Table A2.1 (continued)

Authors	Number of data points		Covered ranges					Statistical analysis[n]							
	total[a]	used[b]	Temp. T/K	Pressure p/MPa	Compos.[c,d] x	N_1	N_2	AAD_1 %	AAD_2 %	$Bias_1$ %	$Bias_2$ %	RMS_1 %	RMS_2 %	$MaxD_1$ %	$MaxD_2$ %
(1 − x) CH_4 + x H_2 (continued)															
***pρT* data (continued)**						**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA
Machado *et al.* (1988)	49	49	130 – 159	9.0 – 104	0.10	48	–	0.601		−0.262		1.068		−4.680	
Machado *et al.* (1988)	33	33	159 – 159	10.2 – 105	0.15	33	–	0.302		0.172		0.329		−0.650	
Machado *et al.* (1988)	17	17	140	20.9 – 106	0.28	17	–	0.228		0.068		0.246		−0.411	
Machado *et al.* (1988)	15	15	130	23.0 – 103	0.29	15	–	0.379		0.309		0.406		0.645	
Machado *et al.* (1988)	37	37	159	15.6 – 98.1	0.30	37	–	0.875		−0.400		1.302		−4.064	
Machado *et al.* (1988)	16	16	140	26.7 – 107	0.59	16	–	0.696		0.023		0.855		−2.274	
Machado *et al.* (1988)	9	9	159	65.6 – 91.5	0.60	9	–	1.573		1.481		1.684		2.191	
Machado *et al.* (1988)	16	16	140	25.4 – 105	0.71	16	–	1.711		1.711		1.838		2.516	
Machado *et al.* (1988)	16	16	130	28.8 – 104	0.77	16	–	1.436		1.436		1.470		1.997	
Machado *et al.* (1988)	22	22	159	14.8 – 101	0.81	22	–	0.540		0.540		0.547		0.773	
Machado *et al.* (1988)	18	18	140	3.4 – 105	0.90	18	–	0.520		0.225		0.736		−2.549	
Machado *et al.* (1988)	20	20	130	1.7 – 105	0.91	20	–	1.057		0.807		1.275		−2.385	
Magee *et al.* (1985)	135	135	273 – 600	3.5 – 58.2	0.20	135	135	0.287	0.217	−0.261	−0.178	0.312	0.251	−0.709	−0.651
Mihara *et al.* (1977)	15	–	298	0.4 – 7.9	0.22	15	15	0.133	0.127	−0.133	−0.127	0.182	0.171	−0.417	−0.384
Mihara *et al.* (1977)	31	–	323 – 348	0.4 – 8.5	0.26	31	31	0.061	0.054	−0.059	−0.052	0.097	0.086	−0.283	−0.252
Mihara *et al.* (1977)	15	–	298	0.4 – 9.1	0.43	15	15	0.276	0.268	−0.276	−0.268	0.362	0.350	−0.808	−0.782
Mihara *et al.* (1977)	30	–	323 – 348	0.4 – 8.7	0.46	30	30	0.134	0.130	−0.134	−0.130	0.186	0.179	−0.469	−0.453
Mihara *et al.* (1977)	15	–	298	0.3 – 7.8	0.58	15	15	0.220	0.212	−0.220	−0.212	0.286	0.276	−0.624	−0.608
Mihara *et al.* (1977)	32	–	323 – 348	0.3 – 9.2	0.66	32	32	0.097	0.100	−0.097	−0.100	0.135	0.139	−0.364	−0.378
Mihara *et al.* (1977)	15	–	298	0.4 – 9.2	0.68	15	15	0.223	0.217	−0.223	−0.217	0.286	0.281	−0.621	−0.623
Solbrig & Ellington (1963)	98	98	139 – 422	1.2 – 22.8	0.91	98	98	0.189	0.253	0.057	0.139	0.230	0.316	−0.859	0.922
VLE data						**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP
Benham & Katz (1957)	13	10	116 – 172	3.4 – 27.6	0.02 – 0.35	11	12	5.702	13.415	0.085	13.255	6.832	15.143	14.356	25.760
Fastowsky & Gonikberg (1940)	31	23	90.3 – 127	3.1 – 22.9	0.02 – 0.16	27	27	9.543	10.308	0.141	5.651	12.681	12.369	28.961	25.154
Freeth & Verschoyle (1931)	13	13	90.7	2.2 – 20.8	0.01 – 0.10	8	7	14.356	15.638	−3.198	−9.667	16.836	18.640	28.492	−28.914
Sagara *et al.* (1972)	28	23	103 – 174	1.0 – 10.8	0.00 – 0.23	28	28	8.316	12.922	−2.686	9.069	10.940	13.469	−24.838	−22.274

Table A2.1 (continued)

Authors	Number of data points		Covered ranges			Statistical analysis[n]									
	total[a]	used[b]	Temp. T/K	Pressure p/MPa	Compos.[c,d] x	N_1	N_2	AAD$_1$ %	AAD$_2$ %	Bias$_1$ %	Bias$_2$ %	RMS$_1$ %	RMS$_2$ %	MaxD$_1$ %	MaxD$_2$ %
(1 − x) CH_4 + x H_2 (continued)															
VLE data (continued)						**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP
Yorizane *et al.* (1968b)	25	21	103 – 163	1.0 – 15.2	0.00 – 0.29	20	18	15.097	14.481	−0.116	8.554	17.560	16.520	−28.392	26.093
(1 − x) CH_4 + x O_2															
VLE data						**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP
Hodges & Burch (1967)	3	–	93.2 – 107	0.1 – 0.4	0.999	3	3	0.130	0.127	−0.130	0.010	0.155	0.137	−0.235	−0.176
(1 − x) CH_4 + x CO															
***pρT* data**						**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA
Calado *et al.* (1984)	22	13	116 – 120	4.9 – 126	0.29	22	–	1.159		−0.892		1.735		−4.057	
Calado *et al.* (1984)	17	17	120	3.6 – 119	0.46	17	–	0.306		−0.013		0.348		−0.631	
Calado *et al.* (1984)	35	35	116 – 125	2.0 – 160	0.48	35	–	0.479		−0.043		0.533		−0.900	
Calado *et al.* (1984)	24	24	116 – 120	2.9 – 128	0.69	24	–	0.229		0.070		0.283		0.629	
Calado *et al.* (1984)	13	13	120	7.6 – 128	0.80	13	–	0.248		0.204		0.335		0.687	
Jaeschke *et al.* (1997)	61	61	273 – 353	0.4 – 30.2	0.03	61	61	0.009	0.006	0.008	0.003	0.012	0.009	0.025	0.027
Jaeschke *et al.* (1997)	284	284	273 – 353	0.5 – 29.4	0.03	284	284	0.007	0.007	0.004	−0.002	0.008	0.009	0.024	−0.028
VLE data						**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP
Cheung & Wang (1964)	22	22	91.4 – 124	0.03 – 0.5	0.03 – 0.25	22	22	10.919	4.323	10.677	−3.742	12.530	5.133	24.171	−13.425
Christiansen *et al.* (1973)	33	32	123 – 178	0.4 – 4.7	0.03 – 0.97	32	32	1.938	3.248	−0.951	−3.248	2.368	3.890	5.231	−8.619
(1 − x) CH_4 + x H_2O															
***pρT* data**						**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA
Abdulagatov *et al.* (1993a)	64	–	523 – 653	2.2 – 63.2	0.15 – 0.95	60	56	2.106	2.206	−0.670	1.045	2.686	3.285	−6.786	9.593
Abdulagatov *et al.* (1993b)	64	–	523 – 653	2.2 – 63.2	0.15 – 0.96	60	58	2.351	2.295	−1.615	0.802	3.089	3.415	−8.124	9.751
Fenghour *et al.* (1996a)	16	16	430 – 698	7.5 – 12.7	0.08	16	16	0.122	0.365	0.122	0.365	0.127	0.390	0.188	0.576
Fenghour *et al.* (1996a)	14	14	466 – 698	9.0 – 14.1	0.17	14	14	0.326	0.947	0.326	0.947	0.358	0.982	0.835	1.696

Table A2.1 (continued)

Authors	Number of data points total[a]	used[b]	Covered ranges Temp. T/K	Pressure p/MPa	Compos.[c,d] x	N_1	N_2	Statistical analysis[n] AAD_1 %	AAD_2 %	Bias_1 %	Bias_2 %	RMS_1 %	RMS_2 %	MaxD_1 %	MaxD_2 %
$(1-x)$ $CH_4 + x$ H_2O (continued)															
***pρT* data (continued)**						**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA
Fenghour *et al.* (1996a)	12	12	501 – 699	10.7 – 15.7	0.26	12	12	0.352	1.390	0.352	1.390	0.367	1.410	0.624	1.880
Fenghour *et al.* (1996a)	11	11	519 – 699	12.1 – 17.2	0.34	11	11	0.437	1.932	0.437	1.932	0.468	1.956	0.863	2.554
Fenghour *et al.* (1996a)	9	9	554 – 699	14.2 – 18.8	0.40	9	9	0.312	2.283	0.312	2.283	0.342	2.303	0.622	2.832
Fenghour *et al.* (1996a)	8	8	572 – 699	15.8 – 20.5	0.46	8	8	0.247	2.774	0.247	2.774	0.308	2.799	0.637	3.435
Fenghour *et al.* (1996a)	6	6	608 – 699	19.3 – 23.5	0.54	6	6	0.153	3.556	−0.028	3.556	0.168	3.578	0.290	4.204
Fenghour *et al.* (1996a)	5	5	625 – 698	22.1 – 26.2	0.60	5	5	0.236	4.525	−0.189	4.525	0.258	4.547	−0.350	5.221
Fenghour *et al.* (1996a)	6	6	653 – 698	27.0 – 30.4	0.68	6	6	0.581	6.031	−0.581	6.031	0.591	6.043	−0.697	6.635
Joffrion & Eubank (1988)	48	48	398 – 498	0.2 – 12.0	0.10	48	48	0.087	0.048	−0.087	0.041	0.114	0.113	−0.262	0.483
Joffrion & Eubank (1988)	61	59	398 – 498	0.1 – 8.7	0.25	59	57	0.080	0.075	−0.036	0.065	0.112	0.144	0.338	0.476
Joffrion & Eubank (1988)	60	59	398 – 498	0.1 – 4.2	0.50	59	59	0.053	0.054	0.049	0.037	0.089	0.123	0.296	0.704
$(1-x)$ $CH_4 + x$ He															
VLE data						**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP
DeVaney *et al.* (1971)	47	47	124 – 191	1.4 – 6.9	0.00 – 0.06	35	–	5.539		5.539		5.944		13.025	
Fontaine (1989)	100	100	100 – 185	0.1 – 9.6	0.00 – 0.06	71	–	14.929		−8.666		17.119		29.556	
Fontaine (1989)	170	170	94.0 – 191	0.5 – 26.2	0.00 – 0.24	110	–	9.243		3.999		11.566		−29.599	
Heck & Hiza (1967)[e,f]	70	45	95.0 – 185	0.5 – 20.5	0.00 – 0.14	27	–	11.434		2.477		13.205		−25.967	
Rhodes *et al.* (1971)	82	82	94.0 – 194	6.9 – 26.2	0.00 – 0.34	47	–	11.682		10.793		13.620		29.322	
Sinor *et al.* (1966)[e]	51	45	93.2 – 191	1.7 – 13.8	0.00 – 0.27	24	–	6.598		−2.046		9.367		−26.868	
$(1-x)$ $CH_4 + x$ Ar															
***pρT* data**						**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA
Barreiros & Nunes da Ponte (1989)	10	10	143	3.5 – 122	0.50	10	–	0.208		0.208		0.209		0.233	
Liu & Miller (1972)	26	26	91.0 – 120	0.1 – 0.8	0.15 – 0.84	26	–	0.430		−0.383		0.485		−1.012	

Table A2.1 (continued)

Authors	Number of data points total[a]	used[b]	Covered ranges Temp. T/K	Pressure p/MPa	Compos.[c,d] x	N_1	N_2	Statistical analysis[n] AAD_1 %	AAD_2 %	Bias_1 %	Bias_2 %	RMS_1 %	RMS_2 %	MaxD_1 %	MaxD_2 %
(1 − x) CH_4 + x Ar (continued)															
VLE data						**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP
Calado & Staveley (1972)	8	6	116	0.3 – 0.8	0.18 – 0.80	8	8	0.701	1.095	0.115	0.427	1.060	1.460	−2.110	2.696
Christiansen *et al.* (1973)	34	29	151 – 178	1.2 – 5.1	0.02 – 0.94	34	33	1.866	1.408	−1.761	−1.270	2.101	1.588	−3.329	−2.764
Duncan & Hiza (1972)[e,f]	72	1	105 – 126	0.2 – 1.5	0.10 – 0.88	71	71	0.530	0.492	−0.234	0.089	0.637	0.607	−2.064	1.514
Elshayal & Lu (1975)	6	5	115	0.2 – 0.9	0.06 – 0.96	6	6	1.558	1.782	1.558	1.729	1.893	2.161	2.836	3.738
Jin *et al.* (1993)	12	10	123	0.3 – 1.3	0.07 – 0.95	12	12	0.840	1.086	0.545	0.682	0.961	1.248	1.866	2.228
Shatskaya & Zhirnova (1976)	31	–	113 – 133	0.2 – 2.2	0.03 – 0.96	31	31	3.178	3.356	1.137	1.254	3.857	3.954	−11.744	−10.614
(1 − x) N_2 + x CO_2															
***pρT* data**						**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA
Arai *et al.* (1971)	2	–	253	6.8 – 13.1	0.47	2	–	1.503		0.038		1.503		1.541	
Arai *et al.* (1971)	10	–	273	2.4 – 14.5	0.49	10	–	0.508		−0.463		0.717		−1.423	
Arai *et al.* (1971)	2	–	253	4.8 – 14.4	0.57	2	–	0.811		−0.221		0.841		−1.032	
Arai *et al.* (1971)	9	–	273	3.0 – 12.9	0.58	9	–	0.464		0.464		0.503		0.717	
Arai *et al.* (1971)	7	–	273	9.1 – 14.5	0.63	6	–	1.009		−1.009		1.046		−1.344	
Arai *et al.* (1971)	8	–	273	2.7 – 9.1	0.63	8	–	0.307		0.241		0.375		0.763	
Arai *et al.* (1971)	2	–	253	3.6 – 14.3	0.65	2	–	1.949		1.949		2.577		3.636	
Arai *et al.* (1971)	7	–	273	6.6 – 14.5	0.69	7	–	0.752		−0.302		0.919		−1.359	
Arai *et al.* (1971)	12	–	273 – 288	2.4 – 14.5	0.70	12	–	0.963		0.866		1.363		3.397	
Arai *et al.* (1971)	7	–	288	2.6 – 14.5	0.74	7	–	1.788		1.788		2.072		3.698	
Arai *et al.* (1971)	7	–	273	5.7 – 14.5	0.75	7	–	2.553		2.553		2.886		4.673	
Arai *et al.* (1971)	2	–	253	2.9 – 12.8	0.76	2	–	2.567		2.567		2.875		3.862	
Arai *et al.* (1971)	5	–	273	2.4 – 4.9	0.79	5	–	0.292		0.292		0.308		0.416	
Arai *et al.* (1971)	9	–	288	8.5 – 14.5	0.80	9	–	1.894		1.894		1.993		2.684	
Arai *et al.* (1971)	1	–	288	9.1	0.80	1	–	2.506		2.506		2.506		2.506	
Arai *et al.* (1971)	8	–	288	8.1 – 13.6	0.81	8	–	2.299		2.296		2.657		3.254	
Arai *et al.* (1971)	2	–	288	8.3 – 9.6	0.81	2	–	0.555		0.555		0.559		0.623	

Table A2.1 (continued)

Authors	Number of data points total[a]	used[b]	Covered ranges Temp. T/K	Pressure p/MPa	Compos.[c,d] x	N_1	N_2	Statistical analysis[n] AAD$_1$ %	AAD$_2$ %	Bias$_1$ %	Bias$_2$ %	RMS$_1$ %	RMS$_2$ %	MaxD$_1$ %	MaxD$_2$ %
$(1-x)$ $N_2 + x$ CO_2 (continued)															
***pρT* data (continued)**						**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA
Arai *et al.* (1971)	4	–	288	2.4 – 7.5	0.81	4	–	0.552		0.552		0.623		0.907	
Arai *et al.* (1971)	7	–	288	7.6 – 13.7	0.83	7	–	2.109		2.097		2.486		4.006	
Arai *et al.* (1971)	2	–	253	2.5 – 10.6	0.83	2	–	2.347		2.347		2.451		3.055	
Arai *et al.* (1971)	6	–	288	7.2 – 11.4	0.85	6	–	1.397		1.397		1.473		2.225	
Arai *et al.* (1971)	11	–	253 – 288	2.4 – 14.5	0.87	10	–	2.026		2.026		2.184		3.113	
Arai *et al.* (1971)	8	–	273	4.3 – 14.5	0.87	8	–	3.123		3.123		3.306		4.465	
Arai *et al.* (1971)	13	–	288	2.4 – 14.5	0.90	13	–	2.232		2.232		2.514		3.428	
Arai *et al.* (1971)	5	–	288	2.4 – 6.0	0.92	5	–	1.881		1.881		1.889		2.200	
Arai *et al.* (1971)	8	–	273	3.9 – 14.5	0.93	8	–	3.298		3.298		3.465		4.582	
Arai *et al.* (1971)	9	–	288	5.7 – 13.7	0.94	9	–	3.187		3.187		3.294		3.653	
Brugge *et al.* (1989b)	38	–	300 – 320	0.2 – 9.8	0.11	38	38	0.008	0.010	−0.001	0.001	0.010	0.013	0.027	0.027
Brugge *et al.* (1989b)	40	20	300 – 320	0.2 – 10.6	0.25	40	40	0.007	0.010	0.003	0.009	0.013	0.017	0.069	0.072
Brugge *et al.* (1989b)	40	–	300 – 320	0.2 – 10.2	0.50	40	40	0.031	0.037	0.002	0.036	0.047	0.079	0.173	0.333
Brugge *et al.* (1989b)	40	20	300 – 320	0.2 – 9.7	0.71	40	40	0.054	0.056	−0.054	0.056	0.059	0.115	−0.105	0.448
Brugge *et al.* (1989b)	38	–	300 – 320	0.2 – 7.3	0.91	38	38	0.074	0.015	−0.074	0.012	0.086	0.033	−0.154	0.137
Brugge *et al.* (1997)	141	74	225 – 450	1.3 – 69.2	0.11	140	–	0.155		−0.006		0.188		0.462	
Brugge *et al.* (1997)	149	115	225 – 450	1.2 – 69.2	0.25	148	–	0.307		−0.061		0.399		−1.008	
Brugge *et al.* (1997)	174	101	225 – 450	1.1 – 69.2	0.50	152	–	0.165		0.036		0.201		0.491	
Brugge *et al.* (1997)	150	90	225 – 450	1.1 – 69.1	0.71	150	–	0.185		0.065		0.241		−0.631	
Brugge *et al.* (1997)	135	74	225 – 450	1.0 – 69.1	0.91	123	–	0.111		0.057		0.149		0.466	
Duarte-Garza *et al.* (1995)	11	10	300	30.1 – 69.0	0.40	11	11	0.366	1.449	0.366	−1.051	0.904	1.479	2.978	2.189
Duarte-Garza *et al.* (1995)	40	–	210 – 300	16.7 – 65.0	0.40	40	–	0.398		−0.282		0.595		−1.890	
Duarte-Garza *et al.* (1995)	6	–	210 – 239	15.9 – 21.3	0.40	6	–	0.805		−0.791		0.953		−1.433	
Duarte-Garza *et al.* (1995)	24	–	222 – 300	18.2 – 64.3	0.45	24	–	0.819		−0.819		0.909		−1.625	
Duarte-Garza *et al.* (1995)	3	–	214 – 225	18.1 – 20.6	0.45	3	–	1.883		−1.883		1.902		−2.266	
Duarte-Garza *et al.* (1995)	40	12	285 – 300	1.2 – 69.2	0.50	40	40	0.173	0.962	−0.020	−0.787	0.223	1.214	−0.742	2.105

Table A2.1 (continued)

Authors	Number of data points total[a]	used[b]	Covered ranges Temp. T/K	Pressure p/MPa	Compos.[c,d] x	Statistical analysis[n] N_1	N_2	AAD$_1$ %	AAD$_2$ %	Bias$_1$ %	Bias$_2$ %	RMS$_1$ %	RMS$_2$ %	MaxD$_1$ %	MaxD$_2$ %
(1 − *x*) N_2 + *x* CO_2 (continued)															
***pρT* data (continued)**						**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA
Duarte-Garza *et al.* (1995)	141	–	214 – 300	7.5 – 77.5	0.50	141	–	1.257		0.689		1.835		4.229	
Duarte-Garza *et al.* (1995)	14	–	209 – 268	10.8 – 21.4	0.50	14	–	2.857		2.152		3.239		4.765	
Ely *et al.* (1989)	64	–	300 – 330	2.3 – 33.1	0.98	64	64	0.140	0.410	0.074	−0.410	0.183	0.532	0.442	−1.302
Esper (1987)	153	113	220 – 320	0.1 – 48.4	0.45	149	–	0.175		−0.102		0.428		−2.406	
Gasunie (1990)	21	–	293 – 308	3.8 – 6.0	0.25	21	21	0.058	0.063	−0.058	−0.063	0.058	0.065	−0.074	−0.083
Gaz de France (1990)	19	19	279 – 308	2.0 – 7.0	0.10	19	19	0.046	0.052	−0.046	−0.052	0.049	0.055	−0.074	−0.085
Gaz de France (1990)	20	20	278 – 308	2.0 – 7.0	0.32	20	20	0.061	0.071	−0.061	−0.071	0.063	0.074	−0.095	−0.121
Hacura *et al.* (1988)	110	–	323 – 348	49.0 – 222	0.25	110	–	0.428		−0.242		0.556		−1.134	
Hacura *et al.* (1988)	72	–	323 – 348	63.3 – 224	0.57	64	–	7.706		−7.706		7.836		−9.964	
Hacura *et al.* (1988)	74	–	323 – 348	56.4 – 274	0.74	74	–	4.220		−4.220		4.366		−7.407	
Haney & Bliss (1944)	22	–	298 – 398	7.6 – 50.7	0.25	22	22	0.227	0.252	0.218	−0.099	0.283	0.338	0.665	−0.958
Haney & Bliss (1944)	22	–	298 – 398	7.6 – 50.7	0.50	22	22	0.176	0.571	0.124	−0.378	0.204	0.788	0.475	−1.680
Jiang *et al.* (1990)	10	–	293	0.6 – 4.5	0.27	10	10	0.002	0.005	0.001	−0.001	0.003	0.006	0.005	−0.015
Jiang *et al.* (1990)	9	–	293	0.6 – 4.1	0.47	9	9	0.059	0.080	0.059	0.080	0.064	0.084	0.088	0.109
Jiang *et al.* (1990)	11	–	293	0.6 – 5.2	0.54	11	11	0.019	0.059	0.017	0.059	0.024	0.062	0.042	0.082
Jiang *et al.* (1990)	11	–	293	0.6 – 4.7	0.70	11	11	0.025	0.099	−0.025	0.099	0.034	0.104	−0.085	0.136
Kosov & Brovanov (1975)	31	–	313 – 353	5.9 – 58.8	0.23	31	31	0.711	0.327	0.616	0.110	0.738	0.517	−1.478	−2.329
Kosov & Brovanov (1975)	31	–	313 – 353	6.0 – 58.8	0.47	31	31	1.853	1.064	1.853	1.057	1.870	1.256	2.321	2.299
Kosov & Brovanov (1975)	31	–	313 – 353	6.0 – 58.8	0.68	31	31	4.822	3.599	4.822	3.599	5.014	3.963	8.507	7.787
Kritschewsky & Markov (1940)	30	–	273 – 473	5.1 – 50.7	0.24	29	29	1.669	1.391	1.669	1.382	1.773	1.614	3.145	3.180
Kritschewsky & Markov (1940)	24	–	323 – 473	5.1 – 50.7	0.47	24	24	2.104	2.175	1.888	1.617	2.813	2.868	6.708	6.773
Rivkin (1975)	43	–	273 – 473	0.4 – 10.0	0.18	43	43	0.061	0.071	0.050	0.063	0.104	0.122	0.345	0.400
Rivkin (1975)	43	–	273 – 472	0.4 – 9.5	0.33	43	43	0.193	0.215	0.189	0.214	0.296	0.320	0.846	0.807
Rivkin (1975)	44	–	273 – 473	0.4 – 9.7	0.42	44	44	0.168	0.193	0.135	0.167	0.274	0.299	0.891	0.931
Rivkin (1975)	45	–	273 – 473	0.4 – 9.4	0.60	45	45	0.172	0.225	0.150	0.212	0.285	0.338	1.071	1.162
Rivkin (1975)	43	–	273 – 473	0.4 – 9.7	0.73	43	43	0.053	0.094	0.003	0.090	0.080	0.135	0.300	0.479

Table A2.1 (continued)

Authors	Number of data points		Temp.	Covered ranges Pressure	Compos.[c,d]			Statistical analysis[n]							
	total[a]	used[b]	T/K	p/MPa	x	N_1	N_2	AAD$_1$ %	AAD$_2$ %	Bias$_1$ %	Bias$_2$ %	RMS$_1$ %	RMS$_2$ %	MaxD$_1$ %	MaxD$_2$ %
$(1-x)$ N_2 + x CO_2 (continued)															
***pρT* data (continued)**						**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA
Rivkin (1975)	39	–	273 – 473	0.4 – 9.1	0.90	39	39	0.084	0.081	−0.042	0.027	0.167	0.151	−0.762	−0.638
Rivkin (1975)	39	–	273 – 473	0.4 – 8.8	0.98	39	39	0.069	0.079	0.036	0.054	0.096	0.114	0.305	0.422
Ruhrgas (1990), Bu	46	46	330	0.2 – 26.2	0.29	46	46	0.023	0.030	0.015	0.020	0.034	0.043	0.121	−0.125
Ruhrgas (1990), Op	109	109	275 – 350	0.2 – 12.0	0.25	109	109	0.009	0.013	−0.004	−0.002	0.013	0.019	−0.084	0.068
Seitz & Blencoe (1996)	5	–	673	19.9 – 99.9	0.10	5	5	0.460	0.481	0.385	0.432	0.490	0.518	0.710	0.642
Seitz & Blencoe (1996)	6	–	673	19.9 – 99.9	0.20	6	6	0.622	0.528	0.607	0.528	0.680	0.576	0.921	0.732
Seitz & Blencoe (1996)	6	–	673	19.9 – 99.9	0.30	6	6	0.640	0.513	0.632	0.513	0.717	0.546	1.047	0.698
Seitz & Blencoe (1996)	6	–	673	19.9 – 99.9	0.40	6	6	0.668	0.550	0.646	0.550	0.739	0.596	1.020	0.865
Seitz & Blencoe (1996)	6	–	673	19.9 – 99.9	0.50	6	6	0.667	0.633	0.667	0.633	0.722	0.679	0.935	0.955
Seitz & Blencoe (1996)	6	–	673	19.9 – 99.9	0.60	6	6	0.546	0.597	0.546	0.597	0.608	0.637	0.851	0.895
Seitz & Blencoe (1996)	6	–	673	19.9 – 99.9	0.70	6	6	0.427	0.572	0.427	0.572	0.478	0.623	0.631	0.921
Seitz & Blencoe (1996)	6	–	673	19.9 – 99.9	0.80	6	6	0.328	0.565	0.328	0.565	0.347	0.627	0.471	0.875
Seitz & Blencoe (1996)	4	–	673	19.9 – 79.9	0.90	4	4	0.097	0.494	0.019	0.494	0.114	0.525	0.196	0.618
Seitz *et al.* (1996a)	15	–	323 – 573	9.9 – 99.9	0.10	15	15	0.432	0.361	0.432	0.129	0.489	0.449	1.165	1.167
Seitz *et al.* (1996a)	21	–	323 – 573	9.9 – 99.9	0.20	21	21	0.607	0.516	0.607	0.227	0.682	0.639	1.545	1.599
Seitz *et al.* (1996a)	24	–	323 – 573	9.9 – 99.9	0.30	24	24	0.566	0.531	0.559	0.127	0.628	0.635	1.342	1.303
Seitz *et al.* (1996a)	22	–	323 – 573	9.9 – 99.9	0.40	22	22	0.552	0.589	0.432	−0.037	0.636	0.724	1.488	1.480
Seitz *et al.* (1996a)	24	–	323 – 573	9.9 – 99.9	0.50	24	24	0.435	0.636	0.422	−0.060	0.543	0.792	1.666	1.682
Seitz *et al.* (1996a)	23	–	323 – 573	9.9 – 99.9	0.60	23	23	0.337	0.617	0.337	−0.119	0.461	0.788	1.472	−1.593
Seitz *et al.* (1996a)	23	–	323 – 573	9.9 – 99.9	0.70	23	23	0.291	0.714	0.274	−0.268	0.422	0.887	1.567	−1.661
Seitz *et al.* (1996a)	22	–	323 – 573	9.9 – 99.9	0.80	22	22	0.270	0.663	0.125	−0.348	0.419	0.807	1.177	−1.945
Seitz *et al.* (1996a)	18	–	323 – 573	9.9 – 99.9	0.90	17	17	0.188	0.547	0.050	−0.351	0.283	0.690	0.958	−1.623
Speed of sound						**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA
Younglove *et al.* (1993)	65	65	250 – 350	0.5 – 10.3	0.50	65	65	0.069	0.225	−0.042	−0.224	0.135	0.304	−0.702	−0.939

Table A2.1 (continued)

Authors	Number of data points total[a]	used[b]	Temp. T/K	Covered ranges Pressure p/MPa	Compos.[c,d] x	N_1	N_2	Statistical analysis[n] AAD$_1$ %	AAD$_2$ %	Bias$_1$ %	Bias$_2$ %	RMS$_1$ %	RMS$_2$ %	MaxD$_1$ %	MaxD$_2$ %
$(1-x)$ $N_2 + x$ CO_2 (continued)															
Isobaric heat capacity						**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA
Bishnoi *et al.* (1972)	107	107	313 – 363	0.2 – 16.5	0.68	107	107	0.671	0.498	−0.592	0.196	0.778	0.661	−1.448	−2.531
Bishnoi *et al.* (1972)	96	96	313 – 363	0.2 – 14.5	0.93	91	91	1.401	1.996	−1.385	−1.709	1.744	3.496	−4.355	−12.320
Saturated liquid density[g]						**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP
Duarte-Garza *et al.* (1995)	23	–	209 – 268	10.8 – 21.4	0.40 – 0.50	23	23	2.194	5.197	0.858	−3.688	2.664	6.063	4.765	−10.162
VLE data						**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP
Al-Sahhaf *et al.* (1983)	27	25	220 – 240	1.5 – 16.7	0.52 – 0.99	27	26	2.030	4.632	−1.997	1.261	2.770	5.539	−6.542	−12.004
Arai *et al.* (1971)[e,f]	40	–	253 – 288	2.4 – 14.4	0.65 – 0.94	9	9	2.129	2.807	−0.655	2.807	2.747	3.128	−6.178	4.440
Bian *et al.* (1993)	13	11	301 – 303	7.2 – 8.1	0.96 – 1.00	8	–	1.221		1.173		1.949		4.755	
Brown *et al.* (1989a)	15	15	250 – 270	2.6 – 14.1	0.70 – 0.99	15	15	1.036	2.555	−0.984	0.633	1.253	2.888	−2.795	−6.120
Brown *et al.* (1989b)[f]	59	15	220 – 270	1.0 – 13.0	0.81 – 0.99	21	22	1.467	3.515	−0.710	3.515	2.093	4.282	−4.881	9.500
Duarte-Garza *et al.* (1995)[x]	23	–	209 – 268	10.8 – 21.4	0.40 – 0.50	9	–	6.350		−6.350		6.933		−10.438	
Kaminishi & Toriumi (1966)[e,f]	22	–	233 – 298	3.7 – 12.7	0.63 – 0.97	17	15	7.786	5.670	−7.786	−5.375	10.651	8.434	−26.939	−19.730
Krichevskii *et al.* (1962)	22	–	288 – 303	6.1 – 10.3	0.81 – 0.99	13	11	2.848	2.036	0.043	0.999	3.573	3.354	9.017	9.917
Somait & Kidnay (1978)[f]	35	26	270	3.4 – 12.3	0.65 – 1.00	32	12	0.520	1.247	−0.146	1.025	0.616	1.366	−1.452	1.979
Tsiklis (1946)	7	–	273	3.9 – 6.9	0.81 – 0.96	2	–	3.732		3.732		4.652		6.509	
Xu *et al.* (1992)	18	17	288 – 293	6.0 – 9.7	0.85 – 1.00	17	13	1.223	1.256	−0.678	1.202	1.453	1.595	−2.846	3.964
Yorizane *et al.* (1970)	15	–	273	4.1 – 11.8	0.70 – 0.99	14	13	1.696	2.226	−1.430	0.014	2.436	2.897	−6.459	−7.014
Yorizane *et al.* (1985)	34	–	273 – 298	4.5 – 11.5	0.60 – 0.94	2	–	12.333		−12.333		12.334		−12.538	
Yucelen & Kidnay (1999)[e,f]	19	6	240 – 270	1.7 – 13.0	0.75 – 0.99	15	14	3.401	2.550	−3.358	−1.080	5.450	3.286	−13.144	−7.075
Zenner & Dana (1963)[e]	31	–	218 – 273	1.3 – 13.9	0.70 – 0.99	25	22	2.168	2.134	−1.729	0.850	2.732	2.724	−6.843	−6.187
$(1-x)$ $N_2 + x$ C_2H_6															
***pρT* data**						**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA
Achtermann *et al.* (1991)	183	141	270 – 350	0.2 – 28.7	0.25	183	183	0.038	0.070	−0.010	−0.066	0.046	0.080	−0.122	−0.140
Achtermann *et al.* (1991)	164	99	270 – 350	0.5 – 28.5	0.50	164	164	0.055	0.090	0.021	0.032	0.071	0.110	0.191	0.267

Table A2.1 (continued)

Authors	Number of data points total[a]	used[b]	Covered ranges Temp. T/K	Pressure p/MPa	Compos.[c,d] x	Statistical analysis[n] N_1	N_2	AAD$_1$ %	AAD$_2$ %	Bias$_1$ %	Bias$_2$ %	RMS$_1$ %	RMS$_2$ %	MaxD$_1$ %	MaxD$_2$ %
(1 − x) N_2 + x C_2H_6 (continued)															
***pρT* data (continued)**						**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA
Achtermann *et al.* (1991)	133	133	270 – 350	0.5 – 28.1	0.75	133	133	0.031	0.090	0.004	−0.009	0.038	0.135	0.108	0.410
Eakin *et al.* (1955)	45	44	217 – 305	2.2 – 28.7	0.30	44	–	0.578		0.518		0.642		1.277	
Eakin *et al.* (1955)	32	–	250 – 305	3.7 – 29.3	0.50	32	–	0.999		0.882		1.330		4.869	
Eakin *et al.* (1955)	34	–	253 – 316	3.4 – 30.7	0.70	31	–	1.069		1.054		1.431		4.788	
Eakin *et al.* (1955)	26	–	261 – 316	2.9 – 26.6	0.85	26	–	0.836		0.408		0.975		2.159	
Eakin *et al.* (1955)	21	–	267 – 316	3.2 – 29.8	0.95	20	–	0.460		0.451		0.579		1.243	
Gasunie (1990)	30	30	282 – 309	3.6 – 7.3	0.25	30	30	0.061	0.152	−0.061	−0.152	0.066	0.156	−0.133	−0.233
Hiza *et al.* (1977)	4	4	105 – 120	0.4 – 0.6	0.94	4	–	0.088		0.088		0.092		0.127	
Raabe & Köhler (2004)	27	–	115 – 139	0.6 – 3.3	0.00 – 0.96	19	–	0.694		0.094		0.872		1.858	
Reamer *et al.* (1952a)	38	38	278 – 478	1.4 – 62.1	0.27	38	38	0.380	0.322	0.376	0.315	0.427	0.364	0.910	0.849
Reamer *et al.* (1952a)	39	39	278 – 478	1.4 – 62.1	0.48	39	39	0.279	0.256	−0.003	0.009	0.354	0.327	0.934	0.896
Reamer *et al.* (1952a)	36	36	278 – 478	1.4 – 62.1	0.73	36	36	0.273	0.243	0.123	0.078	0.360	0.318	0.910	0.794
Speed of sound						**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA
Trusler (2000)	45	45	290 – 400	0.1 – 30.1	0.30	45	45	0.073	0.055	−0.073	0.023	0.142	0.075	−0.513	−0.235
Trusler (2000)	67	67	250 – 400	0.05 – 30.2	0.70	67	67	0.037	0.100	−0.006	−0.049	0.070	0.198	−0.278	−0.895
Isobaric heat capacity						**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA
van Kasteren & Zeldenrust (1979)	36	–	110 – 270	3.0 – 5.1	0.41	5	–	2.942		2.541		4.866		10.436	
Enthalpy differences						**EqG**	EqA	**EqG**[u]	EqA[u]	**EqG**[u]	EqA[u]	**EqG**[u]	EqA[u]	**EqG**[u]	EqA[u]
Grini *et al.* (1998)[h]	77	–	150 – 343	0.2 – 14.2	0.75	69	–	*7.719*		*7.262*		*10.471*		*29.413*	
Grini *et al.* (1998)[p]	77	77	140 – 343	1.0 – 14.2	0.75	76	–	0.434		−0.039		0.602		−1.946	
van Kasteren & Zeldenrust (1979)[p]	34	–	110 – 270	3.0 – 5.1	0.41	3	–	2.128		1.171		2.918		4.948	
Saturated liquid density[g]						**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP
Hiza *et al.* (1977)	4	4	105 – 120	0.4 – 0.6	0.94	4	4	0.085	7.403	0.085	−7.403	0.089	7.408	0.124	−7.742
Raabe & Köhler (2004)	7	–	120 – 138	0.6 – 2.8	0.73 – 0.96	6	6	0.270	8.768	0.089	−8.768	0.344	8.824	0.686	−10.272

Table A2.1 (continued)

Authors	Number of data points total[a]	used[b]	Covered ranges Temp. T/K	Pressure p/MPa	Compos.[c,d] x	Statistical analysis[n] N_1	N_2	AAD_1 %	AAD_2 %	Bias_1 %	Bias_2 %	RMS_1 %	RMS_2 %	MaxD_1 %	MaxD_2 %
$(1-x)$ $N_2 + x$ C_2H_6 (continued)															
VLE data						**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP
Brown *et al.* (1989b)[f]	24	13	220 – 270	1.0 – 12.0	0.59 – 0.98	22	19	1.864	3.403	1.320	−1.510	2.675	4.494	7.654	−12.465
Chang & Lu (1967)	22	–	122 – 171	0.3 – 3.4	0.03 – 0.98	18	17	9.094	9.317	3.443	5.661	11.938	12.804	28.637	25.122
Cheung & Wang (1964)	2	–	92.8	0.02 – 0.04	0.99 – 1.00	–	2		27.649		27.649		27.653		28.115
Eakin *et al.* (1955)[x,y]	320	–	102 – 302	0.5 – 12.2	0.02 – 0.95	193	154	3.186	7.434	−0.553	−5.074	4.828	9.673	19.478	−19.948
Ellington *et al.* (1959)[x,y]	333	–	101 – 301	0.7 – 12.8	0.02 – 0.95	202	175	3.620	6.322	−1.469	−3.768	5.177	8.604	−18.913	−19.764
Grauso *et al.* (1977)	31	20	200 – 290	0.7 – 13.2	0.43 – 0.99	31	29	2.789	6.007	−0.911	−3.261	4.088	8.746	11.461	−27.801
Janisch (2000b)	24	–	170 – 270	0.6 – 10.2	0.64 – 0.98	24	23	1.852	4.946	−1.390	−1.366	2.807	7.400	−8.800	−25.047
Janisch (2000c)	31	–	150 – 270	0.6 – 10.2	0.55 – 0.98	31	29	2.234	5.644	−1.321	−0.946	3.215	8.360	−8.908	−25.047
Kremer (1982)	21	–	120 – 133	0.6 – 3.6	0.01 – 0.96	21	21	1.768	4.235	−1.666	3.209	2.617	6.005	−5.975	13.172
Raabe & Köhler (2004)	21	–	120 – 138	0.9 – 3.3	0.73 – 0.95	21	21	3.808	6.257	−3.808	5.731	4.480	7.083	−8.839	12.136
Raabe *et al.* (2001)	11	11	210 – 270	1.1 – 10.0	0.67 – 0.98	11	11	1.009	2.784	−0.692	−0.998	1.140	4.125	−1.887	−11.705
Stryjek *et al.* (1974b)	48	35	139 – 194	0.3 – 13.5	0.29 – 0.99	43	27	1.732	4.826	−0.930	2.781	2.597	5.711	−9.477	9.542
Wilson (1975)	13	–	111	0.2 – 1.5	0.00 – 0.98	13	13	1.477	5.749	−1.212	4.737	3.022	7.930	−9.989	14.907
$(1-x)$ $N_2 + x$ C_3H_8															
***pρT* data**						**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA
Gasunie (1990)	43	43	293 – 308	3.7 – 6.3	0.05	43	43	0.042	0.032	−0.042	−0.032	0.043	0.033	−0.067	−0.048
Hiza *et al.* (1977)	2	2	100 – 105	0.6 – 0.9	0.93	2	–	0.094		0.056		0.109		0.150	
Hiza *et al.* (1977)	2	2	105 – 110	0.5 – 0.7	0.96	2	–	0.055		−0.055		0.055		−0.060	
Hiza *et al.* (1977)	2	2	110 – 115	0.4 – 0.5	0.98	2	–	0.068		−0.068		0.069		−0.075	
Ruhrgas (1990), Bu	22	22	313 – 353	0.9 – 18.6	0.07	22	22	0.008	0.009	−0.001	−0.001	0.013	0.012	−0.042	−0.033
Ruhrgas (1990), Op	223	223	270 – 353	0.3 – 28.6	0.07	223	223	0.017	0.018	−0.002	−0.004	0.023	0.024	0.073	−0.087
Watson *et al.* (1954)	10	–	399	0.6 – 25.0	0.001	10	10	0.498	0.483	−0.488	−0.474	0.626	0.598	−1.150	−1.072
Watson *et al.* (1954)	11	–	422	0.6 – 42.1	0.32	11	11	1.257	1.008	1.243	0.988	1.707	1.313	3.666	2.378
Watson *et al.* (1954)	10	–	399	0.7 – 27.7	0.44	10	10	1.335	1.637	−1.335	−1.637	1.765	2.182	−4.095	−5.198
Watson *et al.* (1954)	9	–	399	0.9 – 23.3	0.52	9	9	2.384	2.746	−2.384	−2.746	2.737	3.172	−5.207	−6.195

Table A2.1 (continued)

Authors	Number of data points total[a]	used[b]	Temp. T/K	Covered ranges Pressure p/MPa	Compos.[c,d] x	N_1	N_2	Statistical analysis[n] AAD_1 %	AAD_2 %	$Bias_1$ %	$Bias_2$ %	RMS_1 %	RMS_2 %	$MaxD_1$ %	$MaxD_2$ %
(1 − x) N_2 + x C_3H_8 (continued)															
***pρT* data (continued)**						**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA
Watson *et al.* (1954)	10	–	422	1.0 – 41.4	0.71	10	10	1.089	0.947	0.728	0.155	2.015	1.806	5.812	5.510
Watson *et al.* (1954)	9	–	399	1.0 – 26.1	0.79	7	6	5.212	4.846	−5.212	−4.846	5.771	5.259	−9.667	−8.343
Watson *et al.* (1954)	10	–	422	1.0 – 41.6	0.83	10	10	1.774	1.223	1.774	1.223	2.206	1.430	4.784	2.321
Saturated liquid density[g]						**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP
Hiza *et al.* (1977)	2	2	100 – 105	0.6 – 0.9	0.93	2	2	0.094	3.127	0.051	−3.127	0.107	3.127	0.145	−3.198
Hiza *et al.* (1977)	2	2	105 – 110	0.5 – 0.7	0.96	2	2	0.060	3.273	−0.060	−3.273	0.060	3.277	−0.065	−3.431
Hiza *et al.* (1977)	2	2	110 – 115	0.4 – 0.5	0.98	2	2	0.074	3.439	−0.074	−3.439	0.074	3.443	−0.080	−3.591
VLE data						**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP
Blagoi & Orobinskii (1965)[x]	41	–	78.0 – 90.5	0.03 – 0.3	0.66 – 1.00	29	4	6.521	7.728	−5.500	−3.821	9.317	10.596	−28.279	−19.994
Cheung & Wang (1964)[x]	6	–	91.9 – 128	0.1 – 0.6	0.93 – 0.99	1	5	25.353	18.601	−25.353	18.601	25.353	18.936	−25.353	24.637
Grauso *et al.* (1977)[f]	33	32	230 – 290	0.4 – 21.9	0.47 – 0.98	32	32	3.794	6.529	−1.256	−2.044	4.594	8.374	−9.896	−23.244
Hudziak *et al.* (1984)[y]	127	–	188 – 343	0.08 – 5.8	0.09 – 0.74	80	75	6.366	5.238	1.217	−0.532	8.419	7.155	−27.395	−22.031
Kremer (1982)	17	4	120 – 127	0.7 – 6.2	0.87 – 0.97	11	12	15.852	23.651	−12.718	23.651	15.907	23.724	−18.212	26.823
Poon & Lu (1974)[e]	32	32	114 – 122	0.2 – 2.8	0.91 – 0.99	32	–	6.380		3.251		7.883		16.206	
Schindler *et al.* (1966)[e]	60	49	103 – 353	0.7 – 13.8	0.68 – 0.99	51	55	4.571	6.527	−2.793	4.199	7.235	9.632	−25.869	29.069
Yucelen & Kidnay (1999)[e,f]	33	–	240 – 330	1.2 – 15.1	0.68 – 0.98	30	30	3.536	3.384	−3.202	−1.338	3.935	4.595	−7.052	−11.218
(1 − x) N_2 + x n-C_4H_{10}															
***pρT* data**						**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA
Evans & Watson (1956)	131	131	428 – 478	4.6 – 68.9	0.09	131	131	0.171	0.403	−0.114	−0.403	0.223	0.500	−1.378	−1.945
Evans & Watson (1956)	149	147	428 – 478	3.4 – 68.9	0.30	147	147	0.263	1.034	−0.195	−1.020	0.384	1.536	−1.099	−3.505
Evans & Watson (1956)	149	149	428 – 478	3.4 – 68.9	0.50	149	149	0.538	1.411	−0.214	−1.329	0.752	2.021	−2.220	−4.045
Evans & Watson (1956)	155	152	428 – 478	2.9 – 68.9	0.70	155	155	0.780	1.909	−0.440	−0.952	1.202	2.264	−4.132	−4.482
Evans & Watson (1956)	114	102	428 – 461	2.8 – 67.9	0.91	108	82	0.865	2.046	−0.079	0.122	1.190	2.386	−4.919	4.544
Ruhrgas (1990), Bu	22	22	313 – 353	0.4 – 18.4	0.02	22	22	0.013	0.017	−0.012	−0.017	0.014	0.018	−0.031	−0.035

Table A2.1 (continued)

Authors	Number of data points total^a	used^b	Covered ranges Temp. T/K	Pressure p/MPa	Compos.^{c,d} x	Statistical analysis^n N_1	N_2	AAD_1 %	AAD_2 %	$Bias_1$ %	$Bias_2$ %	RMS_1 %	RMS_2 %	$MaxD_1$ %	$MaxD_2$ %
$(1-x)$ $N_2 + x$ n-C_4H_{10} (continued)															
***pρT* data (continued)**						**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA
Ruhrgas (1990), Op	222	222	270 – 353	0.2 – 28.4	0.02	222	222	0.015	0.018	−0.004	−0.007	0.017	0.021	−0.048	−0.048
Saturated liquid density^g						**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP
Malewski & Sandler (1989)	30	–	339 – 380	1.2 – 22.1	0.50 – 0.98	27	27	1.202	3.700	0.361	−3.397	1.577	4.378	−3.283	−8.891
VLE data						**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP
Akers *et al.* (1954b)^f	27	–	311 – 422	3.6 – 29.1	0.46 – 0.99	14	12	9.330	9.544	4.390	4.126	12.700	12.983	27.340	25.185
Brown *et al.* (1989a)	50	50	250 – 344	0.5 – 15.8	0.73 – 1.00	49	42	1.755	4.419	−0.777	4.369	2.609	5.213	−9.254	9.699
Hudziak *et al.* (1984)^y	50	–	240 – 310	0.2 – 6.9	0.05 – 0.13	25	25	8.924	9.838	−1.228	−4.108	9.488	10.831	−15.243	−18.364
Lehigh & McKetta (1966)^{e,f}	21	–	311	13.9 – 28.8	0.39 – 0.77	12	8	5.957	10.770	−3.166	−10.116	7.129	12.335	14.878	−19.484
Malewski & Sandler (1989)	30	25	339 – 380	1.2 – 22.1	0.50 – 0.98	24	25	2.933	4.041	0.792	1.307	3.393	4.937	7.552	−9.269
Roberts & McKetta (1961)^{e,f}	34	–	311 – 411	1.6 – 23.5	0.41 – 0.98	23	22	9.293	8.362	4.444	6.458	11.055	10.389	21.010	23.228
Sauer (1959)	10	–	311 – 378	0.7 – 20.7	0.56 – 1.00	7	6	15.628	12.792	−10.455	−5.090	17.581	14.636	−29.292	−24.453
Shibata & Sandler (1989)	21	–	311 – 411	1.1 – 28.5	0.39 – 0.99	18	16	4.457	7.600	4.192	5.970	6.120	8.591	13.513	17.485
Skripka *et al.* (1969)^e	49	33	153 – 273	0.5 – 19.6	0.72 – 1.00	36	35	7.529	19.453	−2.202	19.453	10.393	20.797	24.921	28.661
$(1-x)$ $N_2 + x$ i-C_4H_{10}															
***pρT* data**						**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA
Kalra *et al.* (1978a)	64	46	255 – 311	0.2 – 20.8	0.03 – 0.99	50	–	1.238		−0.499		1.722		−4.920	
VLE data						**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP
Chen *et al.* (1997)	46	31	120 – 220	0.5 – 15.0	0.73 – 0.99	27	25	7.494	16.669	−0.228	13.899	8.380	18.057	13.950	26.447
Kalra *et al.* (1978a)	52	–	255 – 394	0.2 – 20.8	0.54 – 1.00	44	44	4.260	5.170	0.385	1.430	5.459	6.291	−18.235	14.980
$(1-x)$ $N_2 + x$ n-C_5H_{12}															
***pρT* data**						**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA
Kalra *et al.* (1977)	84	78	277 – 378	0.3 – 20.8	0.01 – 1.00	62	–	1.073		0.909		1.723		4.762	

Table A2.1 (continued)

Authors	Number of data points total[a]	used[b]	Covered ranges Temp. T/K	Pressure p/MPa	Compos.[c,d] x	Statistical analysis[n] N_1	N_2	AAD_1 %	AAD_2 %	Bias_1 %	Bias_2 %	RMS_1 %	RMS_2 %	MaxD_1 %	MaxD_2 %
$(1-x)$ $N_2 + x$ n-C_5H_{12} (continued)															
VLE data						**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP
Kalra *et al.* (1977)	42	37	277 – 378	0.3 – 20.8	0.60 – 1.00	42	42	6.666	4.788	1.750	−0.458	8.330	6.647	−21.235	−25.648
$(1-x)$ $N_2 + x$ i-C_5H_{12}															
***pρT* data**						**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA
Krishnan *et al.* (1977)	94	88	278 – 377	0.2 – 20.8	0.01 – 1.00	78	–	1.803		0.828		2.270		4.938	
VLE data						**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP
Krishnan *et al.* (1977)	47	46	278 – 377	0.2 – 20.8	0.56 – 1.00	47	47	6.463	4.406	3.101	2.777	8.096	6.384	29.072	27.485
$(1-x)$ $N_2 + x$ n-C_6H_{14}															
VLE data						**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP
Poston & McKetta (1966b)	52	25	311 – 444	1.7 – 34.5	0.40 – 0.98	41	48	10.321	6.784	−6.207	1.953	12.479	7.980	−28.837	−21.637
$(1-x)$ $N_2 + x$ n-C_7H_{16}															
VLE data						**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP
Akers *et al.* (1954c)	34	–	305 – 455	7.0 – 69.1	0.28 – 0.92	6	29	19.598	5.535	−15.094	3.132	20.918	7.170	−29.807	15.212
Figuiere *et al.* (1980)	46	33	453 – 497	1.2 – 29.5	0.33 – 0.99	34	41	11.756	9.197	3.467	3.101	13.888	10.824	29.750	27.422
Llave & Chung (1988)[x]	22	–	305 – 366	5.5 – 34.9	0.60 – 0.94	3	22	9.837	7.215	−9.039	5.446	13.457	9.503	−22.553	27.341
Wäterling *et al.* (1991)	12	8	453	1.5 – 27.7	0.42 – 0.98	8	12	8.476	8.936	−0.478	−4.452	10.081	12.286	−21.713	−28.132
$(1-x)$ $N_2 + x$ n-C_8H_{18}															
***pρT* data**						**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA
Daridon *et al.* (1994)	144	143	293 – 373	25.0 – 100	0.79	143	–	0.135		0.029		0.167		−0.563	
Speed of sound						**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA
Daridon *et al.* (1994)	144	144	293 – 373	25.0 – 100	0.79	144	–	0.434		0.087		0.536		−1.975	

Table A2.1 (continued)

Authors	Number of data points total^a	used^b	Covered ranges Temp. T/K	Pressure p/MPa	Compos.^{c,d} x	N_1	N_2	Statistical analysis^n AAD$_1$ %	AAD$_2$ %	Bias$_1$ %	Bias$_2$ %	RMS$_1$ %	RMS$_2$ %	MaxD$_1$ %	MaxD$_2$ %
$(1-x)$ N_2 + x n-C_8H_{18} (continued)															
VLE data						**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP
Daridon *et al.* (1994)^x	9	–	293 – 373	15.8 – 21.2	0.79	–	3		27.058		27.058		27.121		29.169
Graham & Weale (1962)	5	–	323 – 373	15.2 – 20.3	0.99 – 1.00	–	–								
Llave & Chung (1988)^x	12	–	322 – 344	3.2 – 35.0	0.65 – 0.96	3	2	23.403	27.222	23.403	27.222	25.077	27.323	29.793	29.575
$(1-x)$ N_2 + x H_2															
***pρT* data**						**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA
Bartlett *et al.* (1928)	47	46	273 – 573	5.1 – 101	0.75	46	46	0.214	0.955	0.100	0.852	0.279	1.527	0.813	5.192
Bennett & Dodge (1952)	27	26	298 – 398	100 – 306	0.25	27	–	0.675		0.650		0.723		1.239	
Bennett & Dodge (1952)	25	23	298 – 398	101 – 307	0.51	24	–	0.846		0.810		0.901		1.416	
Bennett & Dodge (1952)	25	22	298 – 398	101 – 307	0.75	23	–	0.799		0.799		0.872		1.673	
Jaeschke *et al.* (1997)	47	46	273 – 313	0.4 – 30.2	0.15	46	46	0.010	0.011	−0.006	0.005	0.013	0.015	−0.034	0.058
Jaeschke *et al.* (1997)	230	230	273 – 353	0.4 – 28.5	0.15	230	230	0.028	0.023	−0.009	0.019	0.034	0.029	0.089	0.075
Jaeschke *et al.* (1997)	188	188	270 – 350	0.5 – 28.5	0.25	188	188	0.031	0.021	−0.013	0.010	0.037	0.026	0.103	0.072
Jaeschke *et al.* (1997)	79	79	275 – 350	0.3 – 26.1	0.50	79	79	0.011	0.011	−0.005	−0.004	0.016	0.017	0.056	0.069
Jaeschke *et al.* (1997)	185	184	270 – 350	0.5 – 28.9	0.50	184	184	0.028	0.021	0.002	0.007	0.036	0.025	0.104	0.062
Jaeschke *et al.* (1997)	71	71	275 – 350	0.5 – 26.2	0.75	71	71	0.010	0.015	−0.008	−0.008	0.014	0.020	−0.033	0.085
Jaeschke *et al.* (1997)	199	199	270 – 350	0.5 – 29.1	0.75	199	199	0.017	0.022	−0.011	−0.011	0.020	0.026	−0.050	0.088
Michels & Wassenaar (1949)	37	37	273 – 323	1.9 – 9.1	0.75	37	37	0.013	0.018	0.013	0.016	0.016	0.022	0.032	0.047
Sage *et al.* (1948)	90	90	278 – 511	0.1 – 103	0.76	90	90	0.131	0.705	0.119	0.688	0.177	1.155	0.522	4.073
Verschoyle (1926)	21	21	273 – 293	3.7 – 20.8	0.25	21	21	0.088	0.091	0.060	0.068	0.111	0.113	0.211	0.199
Verschoyle (1926)	21	21	273 – 293	3.7 – 20.8	0.50	21	21	0.104	0.093	0.081	0.068	0.124	0.109	0.238	0.195
Verschoyle (1926)	21	21	273 – 293	3.7 – 20.8	0.75	21	21	0.096	0.083	0.066	0.054	0.120	0.100	0.232	0.183
Wiebe & Gaddy (1938)	43	43	273 – 573	2.5 – 101	0.26	43	43	0.174	0.250	0.169	0.244	0.234	0.402	0.586	1.342
Wiebe & Gaddy (1938)	46	46	273 – 573	2.5 – 101	0.52	46	46	0.210	0.552	0.205	0.538	0.260	0.935	0.658	3.254
Wiebe & Gaddy (1938)	42	42	273 – 573	5.1 – 101	0.76	42	42	0.174	0.968	0.164	0.931	0.230	1.680	0.502	5.744
Wiebe & Gaddy (1938)	44	44	273 – 573	2.5 – 101	0.87	44	44	0.168	1.170	0.167	1.148	0.210	2.002	0.436	6.756

Table A2.1 (continued)

Authors	Number of data points total[a]	used[b]	Covered ranges Temp. T/K	Pressure p/MPa	Compos.[c,d] x	N_1	N_2	Statistical analysis[n] AAD_1 %	AAD_2 %	$Bias_1$ %	$Bias_2$ %	RMS_1 %	RMS_2 %	$MaxD_1$ %	$MaxD_2$ %
(1 − x) N_2 + x H_2 (continued)															
VLE data						**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP
Maimoni (1961)	11	11	90.0 – 95.0	0.8 – 4.6	0.01 – 0.11	1	11	26.930	1.741	−26.930	−1.340	26.930	2.812	−26.930	−7.842
Steckel & Zinn (1939)	23	8	90.0 – 113	0.5 – 9.6	0.04 – 0.39	2	20	17.808	10.932	−17.808	−8.248	17.975	12.908	−20.255	−24.280
Yorizane *et al.* (1968b)	11	–	77.4	1.0 – 15.2	0.02 – 0.36	–	4		13.518		−1.353		18.271		−28.255
(1 − x) N_2 + x O_2															
***pρT* data**						**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA
Blagoi & Rudenko (1958)	19	–	66.9 – 79.2	0.1	0.20 – 0.89	19	–	0.182		0.128		0.242		0.655	
Schilling (2003)	11	–	293	2.1 – 8.0	0.21	11	11	0.007	0.037	0.005	−0.037	0.009	0.041	0.015	−0.059
Wöll (2003)	24	–	233 – 333	0.5 – 2.0	0.21	24	24	0.008	0.012	0.008	−0.010	0.008	0.017	0.015	−0.046
Wöll (2003)	12	–	295	8.0 – 14.4	0.21	12	12	0.029	0.088	−0.001	−0.088	0.038	0.093	−0.072	−0.144
Wöll (2003)	7	–	295	8.0 – 11.5	0.21	7	7	0.032	0.053	0.027	−0.053	0.039	0.065	0.061	−0.108
Wöll (2003)	6	–	295	12.0 – 15.7	0.21	6	6	0.010	0.101	−0.003	−0.101	0.012	0.101	−0.020	−0.120
VLE data						**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP
Armstrong *et al.* (1955)	70	65	64.8 – 78.0	0.003 – 0.1	0.05 – 0.97	68	68	1.388	1.709	1.154	−1.512	1.760	2.095	−4.419	−4.326
Cockett (1957)	62	61	81.1 – 91.0	0.1	0.19 – 0.93	61	61	1.230	0.918	0.828	0.278	1.470	1.256	−3.436	−3.283
Din (1960)	119	104	79.1 – 116	0.1 – 1.0	0.11 – 0.90	108	108	0.883	1.309	−0.728	−1.281	1.085	1.455	−2.044	−2.966
Dodge & Dunbar (1927)	49	48	76.8 – 125	0.06 – 3.0	0.09 – 0.95	49	49	0.876	0.733	−0.125	−0.494	1.143	1.039	−3.179	−2.982
Duncan & Staveley (1966)[x]	9	–	63.2	0.003 – 0.01	0.20 – 0.90	9	9	3.422	1.588	3.422	−1.305	3.627	2.093	4.858	−3.900
Hiza *et al.* (1990)[e]	47	41	63.0 – 99.9	0.01 – 0.7	0.12 – 0.93	47	47	0.917	1.382	−0.088	−1.377	1.205	1.987	2.685	−5.273
Pool *et al.* (1962)[x]	9	–	83.8	0.07 – 0.2	0.10 – 0.90	9	9	0.450	0.445	0.390	−0.445	0.573	0.530	0.929	−0.846
Thorogood & Haselden (1963)	13	13	88.2 – 90.3	0.1	0.92 – 1.00	13	13	1.612	1.550	−1.563	−1.511	1.742	1.684	−2.657	−2.532
Wilson *et al.* (1965)	138	135	77.8 – 136	0.1 – 2.6	0.01 – 0.95	132	129	0.579	0.915	−0.435	−0.860	0.710	0.985	−1.953	−1.982
Yorizane *et al.* (1978)	10	8	79.6 – 80.3	0.05 – 0.1	0.15 – 0.89	8	8	2.846	1.926	2.461	1.408	3.005	2.126	4.588	3.327

Table A2.1 (continued)

Authors	Number of data points total[a]	used[b]	Covered ranges Temp. T/K	Pressure p/MPa	Compos.[c,d] x	N_1	N_2	Statistical analysis[n] AAD_1 %	AAD_2 %	Bias_1 %	Bias_2 %	RMS_1 %	RMS_2 %	MaxD_1 %	MaxD_2 %
(1 − x) N_2 + x CO															
***pρT* data**						**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA
Jaeschke *et al.* (1997)	56	56	273 – 353	0.4 – 30.1	0.03	56	56	0.009	0.011	−0.001	−0.006	0.012	0.014	−0.052	−0.033
Jaeschke *et al.* (1997)	287	287	273 – 353	0.3 – 28.7	0.03	287	287	0.009	0.011	−0.002	−0.003	0.011	0.014	−0.023	0.031
VLE data						**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP
Sprow & Prausnitz (1966)	8	–	83.8	0.1 – 0.2	0.07 – 0.90	8	8	0.266	6.173	0.044	−6.173	0.331	6.537	−0.688	−8.399
Torotscheschnikow (1937)	109	106	70.0 – 123	0.02 – 2.7	0.10 – 1.00	107	93	2.420	4.412	0.611	−3.999	3.290	5.114	9.842	−9.804
(1 − x) N_2 + x H_2O															
***pρT* data**						**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA
Abdulagatov *et al.* (1993b)	55	55	523 – 663	2.1 – 69.3	0.06 – 0.93	53	51	1.333	2.445	0.285	1.518	1.744	3.424	−4.282	9.821
Fenghour *et al.* (1993)	11	11	429 – 697	8.2 – 13.6	0.05	11	11	0.068	0.398	−0.020	0.398	0.075	0.419	0.116	0.649
Fenghour *et al.* (1993)	12	12	456 – 697	9.3 – 14.5	0.11	12	12	0.213	0.661	−0.213	0.661	0.220	0.673	−0.292	0.945
Fenghour *et al.* (1993)	12	12	483 – 698	10.6 – 15.7	0.19	12	12	0.453	0.944	−0.453	0.944	0.461	0.953	−0.539	1.259
Fenghour *et al.* (1993)	11	11	510 – 697	12.0 – 16.9	0.25	11	11	0.557	1.226	−0.557	1.226	0.567	1.233	−0.643	1.504
Fenghour *et al.* (1993)	10	10	536 – 697	13.5 – 18.2	0.30	10	10	0.476	1.654	−0.476	1.654	0.510	1.662	−0.598	2.041
Fenghour *et al.* (1993)	10	10	535 – 697	14.3 – 19.4	0.35	10	10	0.504	1.956	−0.442	1.956	0.541	1.970	−0.682	2.492
Fenghour *et al.* (1993)	10	10	562 – 707	16.8 – 22.3	0.44	10	10	0.482	2.624	−0.252	2.624	0.529	2.646	0.882	3.415
Fenghour *et al.* (1993)	9	9	562 – 698	17.9 – 23.9	0.49	9	9	0.544	3.292	0.164	3.292	0.756	3.332	1.873	4.440
Fenghour *et al.* (1993)	8	8	589 – 698	21.0 – 26.9	0.56	8	8	0.764	4.324	0.723	4.324	1.080	4.361	2.438	5.515
Fenghour *et al.* (1993)	8	8	602 – 697	24.1 – 30.9	0.64	8	8	1.934	6.141	1.934	6.141	2.237	6.196	4.010	7.615
Japas & Franck (1985a)	56	56	673	20.1 – 286	0.13 – 0.90	56	–	1.463		0.396		1.862		4.681	
Japas & Franck (1985a)	63	–	480 – 659	15.5 – 271	0.13 – 0.95	56	–	1.659		0.255		2.048		−4.837	
(1 − x) N_2 + x He															
***pρT* data**						**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA
Canfield *et al.* (1965)	141	–	133 – 273	0.2 – 53.4	0.16	139	–	0.758		0.739		1.311		4.440	

Table A2.1 (continued)

Authors	Number of data points			Covered ranges							Statistical analysis[n]					
	total[a]	used[b]	Temp. T/K	Pressure p/MPa	Compos.[c,d] x	N_1	N_2	AAD_1 %	AAD_2 %	Bias_1 %	Bias_2 %	RMS_1 %	RMS_2 %	MaxD_1 %	MaxD_2 %
$(1-x)$ N_2 + x He (continued)															
***pρT* data (continued)**						**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA
Canfield *et al.* (1965)	154	–	133 – 273	0.2 – 53.6	0.30	148	–	0.975		0.958		1.625		4.957	
Canfield *et al.* (1965)	151	–	133 – 273	0.2 – 53.7	0.45	148	–	0.934		0.914		1.572		4.954	
Canfield *et al.* (1965)	139	–	133 – 273	0.2 – 54.3	0.60	139	–	0.540		0.510		0.965		3.131	
Canfield *et al.* (1965)	154	–	133 – 273	0.2 – 54.6	0.75	154	–	0.277		0.243		0.514		1.844	
Canfield *et al.* (1965)	145	–	133 – 273	0.2 – 53.5	0.88	145	–	0.084		0.074		0.151		0.672	
Davis *et al.* (1963)	30	–	77.2	1.4 – 6.8	0.06	30	–	2.412		2.412		2.440		3.174	
Hall & Canfield (1970)	22	–	103 – 113	0.2 – 2.8	0.30	22	22	1.738	0.448	1.738	0.448	2.246	0.698	5.791	2.243
Hall & Canfield (1970)	24	–	103 – 113	0.3 – 4.2	0.45	24	24	1.687	0.716	1.687	0.716	2.215	1.102	5.839	3.542
Hall & Canfield (1970)	40	–	83.2 – 113	0.2 – 12.6	0.75	40	40	0.631	1.008	0.631	1.008	0.895	1.601	2.512	5.551
Hall & Canfield (1970)	48	–	83.2 – 113	0.2 – 22.2	0.88	48	48	0.312	1.256	0.312	1.256	0.449	2.025	1.114	6.683
Jaeschke *et al.* (1997)	26	26	298	0.5 – 26.6	0.25	26	26	0.039	0.140	−0.025	0.139	0.044	0.245	0.088	0.747
Jaeschke *et al.* (1997)	383	383	270 – 350	0.1 – 28.0	0.25	383	383	0.089	0.258	−0.034	0.252	0.111	0.363	0.311	1.004
Jaeschke *et al.* (1997)	30	30	290 – 310	0.5 – 26.2	0.50	30	30	0.036	0.200	−0.025	0.199	0.041	0.386	0.097	1.254
Jaeschke *et al.* (1997)	328	325	270 – 350	0.1 – 27.2	0.50	325	325	0.060	0.402	−0.024	0.399	0.080	0.562	0.206	1.499
Jaeschke *et al.* (1997)	22	22	298	0.7 – 26.2	0.75	22	22	0.025	0.257	−0.025	0.249	0.030	0.470	−0.053	1.470
Jaeschke *et al.* (1997)	383	379	270 – 350	0.1 – 28.0	0.75	379	379	0.025	0.534	−0.005	0.525	0.031	0.740	0.092	1.925
Ku & Dodge (1967)	11	11	312	0.6 – 25.3	0.16	11	11	0.031	0.116	−0.020	0.116	0.036	0.191	−0.063	0.521
Ku & Dodge (1967)	14	14	373	0.4 – 21.6	0.18	14	14	0.257	0.369	0.257	0.369	0.270	0.419	0.379	0.821
Ku & Dodge (1967)	9	9	312	1.2 – 25.7	0.31	9	9	0.280	0.498	0.280	0.498	0.314	0.614	0.549	1.284
Ku & Dodge (1967)	15	15	373	0.3 – 21.4	0.51	15	15	0.239	0.363	0.239	0.363	0.257	0.454	0.460	1.149
Ku & Dodge (1967)	15	15	312	0.4 – 29.9	0.56	15	15	0.182	0.433	0.177	0.428	0.285	0.743	0.911	2.332
Ku & Dodge (1967)	15	15	373	0.3 – 21.8	0.67	15	15	0.303	0.409	0.303	0.409	0.317	0.492	0.464	1.207
Ku & Dodge (1967)	15	15	312	0.4 – 29.0	0.86	15	15	0.065	0.312	0.046	0.285	0.085	0.614	0.167	1.933
Maslennikova *et al.* (1977)	52	–	298 – 423	100 – 700	0.30	52	–	0.814		0.719		0.998		2.471	
Maslennikova *et al.* (1977)	52	–	298 – 423	100 – 700	0.54	52	–	1.061		0.823		1.265		2.601	
Miller *et al.* (1960)	10	–	294	0.9 – 26.9	0.06	10	10	0.275	0.368	0.275	0.368	0.287	0.405	0.427	0.714

Table A2.1 (continued)

Authors	Number of data points total[a]	used[b]	Temp. T/K	Covered ranges Pressure p/MPa	Compos.[c,d] x	N_1	N_2	Statistical analysis[n] AAD_1 %	AAD_2 %	Bias_1 %	Bias_2 %	RMS_1 %	RMS_2 %	MaxD_1 %	MaxD_2 %
$(1-x)$ N_2 + x He (continued)															
***pρT* data (continued)**						**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA
Miller *et al.* (1960)	10	–	294	0.9 – 27.5	0.16	10	10	0.103	0.255	0.103	0.255	0.117	0.328	0.240	0.755
Miller *et al.* (1960)	10	–	294	0.9 – 27.7	0.20	10	10	0.034	0.176	0.007	0.176	0.053	0.285	0.145	0.742
Miller *et al.* (1960)	10	–	294	0.9 – 27.8	0.28	10	10	0.090	0.288	0.090	0.288	0.114	0.409	0.272	1.022
Miller *et al.* (1960)	10	–	294	0.9 – 27.4	0.34	10	10	0.360	0.577	0.360	0.577	0.403	0.716	0.686	1.536
Miller *et al.* (1960)	10	–	294	0.9 – 27.5	0.44	10	10	0.362	0.623	0.362	0.623	0.391	0.774	0.626	1.700
Miller *et al.* (1960)	10	–	294	0.8 – 26.3	0.52	10	10	0.220	0.497	0.220	0.497	0.247	0.674	0.423	1.598
Miller *et al.* (1960)	10	–	294	0.9 – 27.5	0.61	10	10	0.136	0.455	0.136	0.455	0.151	0.664	0.268	1.637
Miller *et al.* (1960)	10	–	294	0.9 – 27.7	0.68	10	10	0.124	0.453	0.124	0.453	0.140	0.693	0.213	1.765
Miller *et al.* (1960)	10	–	294	0.9 – 28.1	0.74	10	10	0.150	0.483	0.150	0.483	0.151	0.712	0.183	1.829
Miller *et al.* (1960)	8	–	294	1.9 – 27.5	0.84	7	7	0.102	0.440	0.098	0.435	0.131	0.779	0.217	1.943
Miller *et al.* (1960)	10	–	294	0.9 – 27.8	0.90	10	10	0.099	0.447	0.090	0.434	0.109	0.763	0.154	2.053
Miller *et al.* (1960)	10	–	294	0.9 – 27.6	0.94	10	10	0.181	0.568	0.181	0.568	0.217	0.942	0.376	2.444
Miller *et al.* (1960)	10	–	294	0.9 – 27.4	0.98	10	10	0.135	0.652	0.127	0.642	0.153	1.072	0.230	2.789
Miller *et al.* (1960)	10	–	294	0.9 – 27.5	0.99	10	10	0.124	0.753	0.120	0.749	0.137	1.247	0.204	3.244
Zhang *et al.* (1992)	24	–	298	229 – 1027	0.26	24	–	1.343		1.343		1.373		1.743	
Zhang *et al.* (1992)	36	–	298	212 – 1010	0.50	36	–	1.429		1.429		1.508		2.183	
Zhang *et al.* (1992)	43	–	298	200 – 1019	0.75	43	–	1.225		1.225		1.344		2.330	
Speed of sound						**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA
Zhang & Schouten (1992b)	112	–	157 – 298	200 – 1000	0.50	112	–	1.846		−1.815		2.162		−4.032	
VLE data						**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP
Buzyna *et al.* (1963)	30	–	77.2 – 123	1.2 – 6.9	0.00 – 0.08	1	–	8.415		−8.415		8.415		−8.415	
Davis *et al.* (1963)	24	–	77.2	3.6 – 6.8	0.01 – 0.02	–	–								
DeVaney n*et al.* (1963)	277	–	76.5 – 120	1.4 – 13.8	0.00 – 0.14	1	–	29.802		−29.802		29.802		−29.802	
Fontaine (1989)	55	–	64.9 – 125	1.4 – 10.0	0.00 – 0.12	1	–	16.774		−16.774		16.774		−16.774	
Gonikberg & Fastowsky (1940)	25	–	78.0 – 109	1.8 – 28.0	0.01 – 0.18	–	–								

Table A2.1 (continued)

Authors	Number of data points total[a]	used[b]	Covered ranges Temp. T/K	Pressure p/MPa	Compos.[c,d] x	N_1	N_2	Statistical analysis[n] AAD_1 %	AAD_2 %	$Bias_1$ %	$Bias_2$ %	RMS_1 %	RMS_2 %	$MaxD_1$ %	$MaxD_2$ %
$(1-x)$ N_2 + x He (continued)															
VLE data (continued)						**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP
Rodewald *et al.* (1964)	15	–	64.9 – 77.2	1.4 – 6.9	0.00 – 0.01	–	–								
Streett (1967)	89	–	77.6 – 122	6.7 – 83.1	0.01 – 0.58	–	–								
Tully *et al.* (1971)	70	–	122 – 126	3.1 – 21.0	0.01 – 0.41	12	–	13.664		−13.664		15.823		−28.829	
$(1-x)$ N_2 + x Ar															
***pρT* data**						**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA
Crain & Sonntag (1966)	90	90	143 – 273	0.2 – 52.5	0.20	90	87	0.158	0.166	0.154	0.143	0.272	0.343	1.280	1.828
Crain & Sonntag (1966)	90	66	143 – 273	0.2 – 52.1	0.50	84	81	0.370	0.295	0.289	0.241	0.569	0.526	1.877	1.906
Crain & Sonntag (1966)	84	82	143 – 273	0.2 – 51.7	0.80	84	82	0.250	0.253	0.246	0.113	0.450	0.451	1.939	−1.603
Holst & Hamburger (1916)	9	9	73.8 – 83.6	0.03 – 0.1	0.20	9	–	0.067		−0.011		0.090		0.189	
Holst & Hamburger (1916)	13	12	76.2 – 85.9	0.02 – 0.1	0.39	12	–	0.073		−0.043		0.079		−0.136	
Holst & Hamburger (1916)	19	19	80.5 – 90.1	0.01 – 0.2	0.69	19	–	0.208		0.193		0.269		0.756	
Maslennikova *et al.* (1979)	45	–	298 – 423	100 – 800	0.25	43	–	0.773		0.773		0.831		1.325	
Maslennikova *et al.* (1979)	6	6	89.9 – 113	0.3 – 1.3	0.50	6	–	0.373		−0.373		0.375		−0.420	
Maslennikova *et al.* (1979)	43	–	298 – 423	100 – 800	0.74	43	–	1.449		1.366		1.569		2.578	
Palavra (1979)	44	44	93.9 – 106	1.3 – 23.3	0.30	44	–	0.037		−0.037		0.040		−0.060	
Palavra (1979)	42	42	93.9 – 106	1.4 – 23.4	0.41	42	–	0.028		−0.027		0.030		−0.056	
Palavra (1979)	9	9	93.9	1.5 – 22.5	0.51	9	–	0.037		0.037		0.044		0.079	
Palavra (1979)	25	25	97.0 – 103	1.0 – 22.7	0.52	25	–	0.015		0.012		0.019		0.044	
Palavra (1979)	9	9	106	1.4 – 22.5	0.52	9	–	0.017		0.015		0.021		0.037	
Palavra (1979)	31	31	93.9 – 106	1.4 – 24.9	0.60	31	–	0.038		0.038		0.042		0.067	
Palavra (1979)	43	43	93.9 – 106	1.2 – 24.0	0.68	43	–	0.067		0.067		0.070		0.111	
Ricardo *et al.* (1992)	21	21	119	7.4 – 145	0.48	21	–	0.268		0.268		0.271		0.333	
Townsend (1956)	34	34	298 – 323	0.2 – 13.9	0.16	34	34	0.080	0.090	0.074	0.084	0.130	0.150	0.410	0.471
Townsend (1956)	36	36	298 – 323	0.2 – 13.8	0.38	35	35	0.058	0.076	0.051	0.071	0.097	0.129	0.314	0.424
Townsend (1956)	37	37	298 – 323	0.2 – 13.9	0.59	37	37	0.083	0.110	0.077	0.107	0.132	0.178	0.416	0.569

Table A2.1 (continued)

Authors	Number of data points		Covered ranges			Statistical analysis^{n}									
	total^{a}	used^{b}	Temp. T/K	Pressure p/MPa	Compos.^{c,d} x	N_1	N_2	AAD$_1$ %	AAD$_2$ %	Bias$_1$ %	Bias$_2$ %	RMS$_1$ %	RMS$_2$ %	MaxD$_1$ %	MaxD$_2$ %
$(1-x)$ $N_2 + x$ Ar (continued)															
***pρT* data (continued)**						**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA
Townsend (1956)	37	37	298 – 323	0.2 – 13.7	0.84	37	37	0.048	0.046	−0.032	0.010	0.063	0.055	−0.157	0.147
VLE data						**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP
Fastovskii & Petrovskii (1956)	50	–	79.6 – 102	0.1 – 0.4	0.10 – 0.95	50	50	1.578	2.728	−1.137	−2.609	1.852	3.019	−4.217	−6.245
Hiza *et al.* (1990)	28	28	84.9 – 99.9	0.1 – 0.7	0.11 – 0.90	28	28	0.304	1.372	−0.136	−1.372	0.393	1.461	1.140	−2.047
Jin *et al.* (1993)	13	11	123	1.5 – 2.8	0.03 – 0.95	13	13	0.373	1.266	−0.092	−1.266	0.458	1.391	1.001	−2.285
Lewis & Staveley (1975)	6	6	84.5	0.1 – 0.2	0.19 – 0.77	6	6	0.662	0.990	0.662	−0.990	0.755	1.042	1.175	−1.574
Miller *et al.* (1973)^{x,y}	14	–	112	0.8 – 1.5	0.15 – 0.89	14	14	0.689	1.850	−0.689	−1.850	0.744	1.910	−1.309	−2.586
Narinskii (1966)	98	97	80.1 – 120	0.1 – 2.3	0.04 – 0.98	97	68	0.440	1.165	−0.331	−1.165	0.603	1.264	−1.699	−1.991
Pool *et al.* (1962)^{x}	10	–	83.8	0.08 – 0.2	0.12 – 0.94	10	10	0.213	1.650	0.160	−1.650	0.262	1.702	0.443	−2.324
Sprow & Prausnitz (1966)	17	17	83.8	0.08 – 0.2	0.09 – 0.94	17	17	0.244	1.514	0.194	−1.514	0.310	1.580	0.564	−2.197
Thorpe (1968)	68	66	80.9 – 115	0.1 – 1.1	0.09 – 0.90	68	68	0.463	0.888	0.345	−0.888	0.642	1.032	1.912	−2.708
Wilson *et al.* (1965)	183	174	72.2 – 134	0.1 – 2.6	0.00 – 0.95	176	168	1.001	1.732	−0.988	−1.732	1.416	2.000	−4.750	−4.917
$(1-x)$ $CO_2 + x$ C_2H_6															
***pρT* data**						**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA
Brugge *et al.* (1989b)	43	43	300 – 320	0.1 – 6.7	0.10	43	43	0.080	0.073	−0.077	−0.070	0.126	0.105	−0.418	−0.270
Brugge *et al.* (1989b)	44	44	300 – 320	0.1 – 6.7	0.26	43	42	0.025	0.038	0.010	0.007	0.041	0.066	0.143	0.316
Brugge *et al.* (1989b)	35	35	300 – 320	0.1 – 6.8	0.51	35	35	0.073	0.089	0.052	0.019	0.140	0.176	0.503	0.630
Brugge *et al.* (1989b)	44	44	300 – 320	0.1 – 6.1	0.75	44	44	0.035	0.044	0.029	−0.041	0.060	0.068	0.272	−0.206
Brugge *et al.* (1989b)	40	40	300 – 320	0.1 – 4.7	0.90	40	40	0.033	0.071	−0.022	−0.069	0.062	0.131	−0.271	−0.534
Duarte-Garza & Magee (2001)	195	–	220 – 400	3.1 – 34.9	0.26	188	–	0.597		−0.079		0.689		1.767	
Duarte-Garza & Magee (2001)	179	–	220 – 400	3.2 – 34.5	0.51	179	–	0.362		0.198		0.470		1.301	
Duarte-Garza & Magee (2001)	211	–	220 – 400	2.8 – 35.5	0.75	211	–	0.279		0.014		0.328		0.822	
Goodwin & Moldover (1997)	6	–	285 – 293	5.2 – 6.3	0.26	2	–	0.848		0.848		0.905		1.164	
Goodwin & Moldover (1997)	19	–	284 – 291	4.7 – 5.7	0.51	19	–	2.187		0.536		2.368		3.853	
Goodwin & Moldover (1997)	7	–	292 – 297	4.7 – 5.3	0.75	5	–	1.230		−1.180		1.774		−3.515	

Table A2.1 (continued)

Authors	Number of data points total[a]	used[b]	Covered ranges Temp. T/K	Pressure p/MPa	Compos.[c,d] x	N_1	N_2	Statistical analysis[n] AAD_1 %	AAD_2 %	Bias_1 %	Bias_2 %	RMS_1 %	RMS_2 %	MaxD_1 %	MaxD_2 %
$(1-x)$ $CO_2 + x$ C_2H_6 (continued)															
***pρT* data (continued)**						**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA
Lau (1986)	58	58	240 – 350	1.7 – 34.5	0.10	56	–	0.334		−0.314		0.477		−1.583	
Lau (1986)	58	58	240 – 350	1.5 – 34.5	0.26	57	–	0.469		0.378		0.632		1.726	
Lau (1986)	58	58	240 – 350	1.6 – 34.7	0.51	57	–	0.400		0.365		0.573		1.735	
Lau (1986)	60	60	240 – 350	1.6 – 35.3	0.75	60	–	0.211		0.184		0.289		0.729	
Lau *et al.* (1997)	47	47	240 – 350	1.7 – 34.5	0.10	45	–	0.266		−0.220		0.321		−1.088	
Lau *et al.* (1997)	47	47	240 – 350	1.5 – 34.5	0.26	46	–	0.457		0.314		0.622		1.788	
Lau *et al.* (1997)	46	46	240 – 350	1.6 – 34.6	0.51	45	–	0.398		0.324		0.584		1.938	
Lau *et al.* (1997)	48	48	240 – 350	1.6 – 34.5	0.75	48	–	0.212		0.177		0.323		0.835	
Lemming (1989)	54	54	300 – 320	0.03 – 6.7	0.10	54	54	0.051	0.045	−0.051	−0.045	0.095	0.078	−0.340	−0.231
Lemming (1989)	55	55	300 – 320	0.03 – 6.7	0.26	55	55	0.021	0.041	−0.009	0.002	0.038	0.091	0.184	0.491
Lemming (1989)	44	44	300 – 320	0.03 – 6.8	0.51	44	44	0.041	0.065	0.026	−0.001	0.107	0.134	0.464	0.527
Lemming (1989)	55	55	300 – 320	0.04 – 6.1	0.75	55	55	0.025	0.035	0.023	−0.034	0.052	0.065	0.249	−0.219
Lemming (1989)	46	46	300 – 320	0.05 – 4.7	0.90	46	46	0.019	0.051	−0.010	−0.051	0.047	0.113	−0.218	−0.481
McElroy *et al.* (1990)	11	–	333	0.8 – 6.0	0.23	11	11	0.255	0.163	0.255	0.163	0.274	0.208	0.389	0.363
McElroy *et al.* (1990)	10	–	313	1.1 – 5.4	0.24	10	10	0.115	0.111	0.109	0.094	0.147	0.147	0.242	0.253
McElroy *et al.* (1990)	11	–	303	0.8 – 4.9	0.26	11	11	0.385	0.359	−0.278	−0.248	0.429	0.418	−0.614	−0.617
McElroy *et al.* (1990)	11	–	323	0.7 – 5.4	0.27	11	11	0.178	0.145	0.138	0.072	0.209	0.159	0.348	0.250
McElroy *et al.* (1990)	11	–	333	0.7 – 6.2	0.41	11	11	0.410	0.244	0.410	0.244	0.418	0.277	0.549	0.494
McElroy *et al.* (1990)	11	–	323	0.7 – 5.8	0.44	11	11	0.355	0.234	0.355	0.226	0.417	0.286	0.768	0.582
McElroy *et al.* (1990)	11	–	303	0.8 – 4.9	0.47	11	11	0.109	0.114	0.011	−0.003	0.120	0.128	−0.192	−0.222
McElroy *et al.* (1990)	11	–	313	0.7 – 5.2	0.47	11	11	0.231	0.300	−0.116	−0.196	0.282	0.344	−0.519	−0.610
McElroy *et al.* (1990)	11	–	313	0.7 – 5.4	0.63	11	11	0.419	0.299	0.419	0.299	0.452	0.343	0.720	0.606
McElroy *et al.* (1990)	11	–	303	0.7 – 5.2	0.64	11	11	0.187	0.150	0.169	0.110	0.224	0.175	0.353	0.287
McElroy *et al.* (1990)	11	–	323	0.7 – 5.1	0.64	11	11	0.449	0.298	0.449	0.298	0.486	0.380	0.892	0.860
McElroy *et al.* (1990)	11	–	333	0.8 – 5.5	0.64	11	11	0.145	0.158	0.054	−0.132	0.170	0.215	−0.286	−0.571
Reamer *et al.* (1945)	34	–	311 – 478	2.8 – 68.9	0.18	34	34	0.437	0.969	0.393	0.778	0.601	2.244	2.164	9.330

Table A2.1 (continued)

Authors	Number of data points total[a]	used[b]	Temp. T/K	Covered ranges Pressure p/MPa	Compos.[c,d] x	N_1	N_2	Statistical analysis[n] AAD_1 %	AAD_2 %	Bias_1 %	Bias_2 %	RMS_1 %	RMS_2 %	MaxD_1 %	MaxD_2 %
(1 − x) CO_2 + x C_2H_6 (continued)															
***pρT* data (continued)**						**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA
Reamer *et al.* (1945)	35	–	311 – 478	2.8 – 68.9	0.33	35	34	0.712	0.818	0.687	0.574	0.869	1.769	2.373	8.609
Reamer *et al.* (1945)	34	–	311 – 478	2.8 – 68.9	0.51	34	33	0.866	0.631	0.849	0.420	0.984	1.278	1.928	5.944
Reamer *et al.* (1945)	35	–	311 – 478	2.8 – 68.9	0.68	35	35	0.801	0.592	0.777	0.384	0.862	1.342	1.401	6.701
Reamer *et al.* (1945)	34	–	311 – 478	2.8 – 68.9	0.83	34	34	0.229	0.470	0.149	−0.316	0.272	0.577	0.489	1.456
Ruhrgas (1990), Op	98	98	273 – 353	0.3 – 4.0	0.23	98	98	0.041	0.022	0.008	−0.002	0.061	0.028	0.151	0.095
Ruhrgas (1990), Op	102	102	273 – 353	0.2 – 3.9	0.46	102	102	0.072	0.022	0.033	−0.006	0.092	0.030	−0.249	0.094
Ruhrgas (1990), Op	104	104	260 – 360	0.1 – 5.8	0.70	104	104	0.120	0.036	0.082	−0.001	0.169	0.045	0.464	0.131
Ruhrgas (1990), Op	80	80	273 – 353	0.2 – 3.8	0.72	80	80	0.079	0.037	0.031	−0.029	0.106	0.063	−0.344	−0.272
Sherman *et al.* (1989)	83	–	270 – 400	3.2 – 34.8	0.01	83	83	0.212	0.469	0.194	0.432	0.331	0.954	1.336	4.402
Weber (1992)	102	–	293 – 320	0.3 – 12.2	0.26	80	–	3.380		3.375		4.339		9.838	
Weber (1992)	81	–	290 – 320	0.1 – 10.2	0.51	81	–	2.276		2.272		3.090		9.937	
Weber (1992)	70	–	295 – 320	0.3 – 9.6	0.75	69	–	1.822		−1.352		2.898		−8.229	
Isochoric heat capacity						**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA
Magee (1995)	93	–	226 – 337	236^{ρ} – 902^{ρ}	0.26	91	–	1.021		0.770		1.629		6.762	
Magee (1995)	80	–	218 – 337	232^{ρ} – 747^{ρ}	0.51	80	–	1.475		−1.187		1.758		−6.534	
Magee (1995)	86	–	218 – 341	67.6^{ρ} – 617^{ρ}	0.75	85	–	1.554		−1.450		1.826		−5.859	
Speed of sound						**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA
Estrada-Alexanders & Trusler (1999)	8	–	220	0.1 – 0.6	0.40	8	8	0.022	0.237	0.022	0.203	0.027	0.354	0.051	0.804
Estrada-Alexanders & Trusler (1999)	9	–	250	0.07 – 1.2	0.40	9	9	0.012	0.030	0.012	0.016	0.015	0.046	0.028	0.117
Estrada-Alexanders & Trusler (1999)	16	–	275	0.05 – 1.2	0.40	16	16	0.012	0.035	0.011	0.035	0.016	0.040	0.025	0.073
Estrada-Alexanders & Trusler (1999)	9	–	300	0.05 – 1.2	0.40	9	9	0.008	0.035	−0.007	0.035	0.011	0.040	−0.021	0.067
Estrada-Alexanders & Trusler (1999)	9	–	350	0.05 – 1.3	0.40	9	9	0.012	0.039	−0.012	0.039	0.016	0.045	−0.031	0.076
Estrada-Alexanders & Trusler (1999)	9	–	400	0.05 – 1.2	0.40	9	9	0.013	0.043	−0.013	0.033	0.020	0.047	−0.049	0.071
Estrada-Alexanders & Trusler (1999)	9	–	450	0.05 – 1.2	0.40	9	9	0.012	0.034	−0.011	0.030	0.015	0.037	−0.026	0.055

Table A2.1 (continued)

Authors	Number of data points			Covered ranges							Statistical analysis[n]				
	total[a]	used[b]	Temp. *T*/K	Pressure *p*/MPa	Compos.[c,d] *x*	N_1	N_2	AAD$_1$ %	AAD$_2$ %	Bias$_1$ %	Bias$_2$ %	RMS$_1$ %	RMS$_2$ %	MaxD$_1$ %	MaxD$_2$ %
(1 − *x*) CO$_2$ + *x* C$_2$H$_6$ (continued)															
Enthalpy differences						**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA
Möller *et al.* (1993)[p]	16	–	230 – 350	15.2 – 17.8	0.10	16	8	2.189	1.774	−2.189	−0.562	2.641	2.601	−6.314	−6.286
Möller *et al.* (1993)[p]	16	–	230 – 350	15.4 – 18.2	0.26	16	12	2.400	5.884	−2.159	0.154	2.475	6.899	−3.853	−14.493
Möller *et al.* (1993)[p]	16	–	230 – 350	15.5 – 18.2	0.50	16	14	2.684	6.110	−2.545	−1.168	2.804	8.358	−3.798	−19.972
Möller *et al.* (1993)[p]	16	–	230 – 350	15.5 – 18.3	0.75	16	12	3.072	3.752	−3.072	−3.611	3.231	5.336	−5.323	−11.112
Möller *et al.* (1993)[p]	15	–	230 – 350	15.5 – 18.4	0.90	15	10	1.964	6.622	−1.790	−6.622	2.119	8.170	−3.234	−18.089
Isobaric heat capacity						**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA
Ernst & Hochberg (1989)	56	–	303 – 393	0.00 – 52.9	0.50	53	53	0.817	2.744	−0.519	2.707	1.146	4.057	−2.868	11.669
VLE data						**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP
Brown *et al.* (1988)[f]	124	121	207 – 270	0.3 – 3.6	0.01 – 0.99	124	124	2.713	1.215	2.697	0.713	3.499	1.738	8.314	4.944
Clark & Stead (1988)	11	–	260	1.9 – 2.8	0.03 – 0.94	11	11	2.041	1.377	1.672	0.562	2.290	1.562	3.680	2.468
Davalos *et al.* (1976)	13	–	250	1.4 – 2.1	0.03 – 0.96	13	13	1.316	0.483	1.316	0.013	1.430	0.533	2.173	0.818
Fredenslund & Mollerup (1974)	55	50	223 – 293	0.6 – 6.3	0.04 – 0.97	49	48	1.136	0.836	0.910	−0.391	1.532	1.029	4.247	3.098
Gugnoni *et al.* (1974)[x]	50	–	241 – 283	1.2 – 5.0	0.06 – 0.92	50	50	0.668	1.074	0.379	−0.833	0.955	1.163	3.231	2.071
Hakuta *et al.* (1969)	15	–	273	2.5 – 4.0	0.04 – 0.99	15	15	2.804	2.165	2.804	1.947	3.277	2.695	5.158	4.415
Hamam & Lu (1974)	39	–	222 – 289	0.7 – 5.7	0.08 – 0.93	38	36	2.069	0.931	1.756	0.031	2.514	1.146	5.251	−2.538
Nagahama *et al.* (1974)	13	–	253	1.6 – 2.3	0.06 – 0.95	13	13	1.510	1.297	1.510	0.162	2.054	1.502	3.887	2.717
Ohgaki & Katayama (1977)	64	45	283 – 298	3.5 – 6.6	0.03 – 0.93	55	47	0.799	0.831	0.656	0.240	0.992	0.974	2.538	1.861
Robinson & Kalra (1974)	8	–	289	3.6 – 5.7	0.08 – 0.98	7	6	0.977	0.945	0.934	0.537	1.240	1.166	2.066	1.949
Vrabec & Fischer (1996)[z]	24	–	223 – 283	0.7 – 5.0	0.10 – 0.90	24	24	2.239	1.460	2.027	0.545	2.908	1.730	6.412	3.654
Wei *et al.* (1995)	76	–	207 – 270	0.4 – 3.6	0.01 – 0.99	76	76	2.850	0.980	2.848	0.216	3.316	1.309	6.442	−3.595
(1 − *x*) CO$_2$ + *x* C$_3$H$_8$															
***pρT* data**						**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA
de la Cruz de Dios *et al.* (2003)	35	–	314	0.1 – 70.4	0.07	34	–	4.314		2.985		4.967		7.263	
de la Cruz de Dios *et al.* (2003)	35	–	303	0.1 – 70.0	0.10	35	–	0.224		−0.222		0.415		−1.914	

Table A2.1 (continued)

Authors	Number of data points		Covered ranges			Statistical analysis[n]									
	total[a]	used[b]	Temp. T/K	Pressure p/MPa	Compos.[c,d] x	N_1	N_2	AAD$_1$ %	AAD$_2$ %	Bias$_1$ %	Bias$_2$ %	RMS$_1$ %	RMS$_2$ %	MaxD$_1$ %	MaxD$_2$ %
$(1-x)$ CO_2 + x C_3H_8 (continued)															
***pρT* data (continued)**						**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA
de la Cruz de Dios *et al.* (2003)	34	–	303	0.1 – 70.0	0.19	33	–	0.341		−0.227		0.382		−0.989	
de la Cruz de Dios *et al.* (2003)	32	–	323	0.1 – 70.1	0.19	32	–	0.351		−0.284		0.528		−1.600	
de la Cruz de Dios *et al.* (2003)	35	–	314	0.1 – 70.1	0.19	34	–	0.873		0.388		0.920		−1.518	
de la Cruz de Dios *et al.* (2003)	32	–	323	0.1 – 70.2	0.28	31	–	0.918		−0.713		1.015		1.522	
de la Cruz de Dios *et al.* (2003)	29	–	333	0.1 – 70.2	0.29	29	–	0.357		−0.269		0.531		−1.822	
de la Cruz de Dios *et al.* (2003)	31	–	314	0.1 – 70.1	0.30	31	–	0.333		0.038		0.475		1.132	
de la Cruz de Dios *et al.* (2003)	32	–	333	0.1 – 70.2	0.36	32	–	0.349		−0.201		0.496		−1.623	
de la Cruz de Dios *et al.* (2003)	103	–	313 – 328	0.1 – 70.0	0.38	100	–	0.295		−0.228		0.373		−1.734	
de la Cruz de Dios *et al.* (2003)	33	–	304	0.1 – 70.6	0.38	33	–	0.495		0.094		0.637		1.908	
de la Cruz de Dios *et al.* (2003)	34	–	294	5.0 – 70.2	0.38	34	–	0.256		−0.086		0.297		0.696	
de la Cruz de Dios *et al.* (2003)	30	–	333	0.1 – 70.1	0.41	28	–	0.346		0.015		0.456		−1.593	
de la Cruz de Dios *et al.* (2003)	32	–	323 – 324	0.1 – 70.3	0.52	32	–	0.377		−0.252		0.535		−1.498	
de la Cruz de Dios *et al.* (2003)	32	–	344	0.1 – 70.3	0.54	31	–	0.362		−0.351		0.517		−1.700	
Galicia-Luna *et al.* (1994)	55	55	323 – 398	7.5 – 39.5	0.69	55	–	0.395		0.295		0.528		1.839	
Galicia-Luna *et al.* (1994)	58	58	323 – 398	5.0 – 39.5	0.92	57	–	0.150		−0.083		0.184		−0.389	
Galicia-Luna *et al.* (1994)	57	57	323 – 398	5.0 – 39.5	0.97	57	–	0.172		0.128		0.210		−0.412	
Reamer *et al.* (1951)	174	174	278 – 511	1.4 – 68.9	0.21	173	–	0.432		0.161		0.531		1.510	
Reamer *et al.* (1951)	172	172	278 – 511	1.4 – 68.9	0.41	167	–	0.642		0.304		0.774		1.908	
Reamer *et al.* (1951)	173	173	278 – 511	1.4 – 68.9	0.60	170	–	0.733		0.267		0.828		1.908	
Reamer *et al.* (1951)	173	173	278 – 511	1.4 – 68.9	0.80	169	–	0.594		0.101		0.682		1.769	
Saturated liquid density[g]						**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP
Niesen & Rainwater (1990)	37	–	311	1.5 – 6.7	0.22 – 0.98	36	36	0.966	4.687	0.718	3.673	1.331	6.044	3.056	11.948
Reamer *et al.* (1951)	14	–	278	0.7 – 3.8	0.06 – 0.98	14	14	0.341	3.339	−0.230	−1.984	0.428	3.725	−0.750	−5.304
VLE data						**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP
Acosta *et al.* (1984)[x,y]	289	–	211 – 350	0.06 – 5.9	0.56 – 0.92	274	276	5.824	6.236	1.813	2.080	8.618	8.775	28.227	28.205

Table A2.1 (continued)

Authors	Number of data points total[a]	used[b]	Covered ranges Temp. T/K	Pressure p/MPa	Compos.[c,d] x	N_1	N_2	Statistical analysis[n] AAD_1 %	AAD_2 %	$Bias_1$ %	$Bias_2$ %	RMS_1 %	RMS_2 %	$MaxD_1$ %	$MaxD_2$ %
(1 − x) CO_2 + x C_3H_8 (continued)															
VLE data (continued)						**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP
Akers *et al.* (1954d)	9	–	233 – 273	0.3 – 2.8	0.18 – 0.95	9	9	13.097	14.171	−13.097	−14.171	14.983	15.954	−22.297	−26.692
Hamam & Lu (1976)	21	21	244 – 266	0.5 – 2.6	0.18 – 0.91	21	21	2.489	2.027	1.820	1.202	3.254	2.539	7.397	5.124
Meldrum & Nielson (1955)[x]	22	–	289	4.9 – 5.1	0.02 – 0.06	22	22	1.743	2.213	−1.288	−1.959	2.080	2.494	−3.684	−4.173
Nagahama *et al.* (1974)	20	–	253 – 273	0.3 – 3.4	0.05 – 0.99	20	20	4.562	4.491	3.516	2.861	6.410	6.281	14.703	14.005
Niesen & Rainwater (1990)	90	–	311 – 361	1.5 – 6.7	0.22 – 0.99	66	63	1.210	1.605	−0.325	1.352	1.526	1.916	4.102	4.950
Reamer *et al.* (1951)[f]	74	56	278 – 344	0.7 – 6.9	0.02 – 0.99	45	47	2.014	1.767	1.362	0.457	2.570	2.132	4.849	4.896
Webster & Kidnay (2001)[f]	63	–	230 – 270	0.1 – 3.1	0.04 – 0.97	63	63	6.699	5.246	6.233	4.269	10.834	8.365	27.018	21.428
Yucelen & Kidnay (1999)[e,f]	31	12	240 – 330	0.2 – 5.9	0.18 – 0.98	31	31	3.129	1.622	1.312	1.143	3.878	2.370	9.359	7.312
(1 − x) CO_2 + x n-C_4H_{10}															
***pρT* data**						**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA
Tsuji *et al.* (1998)	39	–	311	1.3 – 9.8	0.03	39	–	1.261		0.207		1.505		−3.114	
Tsuji *et al.* (1998)	28	–	311	1.2 – 7.5	0.05	27	–	1.188		0.809		1.333		−3.202	
Tsuji *et al.* (2004)	20	–	360	1.1 – 10.6	0.10	20	20	0.123	1.050	0.083	1.050	0.160	1.351	0.455	3.162
Tsuji *et al.* (2004)	15	–	360	1.6 – 10.0	0.15	15	15	0.322	1.424	0.294	1.416	0.348	1.976	0.567	4.853
Tsuji *et al.* (2004)	23	–	360	1.4 – 9.9	0.20	23	23	0.291	2.086	0.238	2.086	0.357	2.783	0.691	6.292
Excess molar enthalpy															
Guedes *et al.* (1991)	20	20	221 – 242	0.8 – 4.4	0.17 – 0.85										
VLE data						**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP
Besserer & Robinson (1971)[e,f]	16	10	311	0.3 – 7.4	0.10 – 0.97	14	14	3.397	3.426	−0.443	−1.852	4.142	4.259	−10.051	−11.005
Clark & Stead (1988)	9	6	260	0.2 – 2.2	0.10 – 0.98	9	9	9.907	10.699	2.761	0.134	13.139	13.916	27.125	26.841
Hirata & Suda (1968)[e,f]	18	1	273	0.1 – 0.2	0.99 – 1.00	18	18	3.438	3.292	3.238	3.156	4.331	4.101	9.325	9.063
Hsu *et al.* (1985)	54	44	319 – 378	2.2 – 8.1	0.13 – 0.91	49	45	1.544	1.595	0.636	−0.127	1.797	1.872	−3.962	−4.266
Kalra *et al.* (1976)	29	25	228 – 283	0.03 – 4.1	0.07 – 0.99	29	29	4.307	5.282	3.843	1.579	5.735	6.170	12.659	12.240
Leu & Robinson (1987)	27	–	368 – 418	1.5 – 7.9	0.42 – 0.99	24	23	1.790	1.808	1.439	1.510	2.020	2.032	3.940	3.368

Table A2.1 (continued)

Authors	Number of data points total[a]	used[b]	Covered ranges Temp. T/K	Pressure p/MPa	Compos.[c,d] x	N_1	N_2	Statistical analysis[n] AAD_1 %	AAD_2 %	Bias_1 %	Bias_2 %	RMS_1 %	RMS_2 %	MaxD_1 %	MaxD_2 %
$(1-x)$ CO_2 + x n-C_4H_{10} (continued)															
VLE data (continued)						**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP
Nagahama *et al.* (1974)	13	12	273 – 273	0.2 – 3.2	0.09 – 0.97	13	13	5.164	5.883	−3.989	−5.883	6.178	6.818	−12.787	−12.232
Olds *et al.* (1949)[e,f]	67	53	311 – 411	0.4 – 8.2	0.06 – 1.00	56	55	1.559	1.333	1.278	0.803	1.806	1.670	3.437	3.633
Pozo de Fernandez *et al.* (1989)[f]	120	–	278 – 418	0.2 – 8.2	0.07 – 0.98	110	112	1.890	1.724	0.954	0.312	2.394	2.212	8.330	6.707
Shibata & Sandler (1989)	33	28	311 – 411	0.7 – 8.1	0.08 – 0.99	32	29	1.791	2.150	0.781	−0.215	2.289	2.606	5.937	5.081
Weber (1989)	52	44	309 – 394	0.4 – 8.0	0.15 – 0.99	47	46	1.514	1.641	0.574	−0.076	1.915	1.996	4.914	−4.385
$(1-x)$ CO_2 + x i-C_4H_{10}															
***pρT* data**						**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA
Tsuji *et al.* (1998)	39	–	311	1.0 – 9.7	0.03	34	–	1.129		−0.608		1.716		−4.899	
Tsuji *et al.* (1998)	41	–	311	2.8 – 9.2	0.05	35	–	1.614		0.494		1.859		−4.691	
Tsuji *et al.* (2004)	12	–	360	2.1 – 10.5	0.10	12	12	0.246	0.927	0.162	0.927	0.299	1.106	0.612	2.326
Tsuji *et al.* (2004)	15	–	360	1.9 – 10.3	0.15	15	15	0.206	1.086	0.101	1.086	0.228	1.543	−0.414	3.965
Tsuji *et al.* (2004)	19	–	360	1.1 – 10.1	0.20	19	19	0.359	1.690	0.047	1.544	0.404	2.259	−0.849	5.219
Saturated liquid density[g]						**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP
Besserer & Robinson (1973a)	29	–	311 – 394	0.7 – 7.2	0.12 – 0.97	22	22	1.916	5.679	1.586	4.463	2.177	6.979	4.450	12.773
VLE data						**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP
Besserer & Robinson (1973a)	29	14	311 – 394	0.7 – 7.2	0.12 – 0.97	28	28	1.906	2.305	1.591	1.965	2.312	2.706	5.161	5.638
Weber (1989)	65	59	311 – 394	0.6 – 7.4	0.10 – 0.99	62	59	1.094	1.148	0.246	0.532	1.350	1.480	3.385	3.079
$(1-x)$ CO_2 + x n-C_5H_{12}															
***pρT* data**						**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA
Besserer & Robinson (1973b)	96	34	278 – 378	0.2 – 9.6	0.01 – 0.99	94	–	2.232		0.376		2.916		8.777	
Chen *et al.* (2003)	21	–	312	7.8 – 9.6	0.04	11	–	4.447		−4.447		5.267		−9.689	
Chen *et al.* (2003)	24	–	316	7.9 – 11.5	0.05	14	–	3.669		−3.669		4.480		−8.851	
Chen *et al.* (2003)	35	–	323	8.2 – 11.3	0.06	24	–	5.993		−5.993		6.456		−9.956	

Table A2.1 (continued)

Authors	Number of data points			Covered ranges				Statistical analysis^n						
	total^a	used^b	Temp. T/K	Pressure p/MPa	Compos.^{c,d} x	N_1	N_2	AAD_1 %	AAD_2 %	$Bias_1$ %	$Bias_2$ %	RMS_1 %	RMS_2 %	$MaxD_1$ %	$MaxD_2$ %
(1 − x) CO_2 + x n-C_5H_{12} (continued)															
***pρT* data (continued)**						**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA
Chen *et al.* (2003)	27	–	323	8.2 – 14.5	0.08	20	–	3.883		−3.883		4.670		−9.368	
Chen *et al.* (2003)	169	–	318 – 328	7.9 – 14.9	0.10	139	–	3.908		−3.908		4.490		−9.705	
Chen *et al.* (2003)	20	–	323	7.9 – 14.7	0.13	20	–	3.697		−3.697		3.929		−6.356	
Chen *et al.* (2003)	11	–	323	7.2 – 14.5	0.21	11	–	1.296		1.296		1.350		1.737	
Chen *et al.* (2003)	8	–	323	6.2 – 13.8	0.33	8	–	6.507		6.507		6.507		6.595	
Chen *et al.* (2003)	13	–	323	3.6 – 14.8	0.64	13	–	0.372		0.372		0.402		0.609	
Chen *et al.* (2003)	11	–	323	2.3 – 15.2	0.79	11	–	0.550		−0.275		0.820		−2.040	
Kiran *et al.* (1996)	60	59	323 – 423	9.6 – 64.8	0.08	60	–	0.669		0.109		0.913		−2.975	
Kiran *et al.* (1996)	55	47	323 – 423	9.7 – 64.8	0.13	54	–	0.814		−0.677		1.042		−3.892	
Kiran *et al.* (1996)	51	45	323 – 423	14.7 – 64.9	0.19	47	–	2.326		0.370		2.624		4.823	
Kiran *et al.* (1996)	40	26	323 – 398	17.6 – 65.0	0.27	40	–	2.074		−1.107		2.492		−4.019	
Kiran *et al.* (1996)	46	45	323 – 423	13.5 – 64.9	0.38	46	–	1.374		0.533		1.805		3.923	
Kiran *et al.* (1996)	38	36	323 – 398	12.2 – 64.8	0.53	36	–	0.219		0.036		0.268		−0.517	
Kiran *et al.* (1996)	37	36	323 – 398	13.2 – 65.0	0.71	36	–	0.300		0.201		0.400		0.916	
Kiran *et al.* (1996)	42	38	323 – 398	8.6 – 64.9	0.85	38	–	0.594		0.581		0.669		1.177	
VLE data						**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP
Besserer & Robinson (1973b)	48	25	278 – 378	0.2 – 9.6	0.02 – 0.99	45	48	4.954	3.522	4.654	2.059	6.704	5.146	18.729	15.545
Cheng *et al.* (1989)	117	44	253 – 459	0.2 – 9.9	0.03 – 0.99	106	110	5.120	2.369	1.288	−0.187	6.220	3.192	18.854	−9.463
Tochigi *et al.* (1998)	41	–	310 – 363	0.6 – 9.7	0.08 – 0.97	36	41	7.981	5.115	7.981	5.091	9.464	7.453	24.514	25.588
Xu *et al.* (1991)	8	3	343	0.6 – 9.1	0.22 – 0.98	8	8	7.025	5.376	7.025	4.749	8.396	7.444	14.279	13.156
(1 − x) CO_2 + x i-C_5H_{12}															
***pρT* data**						**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA
Besserer & Robinson (1975)	82	69	278 – 378	0.2 – 8.9	0.00 – 0.99	80	–	2.347		1.415		2.969		−7.636	
Bian *et al.* (1993)	24	22	378	2.0 – 9.4	0.22 – 0.92	24	–	3.519		3.519		3.917		6.799	

Table A2.1 (continued)

Authors	Number of data points		Covered ranges			Statistical analysis^n									
	total^a	used^b	Temp. T/K	Pressure p/MPa	Compos.^{c,d} x	N_1	N_2	AAD$_1$ %	AAD$_2$ %	Bias$_1$ %	Bias$_2$ %	RMS$_1$ %	RMS$_2$ %	MaxD$_1$ %	MaxD$_2$ %
(1 − x) CO_2 + x i-C_5H_{12} (continued)															
VLE data						**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP
Besserer & Robinson (1975)	41	28	278 – 378	0.2 – 8.9	0.03 – 0.99	40	41	3.575	2.827	3.119	0.441	4.494	3.319	8.842	7.112
Bian *et al.* (1993)	12	8	378	2.0 – 9.4	0.29 – 0.92	11	10	1.715	1.409	−1.574	−0.124	2.320	1.673	−4.531	−3.484
(1 − x) CO_2 + x n-C_6H_{14}															
VLE data						**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP
Ohgaki & Katayama (1976)	20	20	298 – 313	0.4 – 7.7	0.08 – 0.95	20	20	4.284	5.293	0.403	−0.471	4.958	6.580	8.140	16.234
(1 − x) CO_2 + x n-C_7H_{16}															
***pρT* data**						**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA
Fenghour *et al.* (2001)	8	–	302 – 368	3.5 – 50.0	0.57	8	–	1.048		1.048		1.048		1.062	
Fenghour *et al.* (2001)	9	–	321 – 386	4.0 – 44.5	0.61	9	–	1.626		1.626		1.626		1.664	
Fenghour *et al.* (2001)	10	–	363 – 459	4.4 – 55.5	0.71	9	–	2.536		2.536		2.537		2.615	
Francis (1954)	2	2	299	0.1	0.12 – 0.52	2	–	3.212		3.084		4.453		6.297	
Kalra *et al.* (1978b)	112	99	311 – 394	0.2 – 13.3	0.01 – 0.98	102	–	2.967		0.815		3.590		−9.961	
VLE data						**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP
Kalra *et al.* (1978b)	64	44	311 – 477	0.2 – 13.3	0.05 – 0.98	57	62	5.145	2.339	0.063	−0.374	6.290	3.929	−14.066	−17.034
(1 − x) CO_2 + x n-C_8H_{18}															
VLE data						**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP
Weng & Lee (1992)	20	16	313 – 348	1.5 – 11.4	0.11 – 0.86	18	7	6.039	21.659	2.886	21.659	7.013	22.584	12.202	28.688
(1 − x) CO_2 + x H_2															
***pρT* data**						**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA
Ababio & McElroy (1993)	9	8	342 – 343	2.5 – 12.1	0.36	9	9	0.360	0.147	−0.353	0.036	0.463	0.173	−0.855	−0.331
Ababio & McElroy (1993)	11	11	323	1.0 – 11.4	0.38	11	11	0.234	0.122	−0.174	0.041	0.270	0.137	−0.536	0.270

Table A2.1 (continued)

Authors	Number of data points total[a]	used[b]	Temp. T/K	Covered ranges Pressure p/MPa	Compos.[c,d] x	N_1	N_2	Statistical analysis[n] AAD_1 %	AAD_2 %	Bias_1 %	Bias_2 %	RMS_1 %	RMS_2 %	MaxD_1 %	MaxD_2 %
$(1-x)$ $CO_2 + x$ H_2 (continued)															
***pρT* data (continued)**						**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA
Ababio & McElroy (1993)	9	9	333	0.6 – 12.7	0.40	9	9	0.278	0.057	−0.265	0.047	0.302	0.067	−0.463	0.104
Ababio & McElroy (1993)	11	11	313	0.8 – 11.5	0.43	11	11	0.094	0.145	−0.028	0.102	0.120	0.171	−0.305	0.342
Ababio & McElroy (1993)	13	13	303	0.8 – 10.8	0.49	13	13	0.119	0.117	−0.055	−0.003	0.161	0.148	−0.401	−0.310
Bezanehtak *et al.* (2002)	42	–	278 – 298	4.8 – 19.3	0.01 – 0.16	–	–								
Jaeschke *et al.* (1997)	128	128	275 – 350	0.2 – 12.2	0.50	128	128	0.082	0.019	−0.005	0.015	0.134	0.034	0.645	0.189
Jaeschke *et al.* (1997)	136	136	275 – 350	0.3 – 26.3	0.75	136	136	0.046	0.015	−0.028	0.001	0.076	0.033	0.523	−0.287
Kritschewsky & Markov (1940)	24	–	323 – 473	5.1 – 50.7	0.47	24	24	2.055	1.640	2.055	1.014	2.641	2.314	6.894	7.148
Kritschewsky & Markov (1940)	30	–	273 – 473	5.1 – 50.7	0.74	30	30	1.573	1.165	1.573	0.865	1.683	1.323	3.290	2.615
VLE data						**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP
Barrick *et al.* (1966)	38	–	220 – 290	1.1 – 20.3	0.00 – 0.14	33	13	9.247	20.879	0.874	20.879	10.821	22.104	−25.694	29.143
Bezanehtak *et al.* (2002)[e]	42	34	278 – 298	4.8 – 19.3	0.01 – 0.16	38	11	1.840	5.962	0.234	5.962	2.296	6.396	6.841	9.736
Spano *et al.* (1968)[e,f]	58	34	220 – 290	1.1 – 20.3	0.00 – 0.14	40	14	9.028	20.995	1.512	20.995	10.699	22.185	−25.692	29.144
$(1-x)$ $CO_2 + x$ O_2															
VLE data						**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP
Fredenslund & Sather (1970)[f]	72	–	223 – 283	1.0 – 13.2	0.01 – 0.78	36	51	19.586	18.429	−19.586	17.518	20.717	19.790	−28.466	28.996
Fredenslund & Sather (1970)	72	–	223 – 283	1.0 – 13.2	0.00 – 0.39	40	52	19.063	18.846	−19.063	18.814	20.648	20.363	−29.966	29.625
$(1-x)$ $CO_2 + x$ CO															
***pρT* data**						**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA
Mallu *et al.* (1986)	75	–	323 – 423	0.1 – 6.5	0.43	75	72	0.487	2.736	0.487	−2.736	0.612	3.573	1.435	−8.999
$(1-x)$ $CO_2 + x$ H_2O															
***pρT* data**						**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA
Fenghour *et al.* (1996b)	22	22	415 – 698	5.9 – 10.8	0.06	22	22	0.055	0.508	0.043	0.508	0.068	0.513	0.162	0.640

Table A2.1 (continued)

Authors	Number of data points		Covered ranges			Statistical analysis[n]									
	total[a]	used[b]	Temp. T/K	Pressure p/MPa	Compos.[c,d] x	N_1	N_2	AAD$_1$ %	AAD$_2$ %	Bias$_1$ %	Bias$_2$ %	RMS$_1$ %	RMS$_2$ %	MaxD$_1$ %	MaxD$_2$ %
(1 − *x*) CO_2 + *x* H_2O (continued)															
***pρT* data (continued)**						**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA
Fenghour *et al.* (1996b)	19	19	455 – 698	7.1 – 11.8	0.14	19	19	0.203	0.980	0.203	0.980	0.212	0.985	0.317	1.188
Fenghour *et al.* (1996b)	18	18	470 – 698	7.8 – 12.7	0.21	18	18	0.295	1.369	0.295	1.369	0.308	1.377	0.522	1.709
Fenghour *et al.* (1996b)	16	16	497 – 698	9.1 – 14.0	0.29	16	16	0.091	1.518	0.050	1.518	0.140	1.533	0.411	2.014
Fenghour *et al.* (1996b)	14	14	519 – 693	10.5 – 15.4	0.37	14	14	0.124	2.031	0.039	2.031	0.181	2.050	0.514	2.674
Fenghour *et al.* (1996b)	12	12	544 – 693	12.2 – 17.0	0.43	12	12	0.177	2.482	−0.077	2.482	0.193	2.503	0.371	3.169
Fenghour *et al.* (1996b)	11	11	563 – 698	14.3 – 19.8	0.53	11	11	0.768	4.384	0.768	4.384	0.806	4.411	1.375	5.374
Fenghour *et al.* (1996b)	12	12	580 – 699	16.6 – 22.7	0.60	12	12	0.309	4.843	0.021	4.843	0.367	4.901	0.777	6.169
Fenghour *et al.* (1996b)	10	10	617 – 699	21.4 – 27.3	0.69	10	10	0.353	6.717	−0.257	6.717	0.388	6.761	−0.539	8.116
Fenghour *et al.* (1996b)	9	9	625 – 699	24.2 – 31.4	0.75	9	7	0.395	8.506	−0.214	8.506	0.440	8.536	−0.606	9.682
Fenghour *et al.* (1996b)	8	7	635 – 699	26.8 – 34.6	0.79	8	3	0.440	9.532	−0.287	9.532	0.483	9.537	−0.692	9.923
Patel & Eubank (1988)	75	75	323 – 498	0.1 – 9.3	0.02	75	75	0.010	0.043	−0.005	0.043	0.019	0.080	−0.093	0.362
Patel & Eubank (1988)	75	75	323 – 498	0.1 – 8.9	0.05	75	75	0.048	0.037	−0.048	0.037	0.079	0.074	−0.295	0.276
Patel & Eubank (1988)	63	62	348 – 498	0.1 – 10.2	0.10	62	62	0.042	0.109	−0.042	0.109	0.062	0.224	−0.200	0.838
Patel & Eubank (1988)	47	47	373 – 498	0.1 – 10.1	0.25	47	47	0.029	0.152	−0.019	0.152	0.042	0.352	−0.132	1.737
Patel & Eubank (1988)	37	37	398 – 498	0.1 – 3.7	0.50	37	37	0.049	0.081	0.047	0.077	0.078	0.152	0.255	0.612
VLE data						**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP
Takenouchi & Kennedy (1964)	120	–	383 – 623	10.0 – 150	0.71 – 1.00	–	–								
Tödheide & Franck (1963)	81	–	523 – 623	20.0 – 350	0.57 – 0.99	–	–								
(1 − *x*) CO_2 + *x* He															
***pρT* data**						**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA
Altunin *et al.* (1975)	13	13	343	1.1 – 20.9	0.14	13	13	0.972	0.525	−0.972	−0.104	1.287	0.635	−3.096	1.443
Altunin *et al.* (1975)	11	11	313	1.5 – 14.8	0.15	11	11	0.705	0.355	−0.597	−0.134	1.374	0.413	−4.035	0.834
Altunin *et al.* (1975)	20	–	303 – 313	0.9 – 15.2	0.15	19	19	1.064	1.260	1.055	1.201	1.481	2.003	3.840	5.371
Altunin *et al.* (1975)	16	16	343	0.5 – 24.2	0.20	16	16	0.989	0.591	−0.989	−0.195	1.276	0.723	−2.960	1.861
Altunin *et al.* (1975)	14	14	343	0.9 – 25.1	0.22	14	14	0.843	0.639	−0.843	0.111	1.055	0.899	−2.429	2.425

Table A2.1 (continued)

Authors	Number of data points total[a]	used[b]	Temp. T/K	Covered ranges Pressure p/MPa	Compos.[c,d] x	N_1	N_2	Statistical analysis[n] AAD$_1$ %	AAD$_2$ %	Bias$_1$ %	Bias$_2$ %	RMS$_1$ %	RMS$_2$ %	MaxD$_1$ %	MaxD$_2$ %
$(1-x)$ CO$_2$ + x He (continued)															
***$p\rho T$* data (continued)**						**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA
Altunin *et al.* (1975)	17	17	323	0.4 – 24.4	0.23	17	17	0.450	0.741	−0.450	0.265	0.703	1.171	−2.301	3.221
Altunin *et al.* (1975)	13	13	343	1.1 – 24.9	0.25	13	13	0.741	0.679	−0.741	0.269	0.895	1.030	−1.916	2.809
Altunin *et al.* (1975)	11	11	313	1.2 – 14.9	0.26	11	11	0.302	0.720	−0.016	0.133	0.336	1.015	0.575	2.737
Altunin *et al.* (1975)	12	12	373	1.2 – 25.1	0.29	12	12	0.417	0.737	−0.417	0.737	0.495	1.226	−0.933	3.148
Altunin *et al.* (1975)	11	10	343	1.8 – 24.8	0.30	11	11	0.854	1.013	−0.355	0.687	1.070	1.664	2.742	4.102
Altunin *et al.* (1975)	13	13	323	0.8 – 25.6	0.32	13	13	0.449	1.361	0.449	1.361	0.627	2.392	1.629	6.721
Altunin *et al.* (1975)	11	10	323	0.8 – 14.7	0.35	11	11	0.426	0.819	0.377	0.796	0.810	1.565	2.360	4.473
Altunin *et al.* (1975)	9	–	323	2.0 – 18.7	0.37	6	7	4.929	5.419	−4.929	−5.419	5.389	6.011	−8.672	−9.976
Altunin *et al.* (1975)	10	10	303	0.9 – 12.9	0.39	10	10	1.088	1.301	1.083	1.290	1.624	2.080	3.318	4.771
Altunin *et al.* (1975)	16	14	323	0.4 – 24.6	0.39	16	16	0.629	1.394	0.182	1.078	1.283	2.583	4.233	7.516
Altunin *et al.* (1975)	11	11	313	1.1 – 15.7	0.40	11	11	0.406	0.365	−0.384	0.153	0.476	0.606	−0.802	1.783
Altunin *et al.* (1975)	14	14	373	0.5 – 17.9	0.41	14	14	0.238	0.568	−0.238	0.568	0.320	0.887	−0.708	2.383
Altunin *et al.* (1975)	13	13	323	0.7 – 26.5	0.42	13	13	0.273	1.419	0.251	1.404	0.385	2.199	1.091	5.625
Altunin *et al.* (1975)	11	11	313	1.1 – 15.7	0.44	11	11	0.508	0.389	−0.508	0.203	0.579	0.732	−1.076	2.142
Altunin *et al.* (1975)	12	12	323	0.8 – 21.6	0.44	12	12	0.343	0.701	−0.343	0.682	0.433	1.249	−0.816	3.556
Altunin *et al.* (1975)	15	15	343	0.5 – 24.3	0.47	15	15	0.201	0.929	−0.199	0.929	0.294	1.527	−0.645	4.386
Altunin *et al.* (1975)	10	10	313	1.4 – 15.1	0.51	10	10	0.585	1.562	0.585	1.562	0.638	1.923	1.139	4.076
Altunin *et al.* (1975)	10	10	303	1.1 – 16.1	0.53	10	10	1.165	2.111	1.153	2.111	1.686	3.018	3.238	6.426
Altunin *et al.* (1975)	10	10	313	1.3 – 15.3	0.54	10	10	0.840	0.407	−0.840	0.243	0.919	0.674	−1.345	1.825
Altunin *et al.* (1975)	15	15	343	0.5 – 24.5	0.57	15	15	0.615	0.652	−0.615	0.652	0.763	1.202	−1.386	3.509
Altunin *et al.* (1975)	12	12	343	0.5 – 15.1	0.58	12	12	0.525	0.453	−0.525	0.433	0.612	0.777	−0.979	2.092
Altunin *et al.* (1975)	15	15	373	0.5 – 24.7	0.61	15	15	0.483	0.739	−0.483	0.739	0.597	1.240	−1.052	3.459
Altunin *et al.* (1975)	10	10	313	1.3 – 15.2	0.64	10	10	0.956	0.361	−0.956	0.297	1.064	0.642	−1.636	1.722
Altunin *et al.* (1975)	8	8	343	2.9 – 20.5	0.64	8	8	0.735	1.152	−0.735	1.152	0.799	1.433	−1.241	2.868
Altunin *et al.* (1975)	9	9	343	1.9 – 17.2	0.68	9	9	0.640	0.786	−0.640	0.786	0.705	1.038	−1.173	2.210
Altunin *et al.* (1975)	11	10	323	1.1 – 25.6	0.68	11	11	0.945	1.315	−0.945	0.752	1.281	1.783	−3.326	3.718

Table A2.1 (continued)

Authors	Number of data points total[a]	used[b]	Covered ranges Temp. T/K	Pressure p/MPa	Compos.[c,d] x	N_1	N_2	Statistical analysis[n] AAD_1 %	AAD_2 %	Bias_1 %	Bias_2 %	RMS_1 %	RMS_2 %	MaxD_1 %	MaxD_2 %
$(1-x)$ CO$_2$ + x He (continued)															
***pρT* data (continued)**						**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA
Altunin *et al.* (1975)	10	10	313	1.3 – 15.7	0.74	10	10	0.747	0.467	−0.747	0.467	0.861	0.718	−1.359	1.796
Altunin *et al.* (1975)	9	9	303	0.9 – 11.1	0.80	9	9	0.285	0.492	−0.285	0.484	0.328	0.651	−0.621	1.373
Kessel'man & Alekseenko (1974)	6	6	340 – 440	18.6 – 34.8	0.12	6	6	0.285	3.297	0.024	3.297	0.398	3.409	0.889	5.128
Kessel'man & Alekseenko (1974)	6	6	340 – 440	30.7 – 50.6	0.28	6	6	0.973	5.877	0.973	5.877	1.193	5.938	2.440	7.614
Kessel'man & Alekseenko (1974)	9	9	340 – 600	20.9 – 46.7	0.32	9	9	0.614	3.579	−0.497	3.579	0.714	3.599	−1.130	4.393
Kessel'man & Alekseenko (1974)	4	4	500 – 650	14.2 – 18.9	0.34	4	4	1.582	2.743	0.565	2.743	1.684	3.189	2.305	4.494
Kessel'man & Alekseenko (1974)	6	6	340 – 440	20.2 – 28.9	0.36	6	6	0.808	4.306	0.356	4.306	1.003	4.388	1.888	5.901
Kessel'man & Alekseenko (1974)	4	4	360 – 440	1.8 – 2.2	0.36	4	4	0.072	0.170	−0.072	0.170	0.086	0.170	−0.121	0.197
Kessel'man & Alekseenko (1974)	6	6	340 – 440	22.5 – 32.5	0.42	6	6	0.523	4.485	0.006	4.485	0.632	4.510	1.177	5.353
Kessel'man & Alekseenko (1974)	4	4	500 – 650	24.3 – 32.5	0.44	4	4	0.345	3.596	0.041	3.596	0.438	3.622	0.771	4.310
Kessel'man & Alekseenko (1974)	6	6	500 – 800	1.6 – 2.4	0.47	6	6	1.213	0.945	−1.213	−0.945	1.479	1.266	−2.398	−2.139
Kessel'man & Alekseenko (1974)	6	6	340 – 440	9.2 – 12.3	0.51	6	6	0.809	2.723	0.809	2.723	0.858	2.726	1.293	2.924
Kessel'man & Alekseenko (1974)	6	6	340 – 440	15.7 – 21.4	0.52	6	6	0.920	2.504	−0.860	2.504	1.079	2.571	−2.031	3.242
Kessel'man & Alekseenko (1974)	7	7	500 – 800	6.2 – 9.9	0.52	7	7	0.245	1.168	0.127	1.168	0.411	1.231	1.045	2.073
Kessel'man & Alekseenko (1974)	6	6	340 – 440	19.0 – 25.9	0.55	6	6	0.531	4.492	0.531	4.492	0.638	4.500	1.164	4.953
Kessel'man & Alekseenko (1974)	6	6	340 – 440	32.5 – 45.2	0.55	6	6	0.226	6.160	0.137	6.160	0.350	6.170	0.779	6.821
Kessel'man & Alekseenko (1974)	5	5	340 – 420	33.1 – 43.0	0.58	5	5	0.555	5.571	−0.555	5.571	0.572	5.574	−0.703	5.868
Kessel'man & Alekseenko (1974)	5	5	360 – 440	1.2 – 1.5	0.60	5	5	0.167	0.084	−0.167	0.084	0.171	0.089	−0.197	0.137
Kessel'man & Alekseenko (1974)	39	39	340 – 440	3.3 – 44.0	0.67	39	39	0.639	2.392	−0.513	2.392	0.769	2.700	−1.931	5.269
Kessel'man & Alekseenko (1974)	7	7	500 – 800	10.1 – 16.0	0.70	7	7	0.281	1.495	0.267	1.495	0.326	1.502	0.525	1.710
Kessel'man & Alekseenko (1974)	6	6	340 – 440	1.1 – 1.5	0.78	6	6	0.078	0.101	−0.078	0.101	0.085	0.105	−0.129	0.155
Kessel'man & Alekseenko (1974)	5	5	340 – 440	2.8 – 3.6	0.83	5	5	0.808	1.118	0.808	1.118	0.817	1.122	0.948	1.229
Kessel'man & Alekseenko (1974)	6	6	340 – 440	6.8 – 8.8	0.85	6	6	1.449	2.116	1.449	2.116	1.449	2.116	1.514	2.146
Kessel'man & Alekseenko (1974)	5	5	340 – 440	9.6 – 12.4	0.89	5	5	1.047	1.666	1.047	1.666	1.050	1.666	1.146	1.679
Kessel'man & Alekseenko (1974)	6	6	340 – 440	13.5 – 17.4	0.92	6	6	0.812	1.422	0.812	1.422	0.814	1.423	0.883	1.539
Kessel'man & Alekseenko (1974)	6	6	340 – 440	5.7 – 7.4	0.92	6	6	1.002	1.202	1.002	1.202	1.003	1.202	1.059	1.221

Table A2.1 (continued)

Authors	Number of data points total[a]	used[b]	Covered ranges Temp. T/K	Pressure p/MPa	Compos.[c,d] x	N_1	N_2	AAD_1 %	AAD_2 %	Statistical analysis[n] $Bias_1$ %	$Bias_2$ %	RMS_1 %	RMS_2 %	$MaxD_1$ %	$MaxD_2$ %
(1 − x) CO_2 + x He (continued)															
***pρT* data (continued)**						**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA
Kessel'man & Alekseenko (1974)	6	6	340 – 440	15.5 – 20.0	0.93	6	6	0.458	1.110	0.458	1.110	0.505	1.125	0.637	1.220
Kessel'man & Alekseenko (1974)	5	5	340 – 440	4.6 – 5.9	0.94	5	5	0.402	0.447	0.402	0.447	0.446	0.480	0.525	0.570
Kessel'man & Alekseenko (1974)	6	6	340 – 440	9.3 – 11.9	0.95	6	6	0.965	1.131	0.965	1.131	0.974	1.136	1.057	1.197
Kessel'man & Alekseenko (1974)	6	6	340 – 440	13.9 – 17.9	0.96	6	6	0.981	1.283	0.981	1.283	0.982	1.283	1.030	1.318
Kosov & Brovanov (1975)	15	15	313	18.7 – 58.8	0.28	15	–	0.920		0.920		1.144		2.594	
Kosov & Brovanov (1975)	14	14	353	21.7 – 58.8	0.29	14	–	3.576		3.576		3.589		4.154	
Kosov & Brovanov (1975)	14	14	313	18.7 – 55.8	0.51	14	–	2.787		2.787		2.795		3.048	
Kosov & Brovanov (1975)	13	13	353	19.7 – 58.8	0.53	13	–	4.303		4.303		4.303		4.394	
Kosov & Brovanov (1975)	15	15	313	19.7 – 58.8	0.77	15	–	0.155		0.155		0.177		0.385	
Kosov & Brovanov (1975)	14	14	353	21.6 – 58.8	0.78	14	–	0.566		0.566		0.571		0.746	
Linshits *et al.* (1975)	17	17	323	0.7 – 26.5	0.22	17	17	0.484	1.290	−0.241	0.622	0.557	1.897	−1.275	4.420
Linshits *et al.* (1975)	14	14	323	1.3 – 27.6	0.39	14	14	0.458	1.615	0.243	1.511	0.553	2.510	1.016	6.049
Linshits *et al.* (1975)	17	17	323	0.6 – 31.3	0.54	17	17	0.589	1.036	−0.589	0.977	0.658	1.869	−1.132	5.338
Linshits *et al.* (1975)	17	17	323	0.5 – 28.0	0.59	17	17	0.648	0.852	−0.648	0.833	0.767	1.569	−1.284	4.528
Linshits *et al.* (1975)	16	13	323	0.7 – 29.4	0.74	16	16	1.015	1.335	−0.471	1.016	1.729	2.404	4.139	8.108
Linshits *et al.* (1975)	17	17	323	0.5 – 29.0	0.83	17	17	0.436	0.592	−0.436	0.589	0.524	1.051	−0.921	3.072
Linshits *et al.* (1975)	17	17	323	0.4 – 28.8	0.90	17	17	0.143	0.514	−0.143	0.482	0.160	0.852	−0.260	2.493
Tsiklis *et al.* (1974a)	10	10	373	2.5 – 25.3	0.10	10	10	0.800	1.971	0.329	1.971	0.996	2.468	1.728	3.986
Tsiklis *et al.* (1974a)	10	10	373	2.5 – 25.3	0.20	10	10	0.365	1.649	−0.280	1.628	0.492	2.101	−1.226	3.728
Tsiklis *et al.* (1974a)	10	10	373	2.5 – 25.3	0.30	10	10	0.814	1.299	−0.814	1.271	0.862	1.693	−1.076	3.111
Tsiklis *et al.* (1974a)	10	10	373	2.5 – 25.3	0.40	9	9	1.022	1.240	−1.022	1.239	1.131	1.578	−2.033	2.770
Tsiklis *et al.* (1974a)	10	10	373	2.5 – 25.3	0.50	10	10	1.283	1.294	−1.283	1.294	1.385	1.570	−2.192	2.731
Tsiklis *et al.* (1974a)	10	9	373	2.5 – 25.3	0.60	10	10	1.387	1.522	−1.387	1.255	1.471	1.750	−2.332	2.941
Tsiklis *et al.* (1974a)	10	10	373	2.5 – 25.3	0.70	10	10	1.068	1.347	−1.068	1.347	1.122	1.617	−1.590	2.900
Tsiklis *et al.* (1974a)	10	9	373	2.5 – 25.3	0.80	10	10	1.131	1.590	−0.208	1.590	1.636	2.529	4.616	7.098
Tsiklis *et al.* (1974a)	10	10	373	2.5 – 25.3	0.90	10	10	0.094	0.805	−0.057	0.801	0.108	0.975	−0.179	1.681

Table A2.1 (continued)

Authors	Number of data points total[a]	used[b]	Covered ranges Temp. T/K	Pressure p/MPa	Compos.[c,d] x	Statistical analysis[n] N_1	N_2	AAD$_1$ %	AAD$_2$ %	Bias$_1$ %	Bias$_2$ %	RMS$_1$ %	RMS$_2$ %	MaxD$_1$ %	MaxD$_2$ %
(1 − x) CO$_2$ + x He (continued)															
***pρT* data (continued)**						**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA
Tsiklis *et al.* (1974b)	12	–	423	2.5 – 30.4	0.10	2	2	5.683	5.410	−5.683	−5.410	5.999	5.708	−7.605	−7.229
Tsiklis *et al.* (1974b)	12	–	423	2.5 – 30.4	0.20	3	4	5.617	6.184	−5.617	−6.184	6.048	6.713	−8.343	−9.603
Tsiklis *et al.* (1974b)	12	–	423	2.5 – 30.4	0.30	5	12	5.514	7.059	−5.514	−7.059	6.012	7.522	−8.749	−9.687
Tsiklis *et al.* (1974b)	12	–	423	2.5 – 30.4	0.40	12	12	5.232	2.492	−5.232	−2.492	5.636	2.598	−7.889	−3.095
Tsiklis *et al.* (1974b)	12	12	423	2.5 – 30.4	0.50	12	12	1.181	1.590	−1.181	1.590	1.251	1.880	−1.698	3.122
Tsiklis *et al.* (1974b)	12	12	423	2.5 – 30.4	0.60	12	12	2.819	5.426	2.819	5.426	3.161	6.052	5.101	9.249
Tsiklis *et al.* (1974b)	12	–	423	2.5 – 30.4	0.70	9	6	5.501	5.426	5.501	5.426	6.050	5.992	8.785	8.943
Tsiklis *et al.* (1974b)	12	–	423	2.5 – 30.4	0.80	5	4	6.116	5.795	6.116	5.795	6.727	6.333	9.963	9.157
Tsiklis *et al.* (1974b)	12	–	423	2.5 – 30.4	0.90	3	2	6.450	4.865	6.450	4.865	7.002	5.120	9.861	6.463
Weems & Howard (1970)	7	7	253 – 263	0.7 – 2.8	0.07	7	7	0.658	0.111	0.658	0.111	0.765	0.131	1.349	0.248
Weems & Howard (1970)	7	7	253 – 263	0.7 – 2.8	0.12	7	7	0.977	0.226	0.977	0.211	1.161	0.289	1.987	0.558
Weems & Howard (1970)	9	9	253 – 263	0.7 – 3.4	0.22	9	9	1.597	0.410	1.597	0.410	1.869	0.539	3.238	1.144
Weems & Howard (1970)	10	10	253 – 263	0.7 – 4.1	0.24	10	10	1.868	0.577	1.868	0.575	2.218	0.758	4.136	1.605
Weems & Howard (1970)	13	13	253 – 263	0.7 – 5.5	0.42	13	13	1.403	0.698	1.403	0.698	1.629	0.883	3.032	1.935
Weems & Howard (1970)	14	14	253 – 263	0.7 – 5.5	0.51	14	14	0.885	0.711	0.885	0.711	1.015	0.853	1.695	1.661
Weems & Howard (1970)	17	17	253 – 263	0.7 – 6.9	0.73	17	17	0.102	0.663	−0.102	0.663	0.108	0.784	−0.178	1.552
Weems & Howard (1970)	20	20	253 – 263	0.7 – 6.9	0.83	20	20	0.280	0.496	−0.280	0.496	0.306	0.575	−0.458	1.021
Weems & Howard (1970)	20	20	253 – 263	0.7 – 6.9	0.89	20	20	0.168	0.364	−0.168	0.364	0.184	0.422	−0.271	0.758
Weems & Howard (1970)	20	20	253 – 263	0.7 – 6.9	0.95	20	20	0.032	0.234	0.032	0.234	0.040	0.274	0.077	0.507
Weems & Miller (1969)	40	40	273 – 308	0.3 – 5.2	0.06	40	40	0.515	0.324	0.515	0.324	0.659	0.393	1.715	1.081
Weems & Miller (1969)	37	37	273 – 308	0.4 – 5.5	0.08	37	37	0.683	0.386	0.683	0.386	0.895	0.502	2.449	1.450
Weems & Miller (1969)	39	39	273 – 308	0.2 – 4.6	0.25	39	39	0.560	0.263	0.559	0.251	0.767	0.376	1.840	0.975
Weems & Miller (1969)	38	38	273 – 308	0.2 – 5.6	0.48	38	38	0.228	0.305	0.212	0.293	0.303	0.426	0.742	1.142
Weems & Miller (1969)	40	40	273 – 308	0.2 – 4.6	0.74	40	40	0.181	0.177	−0.181	0.157	0.285	0.234	−1.326	0.583
Weems & Miller (1969)	34	34	273 – 308	0.4 – 6.3	0.89	34	34	0.062	0.149	−0.062	0.148	0.073	0.197	−0.166	0.460
Weems & Miller (1969)	41	41	273 – 308	0.3 – 6.4	0.94	41	41	0.035	0.082	−0.004	0.050	0.048	0.109	−0.117	0.293

Table A2.1 (continued)

Authors	Number of data points			Covered ranges				Statistical analysis[n]							
	total[a]	used[b]	Temp. T/K	Pressure p/MPa	Compos.[c,d] x	N_1	N_2	AAD_1 %	AAD_2 %	Bias_1 %	Bias_2 %	RMS_1 %	RMS_2 %	MaxD_1 %	MaxD_2 %
(1 − x) CO_2 + x He (continued)															
VLE data						**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP
Burfield *et al.* (1970)	30	–	253 – 293	3.0 – 14.1	0.00 – 0.05	12	9	8.096	18.562	−6.263	18.562	10.944	20.327	−24.604	27.802
(1 − x) CO_2 + x Ar															
***pρT* data**						**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA
Abraham & Bennett (1960)	13	13	323	5.1 – 101	0.17	13	13	0.739	1.278	−0.467	−1.266	0.945	1.558	−1.797	−2.539
Abraham & Bennett (1960)	13	13	323	5.1 – 101	0.28	13	13	0.662	1.161	−0.337	−1.161	0.827	1.370	−1.614	−2.198
Abraham & Bennett (1960)	13	13	323	5.1 – 101	0.38	13	13	0.578	0.984	−0.289	−0.984	0.699	1.112	−1.241	−1.655
Abraham & Bennett (1960)	13	13	323	5.1 – 101	0.54	13	13	0.556	0.756	−0.403	−0.756	0.644	0.799	−1.106	−1.153
Abraham & Bennett (1960)	13	13	323	5.1 – 101	0.63	13	13	0.519	0.406	−0.259	−0.399	0.598	0.463	−0.992	−0.726
Abraham & Bennett (1960)	13	13	323	5.1 – 101	0.76	13	13	0.425	0.202	−0.316	−0.182	0.504	0.228	−0.923	−0.388
Abraham & Bennett (1960)	13	13	323	5.1 – 101	0.87	13	13	0.228	0.219	−0.091	0.219	0.291	0.297	0.586	0.642
Altunin & Koposhilov (1977)	15	13	313	0.7 – 18.7	0.19	15	15	0.392	0.999	−0.265	−0.999	0.846	1.500	−2.460	−3.431
Altunin & Koposhilov (1977)	17	16	323	0.4 – 20.8	0.20	17	17	0.433	0.658	0.127	−0.358	0.905	1.037	3.215	2.433
Altunin & Koposhilov (1977)	15	15	343	0.6 – 22.2	0.25	15	15	0.414	0.697	−0.396	−0.697	0.750	1.062	−2.033	−2.422
Altunin & Koposhilov (1977)	15	14	373	0.4 – 20.2	0.33	14	14	0.052	0.086	0.029	−0.064	0.061	0.114	−0.130	−0.292
Altunin & Koposhilov (1977)	12	12	303	0.3 – 6.1	0.34	12	12	0.046	0.339	−0.013	−0.325	0.056	0.466	0.107	−1.067
Altunin & Koposhilov (1977)	16	15	313	0.3 – 14.8	0.34	15	15	0.197	0.669	−0.171	−0.652	0.375	0.959	−1.299	−2.342
Altunin & Koposhilov (1977)	10	10	303	1.0 – 9.3	0.35	10	10	0.352	0.260	0.352	−0.260	0.534	0.291	1.335	−0.444
Altunin & Koposhilov (1977)	15	15	343	0.5 – 18.6	0.39	15	15	0.169	0.123	0.162	−0.033	0.283	0.151	0.645	0.299
Altunin & Koposhilov (1977)	15	15	313	0.3 – 13.2	0.43	15	15	0.181	0.515	−0.178	−0.515	0.286	0.723	−0.871	−1.712
Altunin & Koposhilov (1977)	16	16	323	0.4 – 23.7	0.44	16	16	0.315	0.580	−0.315	−0.580	0.521	0.779	−1.515	−1.709
Altunin & Koposhilov (1977)	14	14	303	0.3 – 10.3	0.47	14	14	0.039	0.305	0.032	−0.305	0.060	0.405	0.156	−0.819
Altunin & Koposhilov (1977)	17	17	323	0.3 – 24.7	0.47	17	17	0.206	0.411	−0.192	−0.407	0.340	0.546	−1.080	−1.193
Altunin & Koposhilov (1977)	14	14	373	0.5 – 20.4	0.47	14	14	0.037	0.066	−0.020	−0.055	0.059	0.078	−0.175	−0.125
Altunin & Koposhilov (1977)	14	14	313	0.7 – 20.9	0.50	14	14	0.383	0.673	−0.383	−0.673	0.627	0.890	−1.729	−1.875
Altunin & Koposhilov (1977)	13	13	323	0.9 – 22.0	0.51	13	13	0.136	0.341	−0.132	−0.341	0.249	0.408	−0.802	−0.842

Table A2.1 (continued)

Authors	Number of data points		Covered ranges					Statistical analysis[n]							
	total[a]	used[b]	Temp. T/K	Pressure p/MPa	Compos.[c,d] x	N_1	N_2	AAD$_1$ %	AAD$_2$ %	Bias$_1$ %	Bias$_2$ %	RMS$_1$ %	RMS$_2$ %	MaxD$_1$ %	MaxD$_2$ %
(1 − x) CO$_2$ + x Ar (continued)															
***pρT* data (continued)**						**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA
Altunin & Koposhilov (1977)	15	15	343	0.4 – 18.2	0.52	15	15	0.407	0.501	−0.407	−0.501	0.630	0.722	−1.634	−1.685
Altunin & Koposhilov (1977)	12	12	303	0.5 – 11.0	0.52	12	12	0.134	0.448	−0.134	−0.448	0.145	0.537	−0.252	−0.990
Altunin & Koposhilov (1977)	14	14	343	0.5 – 20.1	0.57	14	14	0.212	0.274	−0.212	−0.274	0.327	0.365	−0.867	−0.786
Altunin & Koposhilov (1977)	16	16	323	0.4 – 23.1	0.63	16	16	0.269	0.322	−0.257	−0.311	0.389	0.406	−1.017	−0.783
Altunin & Koposhilov (1977)	14	14	303	0.3 – 10.8	0.64	14	14	0.279	0.421	−0.279	−0.421	0.373	0.554	−0.871	−1.191
Altunin & Koposhilov (1977)	13	13	313	0.6 – 14.8	0.65	13	13	0.216	0.278	0.077	−0.031	0.406	0.415	1.341	1.289
Kosov & Brovanov (1975)	31	19	313 – 353	7.5 – 58.9	0.29	27	30	2.140	1.718	2.040	1.557	2.318	2.172	4.560	4.796
Kosov & Brovanov (1975)	30	28	313 – 353	6.0 – 58.8	0.52	28	28	0.393	0.320	0.368	0.031	0.434	0.373	1.058	0.656
Kosov & Brovanov (1975)	30	30	313 – 353	5.9 – 58.8	0.80	30	30	0.199	0.614	0.199	0.614	0.217	0.637	0.431	0.820
Sarashina *et al.* (1971)	5	–	288	8.3 – 14.5	0.06	5	–	1.517		1.517		1.601		1.955	
Sarashina *et al.* (1971)	12	1	288	5.7 – 9.8	0.06 – 0.21	9	–	2.560		0.738		2.844		−4.527	
Sarashina *et al.* (1971)	4	4	288	2.4 – 4.9	0.07	4	–	1.361		1.361		1.395		1.753	
Sarashina *et al.* (1971)	5	–	288	9.9 – 14.5	0.10	5	–	0.781		0.434		0.905		1.456	
Sarashina *et al.* (1971)	5	5	288	2.4 – 5.7	0.10	5	–	1.394		1.394		1.458		1.999	
Sarashina *et al.* (1971)	5	–	288	10.3 – 14.5	0.13	5	–	1.303		−0.398		1.483		−2.375	
Sarashina *et al.* (1971)	6	5	288	2.4 – 6.7	0.15	6	–	0.375		0.105		0.418		0.689	
Sarashina *et al.* (1971)	5	–	288	10.3 – 14.5	0.17	3	–	1.062		−0.815		1.288		−2.068	
Sarashina *et al.* (1971)	5	–	288	10.3 – 14.5	0.19	2	–	2.547		−2.547		2.682		−3.386	
Sarashina *et al.* (1971)	5	–	288	10.3 – 14.5	0.21	2	–	2.917		−2.917		3.031		−3.740	
Sarashina *et al.* (1971)	8	5	288	2.6 – 8.3	0.21	8	–	2.075		2.075		2.274		3.677	
Sarashina *et al.* (1971)	11	5	288	2.6 – 14.5	0.25	11	–	1.891		0.798		2.039		−3.154	
Sarashina *et al.* (1971)	12	6	288	2.8 – 14.5	0.30	10	–	0.973		0.973		1.066		1.697	
VLE data						**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP
Kaminishi *et al.* (1968)[f]	19	10	233 – 273	2.6 – 13.2	0.03 – 0.35	17	15	2.880	14.931	−1.823	14.931	4.476	16.978	−13.158	29.610
Sarashina *et al.* (1971)[x,y]	12	–	288	5.7 – 9.8	0.06 – 0.17	1	3	8.182	7.339	−8.182	7.339	8.182	8.614	−8.182	11.184

Table A2.1 (continued)

Authors	Number of data points		Covered ranges					Statistical analysis[n]							
	total[a]	used[b]	Temp. T/K	Pressure p/MPa	Compos.[c,d] x	N_1	N_2	AAD$_1$ %	AAD$_2$ %	Bias$_1$ %	Bias$_2$ %	RMS$_1$ %	RMS$_2$ %	MaxD$_1$ %	MaxD$_2$ %
$(1-x)$ $C_2H_6 + x$ C_3H_8															
***pρT* data**						**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA
Acosta & Swift (1976)	15	15	228 – 311	3.4 – 13.8	0.25	15	–	0.374		0.038		0.416		−0.732	
Acosta & Swift (1976)	16	16	228 – 311	3.4 – 13.8	0.50	16	–	0.404		0.248		0.440		0.662	
Acosta & Swift (1976)	15	15	228 – 311	3.4 – 13.8	0.75	15	–	0.389		0.389		0.443		0.691	
Kahre (1973)	10	–	289	1.0 – 2.9	0.14 – 0.89	10	–	0.118		−0.049		0.150		0.277	
Miniovich & Sorina (1971)	63	–	304 – 307	4.7 – 5.0	0.002	51	–	3.700		−3.696		4.571		−9.676	
Miniovich & Sorina (1971)	65	–	304 – 307	4.7 – 5.0	0.003	51	–	3.272		−3.272		4.369		−9.717	
Miniovich & Sorina (1971)	60	–	304 – 307	4.7 – 5.0	0.005	49	–	3.332		−2.682		4.458		−9.875	
Miniovich & Sorina (1971)	64	–	305 – 308	4.8 – 5.0	0.011	34	–	4.856		−4.856		5.573		−9.524	
Miniovich & Sorina (1971)	69	–	304 – 308	4.7 – 5.0	0.023	44	–	4.802		−4.802		5.430		−9.404	
Parrish (1984)	21	20	283 – 322	4.1 – 9.7	0.05	20	–	0.058		0.023		0.079		0.208	
Parrish (1984)	32	32	283 – 322	2.8 – 9.7	0.09 – 0.12	32	–	0.066		0.011		0.091		0.257	
Parrish (1984)	34	33	283 – 322	2.8 – 9.7	0.19 – 0.21	33	–	0.076		−0.018		0.091		−0.216	
Parrish (1984)	34	34	283 – 322	2.8 – 9.7	0.30 – 0.32	34	–	0.095		−0.020		0.109		0.204	
Parrish (1984)	70	66	283 – 322	2.8 – 9.7	0.39 – 0.42	66	–	0.108		0.010		0.128		0.274	
Parrish (1984)	50	50	283 – 322	2.8 – 9.7	0.49 – 0.51	50	–	0.113		0.010		0.148		0.390	
Parrish (1984)	42	42	283 – 322	2.8 – 9.7	0.59 – 0.60	42	–	0.066		−0.014		0.074		−0.136	
Parrish (1984)	32	32	283 – 322	2.8 – 9.7	0.69 – 0.70	32	–	0.058		−0.011		0.072		0.176	
Shana'a & Canfield (1968)	1	1	108	0.0005	0.19	1	–	0.668		0.668		0.668		0.668	
Shana'a & Canfield (1968)	1	1	108	0.0005	0.30	1	–	0.800		0.800		0.800		0.800	
Shana'a & Canfield (1968)	1	1	108	0.0005	0.41	1	–	0.646		0.646		0.646		0.646	
Shana'a & Canfield (1968)	1	1	108	0.0005	0.59	1	–	0.419		0.419		0.419		0.419	
Shana'a & Canfield (1968)	1	1	108	0.0005	0.74	1	–	0.168		0.168		0.168		0.168	
Isobaric heat capacity						**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA
van Kasteren & Zeldenrust (1979)	16	–	120 – 270	5.1	0.39	14	–	1.412		1.199		1.969		4.619	

Table A2.1 (continued)

Authors	Number of data points total[a]	used[b]	Covered ranges Temp. T/K	Pressure p/MPa	Compos.[c,d] x	Statistical analysis[n] N_1	N_2	AAD$_1$ %	AAD$_2$ %	Bias$_1$ %	Bias$_2$ %	RMS$_1$ %	RMS$_2$ %	MaxD$_1$ %	MaxD$_2$ %
(1 − x) C_2H_6 + x C_3H_8 (continued)															
Enthalpy differences						**EqG**	EqA	**EqG**[u]	EqA[u]	**EqG**[u]	EqA[u]	**EqG**[u]	EqA[u]	**EqG**[u]	EqA[u]
Grini *et al.* (1998)[h]	70	–	151 – 343	0.1 – 14.2	0.20	53	–	*6.655*		*6.013*		*9.483*		*27.400*	
Grini *et al.* (1998)[p]	70	–	143 – 343	1.0 – 14.2	0.20	67	–	1.186		0.785		1.773		−8.850	
van Kasteren & Zeldenrust (1979)[p]	16	–	110 – 270	5.1	0.39	16	–	0.507		0.277		0.718		1.853	
Excess molar enthalpy															
Ott *et al.* (1997)	157	–	323 – 373	5.0 – 15.0	0.01 – 0.98										
VLE data						**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP
Blanc & Setier (1988)	151	149	195 – 270	0.03 – 2.0	0.08 – 1.00	149	149	1.487	1.709	0.724	−1.208	2.193	1.955	6.945	4.869
Clark & Stead (1988)	22	–	260 – 280	0.4 – 2.6	0.05 – 0.94	22	22	3.281	4.502	−3.271	−4.502	3.654	4.689	−7.117	−7.986
Djordjevich & Budenholzer (1970)	25	–	128 – 172	0.00 – 0.05	0.05 – 0.99	25	25	5.318	4.590	4.598	−4.539	6.340	5.642	11.321	−17.780
Djordjevich & Budenholzer (1970)	22	–	200 – 255	0.03 – 1.4	0.05 – 0.95	22	22	3.908	6.065	−3.843	−6.065	5.410	7.232	−15.266	−16.861
Hirata *et al.* (1969a)	25	–	197 – 202	0.02 – 0.3	0.04 – 0.97	25	25	4.106	4.452	2.192	−0.838	6.223	6.423	19.469	18.117
Hirata *et al.* (1969a)	5	–	273 – 273	0.7 – 1.7	0.29 – 0.83	5	5	3.709	5.386	−3.709	−5.386	3.917	5.493	−5.649	−6.742
Matschke & Thodos (1962)	65	59	311 – 366	1.4 – 5.2	0.07 – 0.99	50	44	0.767	0.776	0.247	−0.016	0.923	1.013	2.635	2.799
Miksovsky & Wichterle (1975)	102	78	303 – 369	1.2 – 5.1	0.00 – 1.00	76	56	1.586	1.446	1.549	1.337	1.897	1.775	3.869	4.605
Price (1957)	17	–	255 – 283	0.3 – 2.8	0.09 – 0.98	17	17	1.982	0.839	1.733	0.507	2.121	0.970	3.164	−1.881
Skripka *et al.* (1970)[x,y]	60	–	203 – 273	0.03 – 2.3	0.05 – 0.95	56	56	3.078	3.282	0.740	−0.732	5.129	5.049	18.168	15.915
(1 − x) C_2H_6 + x n-C_4H_{10}															
***pρT* data**						**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA
Acosta & Swift (1976)	4	2	311	3.4 – 13.8	0.22	4	–	1.128		−1.128		1.313		−2.038	
Acosta & Swift (1976)	4	4	311	3.4 – 13.8	0.50	4	–	0.373		−0.373		0.444		−0.699	
Acosta & Swift (1976)	4	4	311	3.4 – 13.8	0.75	4	–	0.223		−0.223		0.256		−0.366	
Kay (1940)	42	36	269 – 318	1.4 – 5.2	0.05	41	–	0.719		0.009		0.950		2.793	
Kay (1940)	55	47	269 – 344	0.5 – 5.7	0.18	55	–	0.676		−0.120		1.139		−4.812	
Kay (1940)	59	49	270 – 369	0.5 – 5.8	0.34	59	–	0.649		0.092		0.992		−3.682	

Table A2.1 (continued)

Authors	Number of data points total[a]	used[b]	Temp. T/K	Covered ranges Pressure p/MPa	Compos.[c,d] x	N_1	N_2	Statistical analysis[n] AAD_1 %	AAD_2 %	Bias_1 %	Bias_2 %	RMS_1 %	RMS_2 %	MaxD_1 %	MaxD_2 %
$(1-x)$ C_2H_6 + x n-C_4H_{10} (continued)															
***pρT* data (continued)**						**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA
Kay (1940)	55	47	274 – 391	0.5 – 5.3	0.55	54	–	0.538		0.241		0.928		4.069	
Kay (1940)	46	34	280 – 414	0.5 – 4.3	0.83	45	–	0.642		0.592		0.984		2.873	
VLE data						**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP
Benedict *et al.* (1942)	13	13	270 – 403	1.4 – 5.5	0.18 – 0.83	13	13	0.439	1.134	0.272	0.465	0.542	1.362	0.954	2.378
Clark & Stead (1988)	36	30	260 – 280	0.2 – 2.5	0.05 – 0.94	33	33	9.210	10.922	−9.210	−10.922	10.622	12.367	−20.202	−22.449
Dingrani & Thodos (1978)	18	17	310 – 366	1.4 – 5.6	0.22 – 0.75	17	17	1.124	1.450	−0.449	−0.078	1.443	1.793	−2.929	3.712
Kay (1940)[x,y]	250	–	235 – 419	0.7 – 5.8	0.10 – 0.98	220	191	0.953	1.279	−0.196	−0.188	1.424	1.584	−4.887	4.568
Lhoták & Wichterle (1981)	43	36	303 – 363	0.4 – 5.3	0.07 – 0.96	43	43	1.514	1.557	0.822	0.452	2.074	2.062	6.862	−5.276
Mehra & Thodos (1965)	19	18	339 – 394	3.2 – 5.6	0.25 – 0.88	18	18	2.816	4.154	2.784	4.154	2.957	4.389	4.329	5.936
$(1-x)$ C_2H_6 + x i-C_4H_{10}															
VLE data						**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP
Besserer & Robinson (1973c)[e]	39	34	311 – 394	1.1 – 5.4	0.04 – 0.98	37	36	1.346	1.568	−0.166	0.624	1.570	1.938	3.392	4.163
Skripka *et al.* (1970)[x,y]	60	–	203 – 273	0.005 – 2.2	0.05 – 0.95	53	53	5.988	5.594	1.240	0.060	8.941	8.199	29.711	26.923
$(1-x)$ C_2H_6 + x n-C_5H_{12}															
***pρT* data**						**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA
Mu *et al.* (2003)	13	–	309	5.0 – 7.0	0.010	11	–	1.977		1.977		2.293		4.230	
Mu *et al.* (2003)	11	–	309	5.0 – 7.0	0.013	11	–	1.883		1.883		2.822		6.375	
Mu *et al.* (2003)	11	–	309	4.6 – 6.7	0.05	11	–	0.134		−0.099		0.173		−0.347	
Mu *et al.* (2003)	10	–	309	3.8 – 7.0	0.16	10	–	0.376		0.376		0.384		0.507	
Mu *et al.* (2003)	12	–	309	3.1 – 7.1	0.32	12	–	0.392		0.392		0.412		0.587	
Reamer *et al.* (1960)	145	138	278 – 511	0.3 – 68.9	0.10	141	–	0.663		−0.297		1.092		−4.927	
Reamer *et al.* (1960)	150	145	278 – 511	0.1 – 68.9	0.20	145	–	0.469		−0.085		0.807		4.258	
Reamer *et al.* (1960)	151	151	278 – 511	0.1 – 68.9	0.30	151	–	0.486		0.086		0.847		4.525	

Table A2.1 (continued)

Authors	Number of data points total[a]	used[b]	Covered ranges Temp. T/K	Pressure p/MPa	Compos.[c,d] x	Statistical analysis[n] N_1	N_2	AAD_1 %	AAD_2 %	$Bias_1$ %	$Bias_2$ %	RMS_1 %	RMS_2 %	$MaxD_1$ %	$MaxD_2$ %
(1 − x) C_2H_6 + x n-C_5H_{12} (continued)															
***pρT* data (continued)**						**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA
Reamer *et al.* (1960)	158	156	278 – 511	0.1 – 68.9	0.40	157	–	0.521		0.018		0.896		−4.261	
Reamer *et al.* (1960)	162	161	278 – 511	0.1 – 68.9	0.50	161	–	0.367		0.057		0.635		3.007	
Reamer *et al.* (1960)	164	162	278 – 511	0.1 – 68.9	0.60	163	–	0.336		0.086		0.704		4.892	
Reamer *et al.* (1960)	170	167	278 – 511	0.1 – 68.9	0.70	167	–	0.304		0.013		0.589		4.135	
Reamer *et al.* (1960)	174	169	278 – 511	0.08 – 68.9	0.80	169	–	0.333		−0.162		0.593		−3.248	
Reamer *et al.* (1960)	177	173	278 – 511	0.06 – 68.9	0.90	173	–	0.362		−0.238		0.567		−2.537	
Isochoric heat capacity						**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA
Mu *et al.* (2003)	13	–	309	231 – 333	0.010	13	–	2.827		2.827		3.139		5.454	
Mu *et al.* (2003)	11	–	309	247 – 340	0.013	11	–	1.321		1.070		1.573		2.578	
Mu *et al.* (2003)	11	–	309	326 – 363	0.05	11	–	3.852		3.852		5.168		11.802	
Mu *et al.* (2003)	10	–	309	410 – 429	0.16	10	–	3.763		3.580		4.815		9.071	
Mu *et al.* (2003)	12	–	309	478 – 491	0.32	12	–	3.365		−3.173		4.037		−6.660	
VLE data						**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP
Reamer *et al.* (1960)	67	59	278 – 444	0.3 – 6.8	0.02 – 1.00	59	56	1.500	1.319	0.228	0.659	1.912	1.743	4.703	4.722
(1 − x) C_2H_6 + x n-C_6H_{14}															
VLE data						**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP
Ohgaki *et al.* (1976)	7	7	298	0.5 – 3.5	0.09 – 0.85	7	7	0.966	3.973	0.281	3.233	1.405	5.140	3.301	9.590
Zais & Silberberg (1970)	39	36	339 – 450	0.2 – 7.9	0.08 – 0.99	35	35	11.998	11.291	3.432	1.740	14.214	13.563	−28.345	−28.370
(1 − x) C_2H_6 + x n-C_7H_{16}															
***pρT* data**						**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA
Kay (1938)	32	28	275 – 357	0.3 – 6.6	0.03	29	–	1.043		0.059		1.517		−4.807	
Kay (1938)	42	36	278 – 411	0.3 – 8.3	0.11	38	–	1.372		−0.451		1.737		−4.703	
Kay (1938)	44	41	280 – 450	0.7 – 8.6	0.23	41	–	1.718		1.366		1.902		3.006	

Table A2.1 (continued)

Authors	Number of data points		Covered ranges									Statistical analysis[n]			
	total[a]	used[b]	Temp. T/K	Pressure p/MPa	Compos.[c,d] x	N_1	N_2	AAD$_1$ %	AAD$_2$ %	Bias$_1$ %	Bias$_2$ %	RMS$_1$ %	RMS$_2$ %	MaxD$_1$ %	MaxD$_2$ %
$(1-x)$ $C_2H_6 + x$ n-C_7H_{16} (continued)															
***pρT* data (continued)**						**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA
Kay (1938)	43	38	276 – 485	0.3 – 7.9	0.41	39	–	1.359		0.731		1.669		−3.741	
Kay (1938)	27	18	285 – 521	0.3 – 4.8	0.73	24	–	1.406		−0.086		1.865		−4.986	
Wu & Ehrlich (1973)	24	9	353	7.5	0.02 – 0.17	11	–	1.789		−1.132		2.439		−4.900	
VLE data						**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP
Dastur (1964)	62	–	339 – 450	2.8 – 8.8	0.06 – 0.81	54	57	4.381	2.776	−4.113	0.439	5.141	3.472	−11.138	−9.343
Kay (1938)[x,y]	410	–	235 – 540	0.3 – 8.6	0.02 – 1.00	357	324	7.567	2.693	−0.028	0.058	10.280	4.203	−29.924	−20.991
Kay (1938)	61	–	235 – 524	0.7 – 8.6	0.10 – 0.90	53	54	4.989	2.128	−1.963	1.489	6.484	2.758	−16.552	6.767
$(1-x)$ $C_2H_6 + x$ n-C_8H_{18}															
***pρT* data**						**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA
Rodrigues *et al.* (1968)	64	51	273 – 373	0.4 – 5.3	0.02 – 0.95	63	–	0.954		−0.456		1.221		−4.012	
VLE data						**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP
Rodrigues *et al.* (1968)[e]	64	38	273 – 373	0.4 – 5.3	0.02 – 0.95	64	64	2.788	1.556	−0.391	0.024	3.600	2.232	−11.835	−9.018
Weng & Lee (1992)	18	9	318 – 338	1.5 – 6.8	0.08 – 0.75	16	16	2.401	3.133	−2.147	−2.708	3.194	3.783	−10.027	−10.900
$(1-x)$ $C_2H_6 + x$ H_2															
***pρT* data**						**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA
Jaeschke *et al.* (1997)	49	49	330	0.3 – 26.1	0.50	48	48	0.039	0.284	0.023	0.280	0.049	0.379	−0.119	0.769
Jaeschke *et al.* (1997)	144	144	275 – 350	0.2 – 26.2	0.75	144	144	0.026	0.158	−0.016	0.158	0.036	0.221	0.130	0.706
Mihara *et al.* (1977)	14	–	323	0.3 – 5.0	0.22	14	14	0.382	0.144	−0.382	−0.144	0.556	0.225	−1.395	−0.580
Mihara *et al.* (1977)	15	–	298	0.3 – 5.1	0.23	15	15	0.203	0.071	−0.194	0.024	0.292	0.086	−0.684	0.200
Mihara *et al.* (1977)	14	–	348	0.4 – 5.7	0.28	14	14	0.393	0.154	−0.393	−0.154	0.541	0.218	−1.271	−0.513
Mihara *et al.* (1977)	54	–	298 – 348	0.3 – 9.3	0.65	54	54	0.230	0.058	−0.230	−0.058	0.307	0.086	−0.830	−0.259
Mihara *et al.* (1977)	57	–	298 – 348	0.3 – 9.1	0.80	57	57	0.148	0.013	−0.148	−0.009	0.191	0.018	−0.486	−0.051
Solbrig & Ellington (1963)	49	43	294 – 422	2.4 – 19.1	0.10	43	39	0.498	0.835	0.110	0.790	0.658	0.956	−1.835	1.814

Table A2.1 (continued)

Authors	Number of data points total[a]	used[b]	Covered ranges Temp. T/K	Pressure p/MPa	Compos.[c,d] x	Statistical analysis[n] N_1	N_2	AAD_1 %	AAD_2 %	Bias_1 %	Bias_2 %	RMS_1 %	RMS_2 %	MaxD_1 %	MaxD_2 %
(1 − x) C_2H_6 + x H_2 (continued)															
***pρT* data (continued)**						**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA
Solbrig & Ellington (1963)	48	38	305 – 422	2.7 – 21.1	0.20	43	47	0.742	0.780	−0.346	0.634	0.862	0.883	−1.925	1.692
Solbrig & Ellington (1963)	54	54	294 – 422	3.5 – 26.2	0.50	54	54	0.264	0.526	−0.071	0.462	0.320	0.652	0.756	1.526
Solbrig & Ellington (1963)	54	54	294 – 422	1.5 – 24.2	0.80	54	54	0.767	1.026	0.767	1.026	0.807	1.078	1.263	1.715
VLE data						**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP
Cohen *et al.* (1967)	28	16	139 – 200	0.7 – 13.8	0.00 – 0.09	10	15	10.973	24.407	−6.729	24.407	14.074	24.682	−25.958	29.912
Hiza *et al.* (1967)	11	7	150 – 190	2.5 – 15.0	0.01 – 0.08	7	–	16.952		−16.817		19.701		−29.986	
Levitskaja & Priannikow (1939)	29	–	158 – 188	1.2 – 7.8	0.00 – 0.03	10	–	23.591		23.591		24.007		28.447	
Sagara *et al.* (1972)	16	14	148 – 223	2.0 – 8.1	0.01 – 0.06	14	1	15.467	24.425	8.177	24.425	16.932	24.425	24.160	24.425
Williams & Katz (1954)	33	24	144 – 283	1.7 – 53.3	0.00 – 0.40	20	8	14.317	17.423	7.640	17.371	16.419	20.273	25.457	27.175
(1 − x) C_2H_6 + x CO															
VLE data						**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP
Trust & Kurata (1971a)	22	21	173 – 273	0.9 – 11.7	0.01 – 0.83	21	19	1.613	7.090	−0.208	6.719	2.302	9.757	−7.078	26.336
(1 − x) C_3H_8 + x n-C_4H_{10}															
***pρT* data**						**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA
Acosta & Swift (1976)	4	4	311	3.4 – 13.8	0.24	4	–	0.100		−0.038		0.116		−0.180	
Acosta & Swift (1976)	4	4	311	3.4 – 13.8	0.50	4	–	0.186		0.083		0.217		0.356	
Acosta & Swift (1976)	4	4	311	3.4 – 13.8	0.75	4	–	0.126		−0.082		0.151		−0.225	
Kahre (1973)	4	4	289 – 328	0.6 – 1.6	0.16	4	–	0.181		0.181		0.212		0.347	
Kahre (1973)	4	4	289 – 328	0.6 – 1.4	0.30	4	–	0.151		0.151		0.160		0.204	
Kahre (1973)	4	4	289 – 328	0.4 – 1.1	0.52	4	–	0.103		0.103		0.106		0.130	
Kahre (1973)	4	4	289 – 328	0.3 – 0.9	0.69	4	–	0.079		0.079		0.084		0.115	
Kahre (1973)	4	4	289 – 328	0.3 – 0.7	0.85	4	–	0.017		0.015		0.019		0.025	
Kayukawa *et al.* (2005a)	91	–	240 – 380	0.5 – 7.0	0.25	91	–	0.130		−0.115		0.267		−1.253	

Table A2.1 (continued)

Authors	Number of data points total[a]	used[b]	Covered ranges Temp. T/K	Pressure p/MPa	Compos.[c,d] x	N_1	N_2	Statistical analysis[n] AAD_1 %	AAD_2 %	$Bias_1$ %	$Bias_2$ %	RMS_1 %	RMS_2 %	$MaxD_1$ %	$MaxD_2$ %
(1 − x) C_3H_8 + x n-C_4H_{10} (continued)															
***pρT* data (continued)**						**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA
Kayukawa *et al.* (2005a)[s]	7	–	240 – 360	0.1 – 2.8	0.25	7	–	0.171		−0.171		0.309		−0.800	
Kayukawa *et al.* (2005a)	96	–	240 – 380	0.5 – 7.1	0.50	96	–	0.064		0.019		0.093		0.331	
Kayukawa *et al.* (2005a)[s]	7	–	240 – 380	0.1 – 3.1	0.50	7	–	0.096		−0.093		0.122		−0.247	
Kayukawa *et al.* (2005a)	101	–	239 – 380	0.5 – 7.1	0.75	101	–	0.038		−0.026		0.054		−0.247	
Kayukawa *et al.* (2005a)[s]	7	–	260 – 380	0.1 – 2.4	0.75	7	–	0.116		−0.116		0.138		−0.286	
Nysewander *et al.* (1940)	7	–	311 – 378	1.2 – 4.2	0.15	7	–	2.691		−2.084		3.493		−6.773	
Nysewander *et al.* (1940)	7	–	311 – 378	1.0 – 3.7	0.31	7	–	1.728		−1.681		2.280		−4.706	
Nysewander *et al.* (1940)	3	–	344 – 378	2.0 – 3.5	0.32	3	–	1.850		−1.850		2.034		−2.479	
Nysewander *et al.* (1940)	6	–	361 – 394	1.9 – 3.9	0.48	6	–	5.623		−4.947		6.039		−8.902	
Nysewander *et al.* (1940)	11	–	311 – 411	0.7 – 4.2	0.66	10	–	3.402		−3.402		4.034		−8.175	
Nysewander *et al.* (1940)	11	–	311 – 411	0.6 – 3.8	0.80	11	–	3.047		−3.047		3.858		−6.368	
Parrish (1986)	63	63	283 – 333	0.6 – 9.7	0.25	63	–	0.041		0.000		0.050		0.094	
Parrish (1986)	63	63	283 – 333	0.6 – 9.7	0.30	63	–	0.049		−0.009		0.059		0.139	
Parrish (1986)	49	49	283 – 333	0.5 – 9.7	0.39 – 0.40	49	–	0.050		−0.001		0.065		0.154	
Parrish (1986)	118	118	283 – 333	0.5 – 9.7	0.49 – 0.50	118	–	0.050		−0.001		0.065		0.192	
Parrish (1986)	48	48	283 – 333	0.5 – 9.7	0.60	48	–	0.035		0.009		0.043		0.101	
Parrish (1986)	56	56	283 – 333	0.5 – 9.7	0.69 – 0.70	56	–	0.023		0.008		0.031		0.080	
Parrish (1986)	57	57	283 – 333	0.4 – 9.7	0.80	57	–	0.018		−0.001		0.021		0.043	
Parrish (1986)	59	59	283 – 333	0.3 – 9.7	0.90	59	–	0.030		−0.023		0.036		−0.094	
VLE data						**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP
Beranek & Wichterle (1981)	29	29	303 – 363	0.4 – 3.4	0.09 – 0.94	29	29	0.895	1.588	−0.830	−1.587	1.150	1.842	−2.761	−3.821
Clark & Stead (1988)	24	–	260 – 280	0.08 – 0.6	0.06 – 0.94	24	24	1.534	2.330	−1.521	−2.330	1.960	2.703	−4.047	−5.369
Hirata *et al.* (1969a)	31	31	237 – 249	0.03 – 0.2	0.05 – 0.95	31	31	2.771	1.602	2.746	0.892	3.131	1.850	6.314	4.018
Kay (1970)[e,f]	236	–	336 – 420	1.6 – 4.3	0.07 – 0.90	228	191	0.529	0.614	0.349	−0.374	0.665	0.745	1.950	−1.996
Kayukawa *et al.* (2005b)[e,f]	20	–	270 – 310	0.1 – 0.9	0.13 – 0.83	20	20	2.501	2.444	0.203	−0.510	3.266	3.506	−8.537	−8.828
Nysewander *et al.* (1940)[x,y]	48	–	311 – 411	0.6 – 4.2	0.15 – 0.80	47	46	2.338	2.085	1.801	1.029	2.739	2.355	4.941	−4.063

Table A2.1 (continued)

Authors	Number of data points total[a]	used[b]	Covered ranges Temp. T/K	Pressure p/MPa	Compos.[c,d] x	N_1	N_2	Statistical analysis[n] AAD_1 %	AAD_2 %	$Bias_1$ %	$Bias_2$ %	RMS_1 %	RMS_2 %	$MaxD_1$ %	$MaxD_2$ %
(1 − *x*) C_3H_8 + *x* n-C_4H_{10} (continued)															
VLE data (continued)						**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP
Skripka *et al.* (1970)[x,y]	36	–	253 – 273	0.05 – 0.5	0.05 – 0.95	36	36	3.032	3.661	−1.941	−2.773	4.012	4.597	−10.619	−12.161
VonNiederhausern & Giles (2001)	35	–	322 – 366	0.5 – 11.0	0.06 – 0.99	34	34	0.424	0.754	−0.042	−0.754	0.557	0.896	−1.339	−1.812
(1 − *x*) C_3H_8 + *x* i-C_4H_{10}															
***pρT* data**						**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA
Duarte-Garza & Magee (1999)	170	170	200 – 400	2.9 – 35.1	0.30	170	–	0.049		−0.043		0.056		−0.138	
Duarte-Garza & Magee (1999)	67	67	205 – 345	3.9 – 32.4	0.30	67	–	0.099		0.099		0.107		0.172	
Duarte-Garza & Magee (1999)	171	171	200 – 400	1.2 – 35.4	0.70	171	–	0.054		−0.043		0.065		−0.162	
Duarte-Garza & Magee (1999)	68	68	203 – 342	3.3 – 33.0	0.70	68	–	0.103		0.102		0.116		0.196	
Kahre (1973)	3	3	289 – 328	0.7 – 1.7	0.15	3	–	0.115		0.115		0.134		0.174	
Kahre (1973)	4	4	289 – 328	0.6 – 1.5	0.30	4	–	0.074		0.074		0.083		0.121	
Kahre (1973)	4	4	289 – 328	0.5 – 1.3	0.51	4	–	0.061		0.061		0.077		0.126	
Kahre (1973)	4	4	289 – 328	0.4 – 1.0	0.70	4	–	0.055		0.055		0.076		0.133	
Kahre (1973)	4	4	289 – 328	0.3 – 0.9	0.86	4	–	0.026		0.021		0.031		0.053	
Kayukawa *et al.* (2005a)	87	–	240 – 360	0.3 – 7.1	0.25	87	–	0.093		0.055		0.175		0.613	
Kayukawa *et al.* (2005a)[s]	7	–	240 – 360	0.1 – 2.9	0.25	7	–	0.117		−0.108		0.198		−0.503	
Kayukawa *et al.* (2005a)	82	–	250 – 380	0.5 – 7.0	0.50	82	–	0.117		−0.054		0.169		−0.577	
Kayukawa *et al.* (2005a)[s]	7	–	250 – 380	0.1 – 3.4	0.50	6	–	0.198		−0.198		0.274		−0.525	
Kayukawa *et al.* (2005a)	102	–	240 – 380	0.4 – 7.1	0.75	102	–	0.218		0.218		0.258		0.587	
Kayukawa *et al.* (2005a)[s]	8	–	240 – 380	0.1 – 2.8	0.75	8	–	0.212		0.212		0.258		0.534	
Isochoric heat capacity						**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA
Duarte-Garza & Magee (1999)	67	–	205 – 345	484^{ρ} – 631^{ρ}	0.30	67	–	0.897		0.883		0.960		1.627	
Duarte-Garza & Magee (1999)	68	–	203 – 342	508^{ρ} – 649^{ρ}	0.70	68	–	0.677		0.657		0.745		1.255	
Isobaric heat capacity						**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA
Bier *et al.* (1973)	23	–	293 – 353	0.1 – 1.2	0.50	23	23	0.229	0.552	−0.190	−0.434	0.254	0.628	−0.439	−1.262

Table A2.1 (continued)

Authors	Number of data points		Covered ranges					Statistical analysis[n]							
	total[a]	used[b]	Temp. T/K	Pressure p/MPa	Compos.[c,d] x	N_1	N_2	AAD_1 %	AAD_2 %	Bias_1 %	Bias_2 %	RMS_1 %	RMS_2 %	MaxD_1 %	MaxD_2 %
(1 − x) C_3H_8 + x i-C_4H_{10} (continued)															
VLE data						**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP
Higashi *et al.* (1994)	18	–	283 – 313	0.2 – 1.1	0.20 – 0.83	17	17	2.215	1.893	−1.174	0.009	2.760	2.337	−5.460	4.378
Hipkin (1966)	79	65	267 – 394	0.1 – 4.2	0.00 – 1.00	74	72	1.176	1.818	0.164	0.284	1.439	3.926	3.375	−29.448
Hirata *et al.* (1969a)	33	33	237 – 249	0.04 – 0.2	0.08 – 0.96	33	33	3.265	4.756	3.264	4.756	3.504	4.930	5.312	6.794
Hirata *et al.* (1970)	14	14	340	1.1 – 2.4	0.02 – 0.95	14	14	1.029	0.754	−0.841	−0.520	1.157	0.891	−2.001	−1.372
Kayukawa *et al.* (2005b)[e,f]	40	–	260 – 320	0.1 – 1.3	0.12 – 0.82	40	40	1.943	0.876	−1.943	−0.684	2.145	1.139	−5.048	−3.255
Lim *et al.* (2004)	36	36	273 – 303	0.2 – 1.0	0.07 – 0.92	36	36	0.515	1.584	0.338	1.584	0.609	1.673	1.256	2.492
Skripka *et al.* (1970)[x,y]	36	–	253 – 273	0.08 – 0.5	0.05 – 0.95	36	36	1.906	1.091	−1.613	−0.283	2.443	1.602	−7.421	−5.105
VonNiederhausern & Giles (2001)	32	–	322 – 355	0.7 – 3.1	0.01 – 0.95	32	32	0.310	0.793	0.237	0.496	0.418	0.923	0.884	1.855
(1 − x) C_3H_8 + x n-C_5H_{12}															
***pρT* data**						**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA
Kay (1970)	17	14	330 – 389	1.7 – 4.5	0.12	14	–	2.267		2.267		2.975		6.330	
Kay (1970)	20	19	325 – 402	1.4 – 4.6	0.21	19	–	3.153		3.115		4.234		8.667	
Kay (1970)	19	18	321 – 420	1.0 – 4.5	0.38	18	–	3.341		2.433		3.639		6.830	
Kay (1970)	20	17	341 – 442	1.0 – 4.2	0.61	19	–	3.755		1.549		4.162		−9.089	
Kay (1970)	21	19	374 – 461	1.0 – 3.7	0.85	20	–	2.868		2.868		3.319		8.099	
Sage & Lacey (1940)	5	5	327 – 383	1.6 – 4.3	0.14	5	–	1.240		0.722		1.466		2.154	
Sage & Lacey (1940)	39	39	344 – 394	0.1 – 3.4	0.15	39	39	0.506	0.338	0.349	−0.044	0.771	0.440	2.465	1.477
Sage & Lacey (1940)	3	3	361 – 394	1.8 – 4.0	0.18	3	3	1.250	2.144	0.407	−2.144	1.584	2.255	2.487	−2.921
Sage & Lacey (1940)	4	4	328 – 378	1.5 – 3.8	0.18	4	–	0.389		0.024		0.422		−0.589	
Sage & Lacey (1940)	4	4	327 – 377	1.5 – 3.6	0.21	4	–	2.688		2.688		2.701		3.058	
Sage & Lacey (1940)	32	32	344 – 394	0.1 – 2.5	0.35	32	32	0.257	0.547	−0.051	−0.526	0.317	0.695	0.799	−1.791
Sage & Lacey (1940)	7	5	327 – 421	1.1 – 4.5	0.44	6	–	2.489		−2.489		2.759		−4.871	
Sage & Lacey (1940)	9	8	327 – 444	0.7 – 4.2	0.65	8	–	0.756		0.756		0.850		1.473	
Sage & Lacey (1940)	51	49	344 – 444	0.1 – 3.0	0.75	49	46	0.984	0.887	0.984	0.880	1.379	1.277	4.097	3.494
Sage & Lacey (1940)	32	31	361 – 444	0.4 – 2.7	0.86	32	32	1.745	2.400	1.745	2.400	1.828	2.929	2.783	9.950

Table A2.1 (continued)

Authors	Number of data points total[a]	used[b]	Temp. T/K	Covered ranges Pressure p/MPa	Compos.[c,d] x	N_1	N_2	Statistical analysis[n] AAD$_1$ %	AAD$_2$ %	Bias$_1$ %	Bias$_2$ %	RMS$_1$ %	RMS$_2$ %	MaxD$_1$ %	MaxD$_2$ %
$(1-x)$ $C_3H_8 + x$ n-C_5H_{12} (continued)															
VLE data						**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP
Kay (1970)[x,y]	189	–	321 – 468	0.7 – 4.5	0.10 – 0.97	172	147	1.874	2.333	−0.640	−1.972	2.748	3.187	−9.711	−9.780
Sage & Lacey (1940)	69	–	344 – 461	0.4 – 4.5	0.04 – 1.00	69	69	1.086	1.075	0.791	0.339	1.265	1.327	2.496	3.591
$(1-x)$ $C_3H_8 + x$ i-C_5H_{12}															
***pρT* data**						**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA
Vaughan & Collins (1942)	140	140	298 – 573	0.5 – 8.1	0.10	140	140	0.621	0.514	0.511	0.192	0.978	0.728	3.669	−3.497
Vaughan & Collins (1942)	8	6	273 – 378	0.2 – 4.5	0.10	6	–	1.062		0.972		1.472		2.618	
Vaughan & Collins (1942)	135	133	323 – 573	0.5 – 8.1	0.21	133	132	0.830	1.179	−0.785	−1.179	1.033	1.994	−3.342	−8.974
Vaughan & Collins (1942)	10	10	273 – 393	0.1 – 4.5	0.21	10	–	1.262		−0.086		1.569		−3.057	
Vaughan & Collins (1942)	121	119	348 – 573	0.5 – 8.1	0.41	120	121	0.912	1.332	0.685	0.634	1.238	1.787	4.204	−6.655
Vaughan & Collins (1942)	8	7	298 – 413	0.2 – 4.5	0.41	8	–	1.318		0.872		1.976		4.681	
Vaughan & Collins (1942)	108	108	348 – 573	0.5 – 8.1	0.61	108	108	2.068	1.477	−2.059	−0.673	2.122	1.743	−3.820	−4.729
Vaughan & Collins (1942)	9	9	323 – 428	0.3 – 4.1	0.61	9	–	1.257		−0.171		1.516		2.644	
Vaughan & Collins (1942)	93	89	373 – 573	0.5 – 8.1	0.90	91	87	2.826	2.790	−2.826	1.141	2.882	3.649	−4.671	9.532
Vaughan & Collins (1942)	8	7	348 – 448	0.5 – 3.4	0.90	7	–	2.536		−2.536		2.565		−2.854	
VLE data						**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP
Vaughan & Collins (1942)	89	78	273 – 453	0.05 – 4.6	0.02 – 0.97	79	76	2.498	2.305	−1.696	1.692	4.404	3.122	−15.733	16.027
$(1-x)$ $C_3H_8 + x$ n-C_6H_{14}															
***pρT* data**						**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA
Chun *et al.* (1993)	17	15	348 – 393	1.4 – 4.7	0.08	15	–	1.384		0.821		1.539		2.521	
Chun *et al.* (1993)	25	23	348 – 416	0.7 – 5.0	0.18	25	–	2.544		1.172		2.869		4.993	
Chun *et al.* (1993)	29	27	348 – 441	0.8 – 5.0	0.30	27	–	1.718		0.685		2.155		4.212	
Chun *et al.* (1993)	38	36	348 – 472	0.2 – 4.5	0.56	37	–	1.806		1.106		2.094		−4.096	
Chun *et al.* (1993)	37	31	348 – 497	0.1 – 3.6	0.86	34	–	1.304		−0.142		1.918		−4.588	

Table A2.1 (continued)

Authors	Number of data points		Covered ranges			Statistical analysis[n]									
	total[a]	used[b]	Temp. T/K	Pressure p/MPa	Compos.[c,d] x	N_1	N_2	AAD$_1$ %	AAD$_2$ %	Bias$_1$ %	Bias$_2$ %	RMS$_1$ %	RMS$_2$ %	MaxD$_1$ %	MaxD$_2$ %
$(1-x)$ $\mathrm{C_3H_8}$ + x n-$\mathrm{C_6H_{14}}$ (continued)															
$p\rho T$ data (continued)						**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA
Kay (1971)	15	13	328 – 394	1.7 – 4.7	0.08	13	–	1.225		0.370		1.525		3.696	
Kay (1971)	17	11	325 – 419	1.4 – 5.0	0.19	11	–	1.799		1.497		1.881		2.323	
Kay (1971)	11	10	399 – 430	2.8 – 5.0	0.24	10	–	1.756		1.492		2.134		4.243	
Kay (1971)	18	17	338 – 447	1.4 – 4.9	0.35	17	–	1.420		0.679		1.576		−3.284	
Kay (1971)	16	15	356 – 471	1.4 – 4.5	0.54	15	–	1.452		−0.634		1.734		4.596	
Kay (1971)	12	5	383 – 491	1.0 – 3.7	0.78	9	–	2.954		−2.226		3.415		−4.775	
VLE data						**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP
Chun *et al.* (1993)[x,y]	171	–	288 – 497	0.1 – 5.0	0.08 – 0.86	155	127	1.862	2.337	−0.666	1.294	2.913	2.891	9.881	−8.274
Kay (1948)	36	–	333 – 493	1.7 – 4.8	0.02 – 0.96	36	36	2.327	1.006	−2.219	0.248	2.978	1.364	−7.305	−3.332
Kay (1971)[x,y]	194	–	325 – 493	1.0 – 5.0	0.08 – 0.90	179	159	2.784	2.404	−2.322	−1.644	3.615	3.220	−9.503	−8.297
$(1-x)$ $\mathrm{C_3H_8}$ + x n-$\mathrm{C_7H_{16}}$															
VLE data						**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP
Kay (1971)	40	40	333 – 533	2.1 – 4.8	0.02 – 0.98	39	39	1.515	1.603	0.458	1.155	1.931	2.107	4.630	4.952
Kay (1971)[x,y]	157	–	338 – 532	2.1 – 5.2	0.09 – 0.90	146	118	4.699	5.788	−2.324	−4.138	7.253	9.811	−24.360	−28.933
$(1-x)$ $\mathrm{C_3H_8}$ + x n-$\mathrm{C_8H_{18}}$															
$p\rho T$ data						**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA
Kay *et al.* (1974)	24	16	313 – 405	2.1 – 5.1	0.04	16	–	4.332		3.424		4.994		8.210	
Kay *et al.* (1974)	26	24	342 – 453	2.1 – 5.8	0.14	25	–	2.407		1.445		3.062		9.872	
Kay *et al.* (1974)	33	33	329 – 493	1.4 – 5.9	0.28	33	–	2.282		−0.424		3.073		−8.914	
Kay *et al.* (1974)	30	30	345 – 513	1.4 – 5.4	0.43	30	–	2.616		0.338		3.300		−8.320	
Kay *et al.* (1974)	22	17	366 – 540	1.0 – 4.3	0.67	19	–	4.161		2.161		4.713		−8.917	
Kay *et al.* (1974)	20	16	371 – 550	0.7 – 3.6	0.79	16	–	2.972		1.951		3.345		7.238	

Table A2.1 (continued)

Authors	Number of data points		Covered ranges			Statistical analysis[n]									
	total[a]	used[b]	Temp. T/K	Pressure p/MPa	Compos.[c,d] x	N_1	N_2	AAD$_1$ %	AAD$_2$ %	Bias$_1$ %	Bias$_2$ %	RMS$_1$ %	RMS$_2$ %	MaxD$_1$ %	MaxD$_2$ %
(1 − x) C_3H_8 + x H_2															
***pρT* data**						**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA
Mihara *et al.* (1977)	24	–	323 – 348	0.3 – 3.3	0.73	24	24	0.139	0.015	−0.139	−0.003	0.181	0.022	−0.422	−0.073
Mihara *et al.* (1977)	37	–	323 – 348	0.3 – 5.1	0.80	37	37	0.154	0.030	−0.154	0.029	0.205	0.033	−0.505	0.056
Mihara *et al.* (1977)	12	–	298	0.4 – 3.9	0.84	12	12	0.210	0.039	−0.210	−0.039	0.256	0.047	−0.508	−0.089
VLE data						**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP
Burriss *et al.* (1953)[e,f]	133	58	278 – 361	2.5 – 55.2	0.01 – 0.67	63	–	8.566		8.136		9.156		16.163	
Trust & Kurata (1971b)	46	46	173 – 348	1.4 – 20.7	0.01 – 0.24	27	–	7.626		1.976		8.932		−18.247	
Williams & Katz (1954)	36	36	172 – 297	1.7 – 55.1	0.01 – 0.47	19	–	8.524		−2.081		10.752		−24.233	
(1 − x) C_3H_8 + x CO															
VLE data						**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP
Trust & Kurata (1971a)	37	37	148 – 323	1.4 – 15.2	0.02 – 0.43	35	33	4.363	6.498	1.631	3.959	5.962	9.325	17.071	29.003
(1 − x) C_3H_8 + x H_2O															
***pρT* data**						**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA
Sanchez & Coll (1978)	8	8	529 – 585	30.0 – 210	0.29	8	–	2.905		2.822		3.820		8.496	
Sanchez & Coll (1978)	10	10	594 – 646	42.0 – 220	0.52	10	–	1.927		0.525		2.199		3.927	
Sanchez & Coll (1978)	9	8	583 – 658	20.0 – 250	0.67	6	–	3.037		−1.610		3.308		−4.789	
Sanchez & Coll (1978)	5	5	610 – 663	30.0 – 265	0.77	5	–	3.230		−0.903		3.488		−4.495	
Sanchez & Coll (1978)	9	9	618 – 637	23.0 – 195	0.91	6	–	3.707		−0.458		4.446		−7.061	
Sanchez & Coll (1978)	7	5	593 – 628	23.0 – 330	0.96	4	–	3.231		−3.231		3.716		−4.839	
Sanchez & Coll (1978)	7	2	587 – 630	21.0 – 145	0.98	2	–	4.186		−1.726		4.528		−5.912	
(1 − x) n-C_4H_{10} + x i-C_4H_{10}															
***pρT* data**						**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA
Kahre (1973)	4	4	289 – 328	0.2 – 0.6	0.21	4	–	0.027		−0.005		0.029		−0.042	

Table A2.1 (continued)

Authors	Number of data points			Covered ranges						Statistical analysis[n]					
	total[a]	used[b]	Temp. T/K	Pressure p/MPa	Compos.[c,d] x	N_1	N_2	AAD_1 %	AAD_2 %	Bias_1 %	Bias_2 %	RMS_1 %	RMS_2 %	MaxD_1 %	MaxD_2 %
$(1-x)$ n-C_4H_{10} + x i-C_4H_{10} (continued)															
***pρT* data (continued)**						**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA
Kahre (1973)	4	4	289 – 328	0.2 – 0.6	0.36	4	–	0.015		−0.004		0.018		−0.028	
Kahre (1973)	4	4	289 – 328	0.2 – 0.7	0.57	4	–	0.020		0.020		0.027		0.038	
Kahre (1973)	4	4	289 – 328	0.2 – 0.7	0.80	4	–	0.024		−0.016		0.030		−0.049	
Kayukawa *et al.* (2005a)	105	–	240 – 380	0.5 – 7.1	0.25	97	–	0.067		−0.013		0.088		−0.329	
Kayukawa *et al.* (2005a)[s]	8	–	240 – 380	0.03 – 2.0	0.25	8	–	0.117		−0.084		0.149		−0.325	
Kayukawa *et al.* (2005a)	105	–	240 – 380	0.3 – 7.1	0.50	105	–	0.043		0.017		0.053		−0.128	
Kayukawa *et al.* (2005a)[s]	8	–	240 – 380	0.03 – 2.0	0.50	8	–	0.074		−0.055		0.094		−0.199	
Kayukawa *et al.* (2005a)	103	–	240 – 380	0.5 – 7.0	0.75	103	–	0.046		0.003		0.061		−0.278	
Kayukawa *et al.* (2005a)[s]	7	–	240 – 380	0.06 – 2.1	0.75	7	–	0.074		−0.055		0.100		−0.227	
VLE data						**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP
Hirata & Suda (1968)	24	24	273	0.1 – 0.2	0.09 – 0.93	24	24	0.265	0.503	0.183	0.500	0.347	0.582	0.711	1.098
Hirata *et al.* (1969b)	27	27	334 – 374	0.7 – 2.0	0.10 – 0.90	27	27	1.180	1.048	−0.472	−0.717	1.494	1.349	−3.021	−2.923
Martinez-Ortiz & Manley (1978)[x]	30	–	278 – 344	0.1 – 1.0	0.25 – 0.75	30	30	0.064	0.368	0.049	0.339	0.085	0.417	0.187	0.683
Stephan & Hildwein (1987)	147	146	330 – 368	0.8 – 1.4	0.02 – 0.98	146	146	0.179	0.324	−0.150	−0.324	0.257	0.338	−0.708	−0.443
$(1-x)$ n-C_4H_{10} + x n-C_5H_{12}															
***pρT* data**						**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA
Kay *et al.* (1975)	12	11	358 – 431	1.0 – 3.7	0.13	11	–	1.419		1.419		1.457		2.032	
Kay *et al.* (1975)	15	13	363 – 438	1.0 – 3.7	0.25	13	–	2.657		2.657		2.809		4.784	
Kay *et al.* (1975)	18	17	371 – 448	1.0 – 3.7	0.46	17	–	1.725		1.172		1.915		−4.100	
Kay *et al.* (1975)	16	12	380 – 456	1.0 – 3.6	0.65	13	–	1.711		0.512		1.966		−4.463	
Kay *et al.* (1975)	12	12	391 – 464	1.0 – 3.4	0.86	12	–	1.232		−0.550		1.619		−3.837	
VLE data						**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP
Calingaert & Hitchcock (1927)	12	–	298	0.07 – 0.1	0.81 – 0.98	12	12	3.475	0.827	3.475	0.221	3.684	1.017	6.605	2.011
Kay *et al.* (1975)[x,y]	183	–	358 – 464	1.0 – 3.7	0.10 – 0.90	175	152	0.393	2.591	0.268	−2.591	0.584	2.781	2.514	−4.693

Table A2.1 (continued)

Authors	Number of data points		Covered ranges			Statistical analysis[n]									
	total[a]	used[b]	Temp. T/K	Pressure p/MPa	Compos.[c,d] x	N_1	N_2	AAD_1 %	AAD_2 %	Bias_1 %	Bias_2 %	RMS_1 %	RMS_2 %	MaxD_1 %	MaxD_2 %
(1 − x) n-C_4H_{10} + x n-C_6H_{14}															
***pρT* data**						**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA
Kay *et al.* (1975)	22	19	384 – 438	1.7 – 3.9	0.10	18	–	1.675		1.675		1.945		4.702	
Kay *et al.* (1975)	26	26	383 – 447	1.5 – 3.9	0.19	26	–	1.576		1.487		1.669		3.469	
Kay *et al.* (1975)	25	25	375 – 459	1.1 – 3.9	0.30	25	–	0.629		0.163		1.187		4.555	
Kay *et al.* (1975)	28	27	386 – 476	1.0 – 3.7	0.51	27	–	0.769		0.009		1.011		−3.684	
Kay *et al.* (1975)	29	28	391 – 491	0.8 – 3.4	0.72	28	–	0.996		−0.463		1.324		−3.718	
Kay *et al.* (1975)	27	27	399 – 502	0.6 – 3.2	0.90	27	–	0.981		−0.388		1.201		2.730	
VLE data						**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP
Cummings (1933)	55	–	358 – 494	1.0 – 3.7	0.10 – 0.90	52	52	1.066	0.651	−0.856	0.070	1.261	0.946	−2.928	2.625
Kay *et al.* (1975)[x,y]	310	–	374 – 502	0.6 – 3.9	0.10 – 0.90	306	293	0.759	0.953	−0.299	0.104	1.109	1.150	4.992	4.293
(1 − x) n-C_4H_{10} + x n-C_7H_{16}															
***pρT* data**						**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA
Kay (1941)	51	51	329 – 437	0.4 – 3.9	0.06	51	–	0.568		0.008		0.787		−2.489	
Kay (1941)	57	54	335 – 463	0.4 – 4.1	0.20	55	–	0.673		0.198		1.044		−3.765	
Kay (1941)	55	54	333 – 487	0.3 – 4.0	0.37	55	–	0.697		0.301		1.196		4.639	
Kay (1941)	50	50	332 – 509	0.3 – 3.6	0.58	50	–	0.634		0.410		0.850		3.319	
Kay (1941)	42	41	369 – 530	0.3 – 3.0	0.84	41	–	0.515		0.018		0.727		2.653	
VLE data						**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP
Kay (1941)[x,y]	436	–	329 – 540	0.3 – 4.1	0.06 – 0.99	408	384	1.200	1.126	−0.472	−0.163	1.543	1.373	4.967	4.891
Kay (1941)	41	–	355 – 539	0.7 – 4.0	0.02 – 0.98	40	39	0.950	0.948	−0.837	0.524	1.216	1.157	−3.015	2.326
(1 − x) n-C_4H_{10} + x n-C_8H_{18}															
***pρT* data**						**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA
Kay *et al.* (1974)	20	14	339 – 444	0.7 – 4.0	0.05	14	–	1.214		−0.134		1.370		3.081	
Kay *et al.* (1974)	24	18	347 – 486	0.7 – 4.3	0.18	18	–	0.971		0.651		1.223		−2.881	

Table A2.1 (continued)

Authors	Number of data points		Covered ranges					Statistical analysis[n]							
	total[a]	used[b]	Temp. T/K	Pressure p/MPa	Compos.[c,d] x	N_1	N_2	AAD$_1$ %	AAD$_2$ %	Bias$_1$ %	Bias$_2$ %	RMS$_1$ %	RMS$_2$ %	MaxD$_1$ %	MaxD$_2$ %
$(1-x)$ n-C_4H_{10} + x n-C_8H_{18} (continued)															
***pρT* data (continued)**						**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA
Kay *et al.* (1974)	17	13	354 – 501	0.7 – 4.2	0.33	13	–	1.856		0.000		2.064		−3.870	
Kay *et al.* (1974)	21	14	376 – 530	0.7 – 3.9	0.54	15	–	1.478		−0.248		1.943		−4.235	
Kay *et al.* (1974)	15	13	427 – 555	0.7 – 3.0	0.82	14	–	1.763		1.000		2.009		−4.435	
$(1-x)$ n-C_4H_{10} + x H_2															
VLE data						**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP
Klink *et al.* (1975)	60	58	328 – 394	2.8 – 16.9	0.02 – 0.27	59	6	6.843	22.608	4.544	22.608	7.736	23.287	13.898	29.182
Nelson & Bonnell (1943)	4	4	355 – 389	4.3 – 9.5	0.04 – 0.11	4	1	8.990	24.155	8.990	24.155	9.425	24.155	13.830	24.155
$(1-x)$ n-C_4H_{10} + x H_2O															
***pρT* data**						**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA
Reamer *et al.* (1952b)	103	90	311 – 511	0.7 – 17.2	0.59	90	–	2.317		0.892		3.077		−9.606	
Tian *et al.* (2004)	6	–	600 – 698	24.6 – 276	0.65	5	–	3.596		−2.303		3.626		−4.087	
Tian *et al.* (2004)	5	–	616 – 700	34.9 – 265	0.75	5	–	3.444		−3.444		3.606		−5.320	
Tian *et al.* (2004)	5	–	602 – 653	20.1 – 127	0.85	2	–	2.752		2.752		3.294		4.563	
Tian *et al.* (2004)	13	–	617 – 644	19.3 – 190	0.95	8	–	4.822		0.953		5.509		8.750	
Tian *et al.* (2004)	13	–	609 – 642	20.5 – 198	0.98	9	–	7.656		7.656		7.750		9.201	
Yiling *et al.* (1991)	3	2	496 – 509	18.8 – 27.6	0.10	2	–	0.913		−0.025		0.914		−0.938	
Yiling *et al.* (1991)	4	3	502 – 551	9.0 – 41.7	0.20	3	–	3.545		0.722		4.084		6.401	
Yiling *et al.* (1991)	7	6	519 – 597	11.1 – 87.7	0.30	6	–	2.792		−2.792		3.184		−5.007	
Yiling *et al.* (1991)	6	6	525 – 605	9.4 – 87.7	0.40	6	–	3.709		3.094		4.031		6.154	
Yiling *et al.* (1991)	8	8	550 – 625	12.1 – 107	0.50	8	–	2.577		−1.156		3.056		−4.526	
Yiling *et al.* (1991)	11	11	554 – 674	11.7 – 204	0.60	11	–	3.579		−3.312		3.877		−5.149	
Yiling *et al.* (1991)	13	12	580 – 700	16.5 – 270	0.70	12	–	4.213		−4.177		4.837		−8.545	
Yiling *et al.* (1991)	11	9	590 – 707	16.6 – 310	0.80	7	–	3.252		−1.521		3.995		−6.790	
Yiling *et al.* (1991)	5	1	624 – 639	24.6 – 83.1	0.90	1	–	5.314		−5.314		5.314		−5.314	

Table A2.1 (continued)

Authors	Number of data points total[a]	used[b]	Covered ranges Temp. T/K	Pressure p/MPa	Compos.[c,d] x	N_1	N_2	Statistical analysis[n] AAD_1 %	AAD_2 %	Bias_1 %	Bias_2 %	RMS_1 %	RMS_2 %	MaxD_1 %	MaxD_2 %
(1 − x) n-C_4H_{10} + x H_2O (continued)															
$p\rho T$ data (continued)						**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA
Yiling *et al.* (1991)	4	–	616 – 629	22.0 – 47.7	0.93	–	–								
Yiling *et al.* (1991)	2	1	618 – 627	20.5 – 41.9	0.95	–	–								
VLE data						**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP
Tian *et al.* (2004)[y]	51	–	600 – 700	19.3 – 276	0.65 – 0.98	–	–								
(1 − x) n-C_4H_{10} + x Ar															
$p\rho T$ data						**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA
Malewski & Sandler (1989)	46	45	340 – 380	1.4 – 18.5	0.02 – 0.82	46	–	1.672		1.115		2.215		4.535	
Marathe & Sandler (1991)	24	21	366	2.2 – 14.7	0.03 – 0.70	22	–	1.511		1.290		1.864		4.415	
VLE data						**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP
Malewski & Sandler (1989)	23	14	340 – 380	1.4 – 18.5	0.02 – 0.55	22	23	2.512	11.017	−0.067	10.885	3.373	11.899	−8.216	16.201
Marathe & Sandler (1991)	12	7	366	2.2 – 14.7	0.03 – 0.56	10	11	3.970	12.966	3.093	12.966	4.556	13.734	6.957	18.107
(1 − x) i-C_4H_{10} + x H_2															
VLE data						**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP
Dean & Tooke (1946)	21	–	311 – 394	3.4 – 20.7	0.02 – 0.25	–	5		26.503		26.503		26.671		29.404
(1 − x) i-C_4H_{10} + x H_2O															
$p\rho T$ data						**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA
Tian *et al.* (2004)	6	–	547 – 651	13.5 – 189	0.50	–	–								
Tian *et al.* (2004)	7	–	566 – 695	16.7 – 306	0.60	–	–								
Tian *et al.* (2004)	6	–	588 – 693	20.7 – 264	0.70	–	–								
Tian *et al.* (2004)	6	–	605 – 674	22.6 – 191	0.80	–	–								
Tian *et al.* (2004)	13	–	608 – 658	18.9 – 190	0.90	–	–								
Tian *et al.* (2004)	16	–	620 – 657	18.1 – 197	0.93	–	–								

Table A2.1 (continued)

Authors	Number of data points		Covered ranges					Statistical analysis[n]							
	total[a]	used[b]	Temp. T/K	Pressure p/MPa	Compos.[c,d] x	N_1	N_2	AAD$_1$ %	AAD$_2$ %	Bias$_1$ %	Bias$_2$ %	RMS$_1$ %	RMS$_2$ %	MaxD$_1$ %	MaxD$_2$ %
$(1-x)$ i-C_4H_{10} + x H_2O (continued)															
***pρT* data (continued)**						**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA
Tian *et al.* (2004)	12	–	618 – 649	16.7 – 215	0.98	–	–								
VLE data						**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP
Tian *et al.* (2004)[y]	77	–	547 – 695	13.5 – 306	0.50 – 0.98	1	–	25.140		25.140		25.140		25.140	
$(1-x)$ n-C_5H_{12} + x i-C_5H_{12}															
VLE data						**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP
McCormick *et al.* (1963)	13	–	328 – 385	0.2 – 0.8	0.02 – 0.94	13	13	2.060	4.942	1.817	−4.671	2.508	6.522	4.423	−11.578
$(1-x)$ n-C_5H_{12} + x n-C_6H_{14}															
***pρT* data**						**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA
Aucejo *et al.* (1995)	9	–	298	0.1	0.10 – 0.90	9	–	0.202		0.202		0.207		0.249	
Pecar & Dolecek (2003)	15	–	298 – 348	0.1 – 40.0	0.13	15	–	0.110		0.062		0.120		0.223	
Pecar & Dolecek (2003)	15	–	298 – 348	0.1 – 40.0	0.13	15	–	0.092		0.082		0.108		0.183	
Pecar & Dolecek (2003)	15	–	298 – 348	0.1 – 40.0	0.25	15	–	0.103		0.064		0.120		−0.219	
Pecar & Dolecek (2003)	15	–	298 – 348	0.1 – 40.0	0.26	15	–	0.108		0.098		0.125		0.238	
Pecar & Dolecek (2003)	15	–	298 – 348	0.1 – 40.0	0.38	15	–	0.109		0.104		0.127		0.230	
Pecar & Dolecek (2003)	15	–	298 – 348	0.1 – 40.0	0.38	15	–	0.112		0.104		0.130		0.255	
Pecar & Dolecek (2003)	15	–	298 – 348	0.1 – 40.0	0.50	15	–	0.113		0.096		0.131		0.266	
Pecar & Dolecek (2003)	15	–	298 – 348	0.1 – 40.0	0.50	15	–	0.106		0.094		0.123		0.236	
Pecar & Dolecek (2003)	15	–	298 – 348	0.1 – 40.0	0.63	15	–	0.074		0.019		0.094		0.193	
Pecar & Dolecek (2003)	15	–	298 – 348	0.1 – 40.0	0.63	15	–	0.108		0.084		0.125		0.267	
Pecar & Dolecek (2003)	15	–	298 – 348	0.1 – 40.0	0.75	15	–	0.081		0.033		0.099		0.201	
Pecar & Dolecek (2003)	15	–	298 – 348	0.1 – 40.0	0.75	15	–	0.078		0.056		0.098		0.205	
Pecar & Dolecek (2003)	15	–	298 – 348	0.1 – 40.0	0.88	15	–	0.081		−0.042		0.095		−0.186	
Pecar & Dolecek (2003)	15	–	298 – 348	0.1 – 40.0	0.88	15	–	0.092		−0.055		0.107		−0.201	

Table A2.1 (continued)

Authors	Number of data points total[a]	used[b]	Covered ranges Temp. T/K	Pressure p/MPa	Compos.[c,d] x	N_1	N_2	Statistical analysis[n] AAD_1 %	AAD_2 %	$Bias_1$ %	$Bias_2$ %	RMS_1 %	RMS_2 %	$MaxD_1$ %	$MaxD_2$ %
(1 − *x*) n-C_5H_{12} + *x* n-C_6H_{14} (continued)															
***pρT* data (continued)**						**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA
Ramos-Estrada *et al.* (2006)	11	–	273 – 323	0.1	0.10	11	–	0.270		0.270		0.271		0.276	
Ramos-Estrada *et al.* (2006)	10	–	273 – 318	0.1	0.20	10	–	0.249		0.249		0.249		0.253	
Ramos-Estrada *et al.* (2006)	10	–	273 – 318	0.1	0.30	10	–	0.341		0.341		0.342		0.377	
Ramos-Estrada *et al.* (2006)	12	–	273 – 328	0.1	0.40	12	–	0.283		0.283		0.283		0.289	
Ramos-Estrada *et al.* (2006)	12	–	273 – 328	0.1	0.50	12	–	0.240		0.240		0.241		0.269	
Ramos-Estrada *et al.* (2006)	10	–	273 – 318	0.1	0.61	10	–	0.207		0.207		0.207		0.220	
Ramos-Estrada *et al.* (2006)	9	–	273 – 313	0.1	0.70	9	–	0.162		0.162		0.163		0.190	
Ramos-Estrada *et al.* (2006)	13	–	273 – 333	0.1	0.80	13	–	0.158		0.158		0.159		0.183	
Ramos-Estrada *et al.* (2006)	13	–	273 – 333	0.1	0.90	13	–	0.071		0.071		0.078		0.107	
VLE data						**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP
Chen & Zwolinski (1974)[x]	8	–	298	0.03 – 0.06	0.10 – 0.89	8	8	2.574	1.552	−2.574	−1.552	2.843	1.755	−3.778	−2.278
(1 − *x*) n-C_5H_{12} + *x* n-C_7H_{16}															
***pρT* data**						**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA
Aucejo *et al.* (1995)	9	–	298	0.1	0.11 – 0.90	9	–	0.413		0.413		0.429		0.534	
Pecar & Dolecek (2003)	15	–	298 – 348	0.1 – 40.0	0.12	15	–	0.244		0.244		0.255		0.377	
Pecar & Dolecek (2003)	15	–	298 – 348	0.1 – 40.0	0.13	15	–	0.224		0.224		0.233		0.325	
Pecar & Dolecek (2003)	15	–	298 – 348	0.1 – 40.0	0.25	15	–	0.404		0.404		0.410		0.525	
Pecar & Dolecek (2003)	15	–	298 – 348	0.1 – 40.0	0.25	15	–	0.369		0.369		0.378		0.534	
Pecar & Dolecek (2003)	30	–	298 – 348	0.1 – 40.0	0.38	30	–	0.458		0.458		0.466		0.640	
Pecar & Dolecek (2003)	15	–	298 – 348	0.1 – 40.0	0.50	15	–	0.420		0.420		0.425		0.540	
Pecar & Dolecek (2003)	15	–	298 – 348	0.1 – 40.0	0.50	15	–	0.422		0.422		0.429		0.590	
Pecar & Dolecek (2003)	15	–	298 – 348	0.1 – 40.0	0.63	15	–	0.329		0.329		0.336		0.454	
Pecar & Dolecek (2003)	15	–	298 – 348	0.1 – 40.0	0.63	15	–	0.359		0.359		0.369		0.521	
Pecar & Dolecek (2003)	30	–	298 – 348	0.1 – 40.0	0.75	30	–	0.239		0.239		0.253		0.406	
Pecar & Dolecek (2003)	15	–	298 – 348	0.1 – 40.0	0.87	15	–	0.103		0.097		0.124		0.254	

Table A2.1 (continued)

Authors	Number of data points		Covered ranges			Statistical analysis[n]									
	total[a]	used[b]	Temp. T/K	Pressure p/MPa	Compos.[c,d] x	N_1	N_2	AAD$_1$ %	AAD$_2$ %	Bias$_1$ %	Bias$_2$ %	RMS$_1$ %	RMS$_2$ %	MaxD$_1$ %	MaxD$_2$ %
$(1-x)$ n-C_5H_{12} + x n-C_7H_{16} (continued)															
***pρT* data (continued)**						**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA
Pecar & Dolecek (2003)	15	–	298 – 348	0.1 – 40.0	0.88	15	–	0.062		0.020		0.067		0.113	
Ramos-Estrada *et al.* (2006)	7	–	273 – 303	0.1	0.10	7	–	0.231		0.231		0.231		0.235	
Ramos-Estrada *et al.* (2006)	11	–	273 – 323	0.1	0.20	11	–	0.371		0.371		0.371		0.373	
Ramos-Estrada *et al.* (2006)	11	–	273 – 323	0.1	0.30	11	–	0.466		0.466		0.466		0.471	
Ramos-Estrada *et al.* (2006)	9	–	273 – 313	0.1	0.40	9	–	0.497		0.497		0.497		0.503	
Ramos-Estrada *et al.* (2006)	14	–	273 – 338	0.1	0.50	14	–	0.568		0.568		0.569		0.576	
Ramos-Estrada *et al.* (2006)	15	–	273 – 343	0.1	0.60	15	–	0.532		0.532		0.532		0.570	
Ramos-Estrada *et al.* (2006)	13	–	273 – 333	0.1	0.70	13	–	0.384		0.384		0.384		0.389	
Ramos-Estrada *et al.* (2006)	12	–	273 – 328	0.1	0.80	12	–	0.274		0.274		0.274		0.279	
Ramos-Estrada *et al.* (2006)	15	–	273 – 343	0.1	0.90	15	–	0.156		0.156		0.156		0.171	
VLE data						**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP
Cummings *et al.* (1933)	26	–	404 – 526	1.0 – 3.1	0.10 – 0.90	24	23	0.529	0.487	−0.452	−0.109	0.632	0.679	−1.213	−1.754
$(1-x)$ n-C_5H_{12} + x n-C_8H_{18}															
***pρT* data**						**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA
Aucejo *et al.* (1995)	9	–	298	0.1	0.10 – 0.89	9	–	2.305		2.305		2.412		3.090	
VLE data						**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP
Chueh & Prausnitz (1982)[z]	61	–	292 – 434	0.05 – 1.5	0.05 – 0.95	60	51	0.487	0.897	−0.004	−0.173	0.558	1.033	−1.250	−1.940
$(1-x)$ n-C_5H_{12} + x H_2O															
***pρT* data**						**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA
Abdulagatov *et al.* (1998)	6	6	647	4.6 – 37.9	0.31	6	6	3.714	3.505	3.714	−3.505	4.169	3.996	5.820	−6.212
Abdulagatov *et al.* (1998)	6	6	647	4.3 – 40.4	0.61	6	6	6.366	2.768	6.366	−0.247	6.660	3.628	9.173	5.761
Abdulagatov *et al.* (1998)	8	8	647	4.6 – 40.9	0.82	8	8	0.983	4.919	0.458	−2.945	1.269	5.245	2.225	−7.893
Abdulagatov *et al.* (1998)	8	8	647	4.6 – 40.0	0.91	8	8	1.697	3.631	−1.433	−3.631	2.557	4.407	−6.535	−6.710

Table A2.1 (continued)

Authors	Number of data points total[a]	used[b]	Covered ranges Temp. T/K	Pressure p/MPa	Compos.[c,d] x	N_1	N_2	Statistical analysis[n] AAD$_1$ %	AAD$_2$ %	Bias$_1$ %	Bias$_2$ %	RMS$_1$ %	RMS$_2$ %	MaxD$_1$ %	MaxD$_2$ %
(1 − x) n-C_5H_{12} + x H_2O (continued)															
$p\rho T$ data (continued)						**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA
Abdulagatov *et al.* (1998)	9	9	647	4.7 – 39.6	0.94	9	6	1.583	2.866	−1.071	−2.866	2.820	3.643	−7.369	−5.971
Abdulagatov *et al.* (1998)	9	9	647	4.6 – 39.0	0.96	9	6	2.324	3.751	−1.767	−3.608	3.485	5.220	−7.115	−8.996
Abdulagatov *et al.* (1998)	9	9	647	4.7 – 38.5	0.97	9	4	2.935	1.298	−0.739	1.298	3.530	1.431	−6.018	2.303
(1 − x) n-C_6H_{14} + x n-C_7H_{16}															
$p\rho T$ data						**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA
Assael *et al.* (2001a)	1	1	293	0.1	0.09	1	–	0.249		0.249		0.249		0.249	
Assael *et al.* (2001a)	1	1	298	0.1	0.10	1	–	0.064		0.064		0.064		0.064	
Assael *et al.* (2001a)	1	1	293	0.1	0.30	1	–	0.326		0.326		0.326		0.326	
Assael *et al.* (2001a)	1	1	298	0.1	0.30	1	–	0.143		0.143		0.143		0.143	
Assael *et al.* (2001a)	12	12	293 – 323	0.1 – 71.7	0.36	12	–	0.169		−0.127		0.191		−0.288	
Assael *et al.* (2001a)	1	1	298	0.1	0.49	1	–	0.032		0.032		0.032		0.032	
Assael *et al.* (2001a)	1	1	293	0.1	0.50	1	–	0.225		0.225		0.225		0.225	
Assael *et al.* (2001a)	13	13	288 – 323	0.1 – 61.7	0.67	13	–	0.065		0.035		0.089		0.201	
Assael *et al.* (2001a)	1	1	293	0.1	0.70	1	–	0.128		0.128		0.128		0.128	
Assael *et al.* (2001a)	1	1	298	0.1	0.70	1	–	0.080		0.080		0.080		0.080	
Assael *et al.* (2001a)	1	1	298	0.1	0.89	1	–	0.022		−0.022		0.022		−0.022	
Assael *et al.* (2001a)	1	1	293	0.1	0.91	1	–	0.156		0.156		0.156		0.156	
Aucejo *et al.* (1995)	9	–	298	0.1	0.10 – 0.89	9	–	0.072		0.072		0.076		0.098	
Chevalier *et al.* (1990)	9	–	298	0.1	0.10 – 0.87	9	–	0.081		0.081		0.085		0.104	
Cooper & Asfour (1991)	9	–	293	0.1	0.09 – 0.91	9	–	0.225		0.225		0.233		0.292	
Goates *et al.* (1981)	31	–	283 – 313	0.1	0.10 – 0.91	31	–	0.064		0.064		0.075		0.135	
Pecar & Dolecek (2003)	15	–	298 – 348	0.1 – 40.0	0.13	15	–	0.087		−0.053		0.100		−0.186	
Pecar & Dolecek (2003)	15	–	298 – 348	0.1 – 40.0	0.16	15	–	0.084		−0.050		0.101		−0.199	
Pecar & Dolecek (2003)	15	–	298 – 348	0.1 – 40.0	0.25	15	–	0.072		−0.021		0.087		−0.158	
Pecar & Dolecek (2003)	15	–	298 – 348	0.1 – 40.0	0.27	15	–	0.071		−0.021		0.086		−0.160	

Table A2.1 (continued)

Authors	Number of data points total[a]	used[b]	Temp. T/K	Covered ranges Pressure p/MPa	Compos.[c,d] x	N_1	N_2	Statistical analysis[n] AAD$_1$ %	AAD$_2$ %	Bias$_1$ %	Bias$_2$ %	RMS$_1$ %	RMS$_2$ %	MaxD$_1$ %	MaxD$_2$ %
(1 − x) n-C_6H_{14} + x n-C_7H_{16} (continued)															
***pρT* data (continued)**						**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA
Pecar & Dolecek (2003)	30	–	298 – 348	0.1 – 40.0	0.38	30	–	0.069		−0.028		0.083		0.172	
Pecar & Dolecek (2003)	30	–	298 – 348	0.1 – 40.0	0.50	30	–	0.080		−0.057		0.097		−0.193	
Pecar & Dolecek (2003)	15	–	298 – 348	0.1 – 40.0	0.62	15	–	0.068		−0.038		0.087		−0.167	
Pecar & Dolecek (2003)	15	–	298 – 348	0.1 – 40.0	0.63	15	–	0.061		−0.034		0.077		−0.150	
Pecar & Dolecek (2003)	30	–	298 – 348	0.1 – 40.0	0.75	30	–	0.096		−0.085		0.120		−0.238	
Pecar & Dolecek (2003)	15	–	298 – 348	0.1 – 40.0	0.88	15	–	0.079		−0.074		0.098		−0.186	
Pecar & Dolecek (2003)	15	–	298 – 348	0.1 – 40.0	0.88	15	–	0.082		−0.071		0.106		−0.192	
Ramos-Estrada *et al.* (2006)	14	–	273 – 338	0.1	0.10	14	–	0.045		0.035		0.052		0.085	
Ramos-Estrada *et al.* (2006)	14	–	273 – 338	0.1	0.20	14	–	0.052		0.049		0.060		0.092	
Ramos-Estrada *et al.* (2006)	16	–	273 – 348	0.1	0.30	16	–	0.103		0.103		0.111		0.161	
Ramos-Estrada *et al.* (2006)	13	–	273 – 333	0.1	0.40	13	–	0.073		0.073		0.077		0.105	
Ramos-Estrada *et al.* (2006)	16	–	273 – 348	0.1	0.50	16	–	0.091		0.091		0.093		0.109	
Ramos-Estrada *et al.* (2006)	19	–	273 – 363	0.1	0.60	19	–	0.152		0.152		0.154		0.172	
Ramos-Estrada *et al.* (2006)	19	–	273 – 363	0.1	0.70	19	–	0.096		0.096		0.097		0.109	
Ramos-Estrada *et al.* (2006)	19	–	273 – 363	0.1	0.80	19	–	0.127		0.127		0.127		0.139	
Ramos-Estrada *et al.* (2006)	19	–	273 – 363	0.1	0.90	19	–	0.020		0.011		0.022		−0.036	
Speed of sound						**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA
Aicart *et al.* (1983)	28	–	298	0.1	0.01 – 0.96	28	–	1.223		1.223		1.322		1.878	
VLE data						**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP
Smyth & Engel (1929)	15	–	303 – 323	0.01 – 0.05	0.11 – 0.86	15	15	3.071	0.673	−3.071	−0.014	3.380	0.793	−5.553	−1.378
Wisniak *et al.* (1997a)	14	14	340 – 367	0.1	0.03 – 0.97	14	14	0.409	2.751	0.212	2.751	0.516	2.911	1.073	4.067
(1 − x) n-C_6H_{14} + x n-C_8H_{18}															
***pρT* data**						**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA
Aucejo *et al.* (1995)	9	–	298	0.1	0.10 – 0.89	9	–	0.205		0.205		0.211		0.259	

Table A2.1 (continued)

Authors	Number of data points		Covered ranges			Statistical analysis^n									
	total^a	used^b	Temp. T/K	Pressure p/MPa	Compos.^{c,d} x	N_1	N_2	AAD$_1$ %	AAD$_2$ %	Bias$_1$ %	Bias$_2$ %	RMS$_1$ %	RMS$_2$ %	MaxD$_1$ %	MaxD$_2$ %
(1 − x) n-C_6H_{14} + x n-C_8H_{18} (continued)															
***pρT* data (continued)**						**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA
Chevalier *et al.* (1990)	9	–	298	0.1	0.10 – 0.90	9	–	0.209		0.209		0.216		0.264	
Cooper & Asfour (1991)	9	–	293	0.1	0.10 – 0.90	9	–	0.361		0.361		0.371		0.438	
Goates *et al.* (1981)	34	–	283 – 313	0.1	0.07 – 0.94	34	–	0.217		0.217		0.231		0.353	
(1 − x) n-C_6H_{14} + x H_2															
***pρT* data**						**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA
Nichols *et al.* (1957)	163	80	278 – 511	1.4 – 68.9	0.19	140	–	2.160		−1.304		3.284		−9.618	
Nichols *et al.* (1957)	139	32	278 – 511	5.5 – 68.9	0.48	77	–	3.281		−1.853		4.224		−9.783	
Nichols *et al.* (1957)	121	81	278 – 511	8.6 – 68.9	0.79	92	–	2.784		−2.331		3.941		−9.743	
VLE data						**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP
Gao *et al.* (2001)^x	34	–	344 – 411	1.2 – 15.1	0.01 – 0.14	16	9	27.779	27.294	27.779	27.294	27.806	27.386	29.633	29.456
Nichols *et al.* (1957)	100	98	278 – 478	0.03 – 68.9	0.03 – 0.69	56	34	13.350	21.655	7.932	21.655	15.673	22.543	28.528	29.836
(1 − x) n-C_6H_{14} + x H_2O															
***pρT* data**						**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA
Abdulagatov & Magomedov (1992)	4	–	463 – 505	2.6 – 6.7	0.25	–	–								
Abdulagatov & Magomedov (1992)	4	–	433 – 485	1.8 – 5.2	0.50	–	–								
Abdulagatov & Magomedov (1992)	4	–	381 – 444	0.7 – 2.8	0.75	–	–								
Abdulagatov & Magomedov (1992)	3	–	399 – 440	0.7 – 2.1	0.85	–	–								
Abdulagatov *et al.* (1992)	8	–	523	2.1 – 7.1	0.01	–	–								
Abdulagatov *et al.* (1992)	6	–	623	3.1 – 14.8	0.02	–	–								
Abdulagatov *et al.* (1992)	5	–	573	4.0 – 8.0	0.02	–	–								
Abdulagatov *et al.* (1992)	5	–	573	2.1 – 8.0	0.04	–	–								
Abdulagatov *et al.* (1992)	4	–	523	2.1 – 4.0	0.05	–	–								
Abdulagatov *et al.* (1992)	6	–	623	3.1 – 15.0	0.07	–	–								

Table A2.1 (continued)

Authors	Number of data points		Covered ranges			Statistical analysis[n]									
	total[a]	used[b]	Temp. T/K	Pressure p/MPa	Compos.[c,d] x	N_1	N_2	AAD_1 %	AAD_2 %	Bias_1 %	Bias_2 %	RMS_1 %	RMS_2 %	MaxD_1 %	MaxD_2 %
$(1-x)$ n-C_6H_{14} + x H_2O (continued)															
***pρT* data (continued)**						**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA
Abdulagatov *et al.* (1992)	4	–	573	2.1 – 8.1	0.13	–	–								
Abdulagatov *et al.* (1992)	3	–	523	2.1 – 4.1	0.14	–	–								
Abdulagatov *et al.* (1992)	5	–	623	3.1 – 15.1	0.18	–	–								
Abdulagatov *et al.* (1992)	4	–	573	2.2 – 8.2	0.33	–	–								
Abdulagatov *et al.* (1992)	2	–	523	2.1 – 4.2	0.35	–	–								
Abdulagatov *et al.* (1992)	5	–	623	3.1 – 15.0	0.46	–	–								
Abdulagatov *et al.* (1993b)	8	8	523	2.1 – 7.1	0.06	4	4	5.701	5.686	5.701	5.686	5.826	5.880	7.109	7.535
Abdulagatov *et al.* (1993b)	6	6	573	2.1 – 8.0	0.08	6	6	5.797	3.622	5.797	3.622	5.918	3.739	7.225	4.595
Abdulagatov *et al.* (1993b)	6	6	623	3.1 – 14.8	0.11	6	6	3.574	0.654	3.574	0.654	3.727	0.778	5.029	1.246
Abdulagatov *et al.* (1993b)	5	5	573	2.1 – 8.0	0.16	5	5	7.363	2.089	5.528	−2.089	7.644	3.455	9.318	−7.542
Abdulagatov *et al.* (1993b)	4	4	523	2.1 – 4.0	0.19	4	4	6.790	3.461	6.790	−3.118	6.910	4.055	8.797	−6.217
Abdulagatov *et al.* (1993b)	6	6	623	3.1 – 15.0	0.26	6	6	4.429	4.326	4.429	−4.326	4.617	4.449	5.662	−5.393
Abdulagatov *et al.* (1993b)	4	4	573	2.1 – 8.1	0.41	4	2	2.020	3.697	2.020	−3.697	2.085	4.548	2.686	−6.346
Abdulagatov *et al.* (1993b)	3	3	523	2.1 – 4.1	0.44	3	2	0.922	5.301	0.922	−5.301	1.121	5.812	1.822	−7.684
Abdulagatov *et al.* (1993b)	5	5	623	3.1 – 15.1	0.52	5	2	2.508	6.362	−2.508	−6.362	2.666	6.759	−3.674	−8.645
Abdulagatov *et al.* (1993b)	4	4	573	2.2 – 8.3	0.70	3	2	5.039	5.456	−5.039	−5.456	5.481	5.755	−7.748	−7.288
Abdulagatov *et al.* (1993b)	2	2	523	2.1 – 4.2	0.72	2	1	2.893	1.444	−2.893	−1.444	4.010	1.444	−5.670	−1.444
Abdulagatov *et al.* (1993b)	5	5	623	3.1 – 15.1	0.80	3	3	5.247	5.535	−5.247	−5.535	5.950	6.172	−8.699	−8.830
Kamilov *et al.* (1996)	123	–	380 – 496	0.4 – 5.6	0.26	–	–								
Kamilov *et al.* (1996)	77	–	365 – 622	0.3 – 24.1	0.62	4	–	5.174		3.932		5.762		8.130	
Rasulov & Rasulov (2001)	42	–	373 – 500	0.4 – 3.8	0.17	1	–	7.905		7.905		7.905		7.905	
Rasulov & Rasulov (2001)	42	–	433 – 580	1.7 – 11.2	0.26	6	–	4.615		−0.883		5.157		9.175	
Rasulov & Rasulov (2001)	69	–	428 – 581	1.4 – 59.2	0.35	14	–	7.323		7.323		7.387		8.935	
Rasulov & Rasulov (2001)	125	–	327 – 625	0.1 – 65.3	0.62	64	–	6.006		5.878		6.812		9.757	
Rasulov & Rasulov (2001)	74	–	396 – 626	0.8 – 60.3	0.83	33	–	3.079		−2.171		4.024		−8.441	
Rasulov & Rasulov (2001)	113	–	428 – 647	1.4 – 64.6	0.94	34	–	3.044		−0.677		3.766		−8.243	

Table A2.1 (continued)

Authors	Number of data points total[a]	used[b]	Covered ranges Temp. T/K	Pressure p/MPa	Compos.[c,d] x	N_1	N_2	Statistical analysis[n] AAD_1 %	AAD_2 %	Bias_1 %	Bias_2 %	RMS_1 %	RMS_2 %	MaxD_1 %	MaxD_2 %
(1 − x) n-C_6H_{14} + x H_2O (continued)															
***pρT* data (continued)**						**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA
Rasulov & Rasulov (2001)	115	–	418 – 635	0.8 – 60.8	0.96	30	–	2.752		−2.152		3.621		−9.624	
Yiling *et al.* (1991)	6	6	555 – 650	19.8 – 227	0.39	6	–	2.489		1.741		3.612		8.089	
Yiling *et al.* (1991)	6	6	596 – 684	39.9 – 247	0.50	6	–	0.674		−0.074		0.726		1.210	
Yiling *et al.* (1991)	6	6	591 – 687	24.8 – 203	0.60	6	–	0.695		−0.516		0.806		−1.277	
Yiling *et al.* (1991)	5	5	601 – 681	22.9 – 153	0.70	5	–	3.374		−3.374		3.526		−4.969	
Yiling *et al.* (1991)	7	7	609 – 699	22.1 – 170	0.80	4	–	5.717		−5.717		6.082		−9.106	
(1 − x) n-C_7H_{16} + x n-C_8H_{18}															
***pρT* data**						**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA
Aucejo *et al.* (1995)	9	–	298	0.1	0.10 – 0.89	9	–	0.248		0.248		0.260		0.340	
Chevalier *et al.* (1990)	9	–	298	0.1	0.10 – 0.90	9	–	0.263		0.263		0.272		0.348	
Cooper & Asfour (1991)	9	–	293	0.1	0.10 – 0.90	9	–	0.359		0.359		0.371		0.466	
VLE data						**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP
Beatty & Calingaert (1934)[x]	3	–	370	0.06 – 0.08	0.35 – 0.67	3	3	1.518	0.312	−1.518	−0.312	1.521	0.390	−1.639	−0.639
Leslie & Carr (1925)[x]	9	–	374 – 394	0.1	0.09 – 0.89	9	9	0.507	1.144	0.020	1.059	0.642	1.318	1.313	2.156
Wisniak *et al.* (1997b)	20	20	370 – 394	0.1	0.04 – 0.97	20	20	0.529	1.135	0.272	1.135	0.638	1.252	1.235	2.283
Zielkiewicz (1992)[x]	11	–	313	0.005 – 0.01	0.08 – 0.93	11	11	1.098	2.014	−1.060	−2.014	1.258	2.049	−1.889	−2.752
(1 − x) n-C_7H_{16} + x H_2															
VLE data						**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP
Peter & Reinhartz (1960)	29	27	424 – 499	2.5 – 78.5	0.02 – 0.81	27	8	9.482	22.406	−0.121	22.406	10.982	23.232	−18.960	29.726
(1 − x) n-C_8H_{18} + x H_2O															
***pρT* data**						**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA
Abdulagatov *et al.* (1993b)	9	9	623	3.1 – 15.3	0.15	9	9	5.389	2.124	2.711	1.645	6.035	2.499	9.197	4.086

Table A2.1 (continued)

Authors	Number of data points total[a]	used[b]	Covered ranges Temp. T/K	Pressure p/MPa	Compos.[c,d] x	N_1	N_2	Statistical analysis[n] AAD_1 %	AAD_2 %	$Bias_1$ %	$Bias_2$ %	RMS_1 %	RMS_2 %	$MaxD_1$ %	$MaxD_2$ %
(1 − *x*) n-C_8H_{18} + *x* H_2O (continued)															
***pρT* data (continued)**						**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA
Abdulagatov *et al.* (1993b)	6	6	623	3.1 – 14.9	0.28	6	6	5.606	3.222	1.528	−3.222	5.907	3.357	−7.869	−4.937
Abdulagatov *et al.* (1993b)	7	7	623	3.1 – 14.8	0.46	6	5	3.073	6.340	−0.238	−6.340	3.656	6.610	−7.278	−9.280
Abdulagatov *et al.* (1993b)	6	6	623	3.1 – 15.0	0.77	5	3	3.805	6.248	−3.805	−6.248	4.573	6.548	−8.262	−8.559
(1 − *x*) H_2 + *x* CO															
***pρT* data**						**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA
Scott (1929)	18	18	298	0.1 – 17.2	0.34	18	18	0.066	0.081	−0.056	0.019	0.087	0.091	−0.169	−0.170
Scott (1929)	18	18	298	0.1 – 17.2	0.48	18	18	0.031	0.134	−0.023	0.134	0.037	0.144	−0.079	0.212
Scott (1929)	18	18	298	0.1 – 17.2	0.67	18	18	2.610	2.818	2.610	2.818	2.888	3.111	3.979	4.206
VLE data						**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP
Akers & Eubanks (1960)	21	20	83.3 – 122	2.2 – 24.1	0.35 – 0.97	10	14	22.863	8.911	22.863	−1.094	23.672	10.752	29.571	−28.142
Verschoyle (1931)	60	60	68.2 – 88.2	1.7 – 22.8	0.46 – 0.97	32	10	17.481	21.662	4.153	−19.761	19.396	22.512	−29.279	−28.932
(1 − *x*) H_2 + *x* He															
VLE data						**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP
Hiza (1981)[x,y]	40	–	20.0 – 28.0	0.6 – 2.1	0.01 – 0.05	23	–	17.394		17.394		17.909		23.002	
Sneed *et al.* (1968)	60	–	15.5 – 29.8	2.4 – 10.4	0.01 – 0.36	12	–	16.822		16.822		17.467		24.523	
Sneed *et al.* (1968)	16	–	20.4 – 29.0	2.0 – 10.3	0.04 – 0.31	6	–	15.299		15.299		15.597		20.904	
Sonntag *et al.* (1964)[e,f]	53	–	20.4 – 31.5	0.2 – 3.4	0.00 – 0.18	44	–	12.294		11.029		14.297		29.142	
Streett *et al.* (1964)[e,f]	95	–	15.5 – 32.5	0.2 – 3.4	0.00 – 0.21	77	–	9.621		3.898		12.102		24.419	
(1 − *x*) O_2 + *x* H_2O															
***pρT* data**						**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA
Japas & Franck (1985b)	154	154	472 – 673	19.5 – 324	0.06 – 0.94	148	–	1.615		−0.321		1.902		−4.678	

Table A2.1 (continued)

Authors	Number of data points total[a]	used[b]	Temp. T/K	Covered ranges Pressure p/MPa	Compos.[c,d] x	N_1	N_2	Statistical analysis[n] AAD$_1$ %	AAD$_2$ %	Bias$_1$ %	Bias$_2$ %	RMS$_1$ %	RMS$_2$ %	MaxD$_1$ %	MaxD$_2$ %
(1 − x) O_2 + x He															
VLE data						**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP
Sinor & Kurata (1966)[x]	37	–	77.4 – 143	1.7 – 13.8	0.00 – 0.09	–	1		23.017		23.017		23.017		23.017
(1 − x) O_2 + x Ar															
***pρT* data**						**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA
Blagoi & Rudenko (1958)	36	–	70.4 – 88.8	0.1	0.10 – 0.87	36	–	0.422		−0.390		0.527		−1.067	
VLE data						**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP
Bourbo & Ischkin (1936)	27	27	87.0 – 95.0	0.07 – 0.2	0.04 – 0.86	27	27	0.793	0.938	0.682	0.890	0.896	1.070	1.438	1.790
Burn & Din (1962)	140	139	84.8 – 118	0.06 – 1.0	0.10 – 0.91	140	140	0.218	0.580	0.157	0.484	0.291	0.650	−1.591	1.697
Clark *et al.* (1954)	45	45	90.0 – 110	0.1 – 0.7	0.10 – 0.90	45	45	0.340	0.282	−0.276	0.120	0.424	0.315	−0.942	−0.683
Fastovskii & Petrovskii (1955)	24	22	89.3 – 96.4	0.1 – 0.2	0.21 – 0.83	23	23	0.421	0.465	−0.210	0.193	0.515	0.558	−1.088	1.166
Hiza *et al.* (1990)	12	12	94.9 – 99.9	0.2 – 0.3	0.11 – 0.79	12	12	0.877	0.724	−0.865	−0.348	1.117	0.873	−1.858	−1.688
Narinskii (1957)	55	55	90.5 – 120	0.1 – 1.2	0.03 – 0.96	55	55	0.238	0.429	−0.236	−0.035	0.321	0.540	−0.695	−1.441
Pool *et al.* (1962)[x]	20	–	83.8 – 89.6	0.05 – 0.1	0.10 – 0.90	20	19	7.781	6.956	−0.686	0.797	12.236	10.825	−29.569	−26.433
Wang (1960)[x]	35	–	90.4 – 95.9	0.1 – 0.2	0.02 – 1.00	35	35	1.401	1.563	0.623	0.736	1.879	2.028	4.282	4.435
Wilson *et al.* (1965)	200	197	87.5 – 139	0.1 – 2.6	0.00 – 0.98	199	199	0.402	0.472	−0.343	−0.325	0.651	0.705	−2.555	−3.037
Yorizane *et al.* (1978)	58	55	89.4 – 91.5	0.1	0.00 – 0.76	57	57	0.694	0.663	−0.026	0.023	1.103	1.072	3.317	3.315
(1 − x) CO + x He															
VLE data						**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP
Parrish & Steward (1975)[x]	27	–	79.5 – 120	3.6 – 13.8	0.00 – 0.10	–	–								
Parrish & Steward (1975)[y]	42	–	80.0 – 120	0.7 – 13.8	0.24 – 0.99	–	–								
Sinor & Kurata (1966)[x]	29	–	77.4 – 128	1.7 – 13.8	0.00 – 0.17	–	–								

Table A2.1 (continued)

Authors	Number of data points		Covered ranges			Statistical analysis^n									
	total^a	used^b	Temp. T/K	Pressure p/MPa	Compos.^{c,d} x	N_1	N_2	AAD$_1$ %	AAD$_2$ %	Bias$_1$ %	Bias$_2$ %	RMS$_1$ %	RMS$_2$ %	MaxD$_1$ %	MaxD$_2$ %
(1 − x) CO + x Ar															
VLE data						**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP
Christiansen *et al.* (1973)	16	15	123 – 137	1.5 – 3.8	0.06 – 0.92	15	15	0.496	0.631	0.026	−0.228	0.601	0.724	1.021	−1.328
(1 − x) H_2O + x Ar															
***pρT* data**						**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA
Wu *et al.* (1990)	4	4	584 – 640	33.1 – 171	0.05	4	–	4.354		−3.760		5.458		−8.638	
Wu *et al.* (1990)	6	6	601 – 645	29.6 – 129	0.08	4	–	2.313		−2.016		2.729		−4.560	
Wu *et al.* (1990)	10	10	623 – 642	22.6 – 227	0.11	7	–	4.050		−3.581		5.120		−8.816	
Wu *et al.* (1990)	12	12	607 – 654	18.4 – 337	0.14	9	–	4.200		−1.682		4.984		7.556	
Wu *et al.* (1990)	13	13	570 – 658	12.5 – 321	0.20	11	–	3.052		0.702		3.709		7.005	
Wu *et al.* (1990)	11	11	567 – 649	11.4 – 201	0.24	8	–	1.568		0.791		2.117		4.136	
Wu *et al.* (1990)	11	11	561 – 657	10.4 – 265	0.28	10	–	2.887		2.041		3.986		9.357	
Wu *et al.* (1990)	13	13	600 – 663	28.1 – 304	0.33	13	–	2.564		1.473		3.354		7.323	
Wu *et al.* (1990)	12	12	601 – 659	34.2 – 272	0.40	12	–	2.440		0.560		3.117		−5.781	
Wu *et al.* (1990)	5	5	629 – 659	82.6 – 270	0.45	5	–	1.702		−0.577		2.063		−3.390	
Wu *et al.* (1990)	13	13	569 – 651	27.1 – 228	0.50	13	–	2.900		1.817		4.036		9.320	
Wu *et al.* (1990)	6	6	613 – 656	74.2 – 268	0.55	6	–	1.346		−0.473		1.806		−3.768	
Wu *et al.* (1990)	11	11	534 – 642	24.4 – 228	0.60	10	–	2.363		1.020		3.419		8.673	
Wu *et al.* (1990)	7	7	581 – 660	61.1 – 313	0.65	7	–	1.347		−0.240		1.740		−3.649	
Wu *et al.* (1990)	10	10	477 – 623	21.0 – 256	0.70	9	–	1.699		0.600		2.376		5.740	
Wu *et al.* (1990)	4	4	566 – 596	87.0 – 218	0.75	4	–	0.911		0.696		1.052		1.790	
Wu *et al.* (1990)	4	4	513 – 564	56.0 – 186	0.80	4	–	3.151		3.151		4.719		9.208	
(1 − x) He + x Ar															
***pρT* data**						**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA
Blancett *et al.* (1970)	72	–	223 – 323	0.3 – 71.9	0.20	72	72	0.329	0.922	0.329	0.920	0.558	1.938	2.268	7.630
Blancett *et al.* (1970)	72	–	223 – 323	0.3 – 71.3	0.41	72	72	0.644	0.817	0.644	0.816	1.087	1.699	4.089	6.721

Table A2.1 (continued)

Authors	Number of			Covered ranges						Statistical analysis[n]					
	data points		Temp.	Pressure	Compos.[c,d]	N_1	N_2	AAD_1	AAD_2	Bias_1	Bias_2	RMS_1	RMS_2	MaxD_1	MaxD_2
	total[a]	used[b]	T/K	p/MPa	x			%	%	%	%	%	%	%	%
$(1-x)$ He + x Ar (continued)															
$p\rho T$ data (continued)						**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA
Blancett *et al.* (1970)	72	–	223 – 323	0.3 – 71.2	0.59	72	72	0.956	0.692	0.956	0.691	1.555	1.421	5.173	5.476
Blancett *et al.* (1970)	72	–	223 – 323	0.3 – 72.3	0.78	72	72	1.079	0.526	1.079	0.526	1.689	1.023	4.647	3.540
Provine & Canfield (1971)	60	–	143 – 183	0.2 – 68.5	0.20	60	59	0.668	1.577	0.668	1.577	1.117	2.906	3.431	9.126
Provine & Canfield (1971)	46	–	143 – 183	0.3 – 68.0	0.41	46	45	1.786	1.621	1.786	1.621	2.741	2.817	7.911	8.104
Provine & Canfield (1971)	54	–	143 – 183	0.2 – 68.3	0.59	49	50	2.273	1.439	2.273	1.439	3.233	2.457	7.757	8.067
Provine & Canfield (1971)	52	–	143 – 183	0.2 – 68.6	0.78	47	48	2.467	1.083	2.467	1.073	3.496	2.128	8.352	9.696
Speed of sound						**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA
Hanayama (1979)	16	–	298	250 – 1697	0.10	4	–	8.386		−8.386		8.440		−9.871	
Hanayama (1979)	15	–	298	198 – 1569	0.25	–	–								
Hanayama (1979)	19	–	298	201 – 1971	0.50	2	–	8.656		−8.656		8.718		−9.692	
VLE data						**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP
Sinor & Kurata (1966)[x]	29	–	93.2 – 148	1.7 – 13.8	0.86 – 1.00	–	–								
Streett & Hill (1971)[e,f]	202	–	98.0 – 160	9.6 – 422	0.40 – 0.98	–	–								
Streett (1969)[e,f]	57	–	91.4 – 148	1.4 – 68.9	0.56 – 1.00	–	–								

[a] Number of all available data points.

[b] Number of data points used for the development of the GERG-2004 equation of state.

[c] Mole fractions. Values of 0.00 and 1.00 result from a mixture composition close to a pure component.

[d] Mole fractions of component X in the saturated liquid phase for VLE data. For VLE data sets containing pTy data only, the specified composition range indicates mole fractions of component X in the saturated vapour phase.

[e] VLE data set also contains pTx data.

[f] VLE data set also contains pTy data.

[g] Listed separately due to a different data format. Saturated liquid (and vapour) densities may also be tabulated as ordinary $p\rho T$ or VLE data.

[h] Isenthalpic measurements.

[n] Nomenclature of the statistical analysis:

- N: Number of data points used for the statistical analysis.

Table A2.1 (continued)

- AAD: Average absolute deviation.
- Bias: Average deviation.
- RMS: Root-mean-squared deviation.
- MaxD: Maximum deviation.
- EqG: GERG-2004 equation of state.
- EqA: AGA8-DC92 equation of state of Starling and Savidge (1992) (used for comparison with GERG-2004 for properties in the homogeneous gas phase only).
- EqP: Cubic equation of state of Peng and Robinson (1976) (used for comparison with GERG-2004 for liquid and saturated liquid densities and VLE properties).

Subscripts:

- 1: GERG-2004 equation of state (EqG).
- 2: AGA8-DC92 equation of state of Starling and Savidge (1992) (EqA) or cubic equation of state of Peng and Robinson (1976) (EqP).

Notes:

- The AGA8-DC92 equation of state of Starling and Savidge (1992) is not valid for the liquid phase and saturated/VLE properties.
- Density deviations are tabulated for $p\rho T$ data.
- Vapour pressure deviations are tabulated for VLE data.

[p] Isobaric measurements.

[s] Saturated liquid densities.

[T] Isothermal measurements.

[u] Values printed in italics indicate deviations in $\mathrm{J{\cdot}mol^{-1}}$.

[x] VLE data set contains pTx data only (or pTx and pTy data).

[y] VLE data set contains pTy data only (or pTy and pTx data).

[z] Calculated data.

[ρ] Density in $\mathrm{kg{\cdot}m^{-3}}$ instead of pressure.

Note

The tabulated VLE data sets contain $pTxy$ data only, unless otherwise stated.

Table A2.2 Data sets for thermal and caloric properties of natural gases and other multi-component mixtures used for the evaluation of the new equation of state (GERG-2004), Eqs. (7.1) – (7.10), and statistical analysis

Authors/Mixture	N_P[a]	Covered ranges		N_C[b]	M[m]	Statistical analysis[n]									
		Temperature T/K	Pressure p/MPa		$\mathrm{g{\cdot}mol^{-1}}$	N_1 %	N_2 %	AAD_1 %	AAD_2 %	Bias_1 %	Bias_2 %	RMS_1 %	RMS_2 %	MaxD_1 %	MaxD_2 %
***pρT* data**						**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA
GERG TM7 [Jaeschke *et al.* (1997)], C-file (ternary mixtures)[c]															
C1231 (DEH), CH_4–N_2–CO_2	33	279 – 308	3.7 – 6.3	3	25.972	33	33	0.056	0.018	−0.056	0.013	0.058	0.020	−0.094	0.034
C1241 (DEH), CH_4–N_2–C_2H_6	22	280 – 308	3.7 – 6.3	3	22.548	22	22	0.033	0.021	0.032	−0.004	0.038	0.025	0.073	−0.046
C1242 (BUR), CH_4–N_2–C_2H_6	99	275 – 345	0.2 – 58.8	3	21.033	99	99	0.138	0.145	−0.073	−0.080	0.295	0.297	−1.630	−1.603
C1341 (DEH), CH_4–CO_2–C_2H_6	22	279 – 308	3.7 – 6.4	4	26.453	22	22	0.132	0.299	0.132	0.299	0.137	0.332	0.209	0.632
C1342 (DEH), CH_4–CO_2–C_2H_6	33	293 – 308	3.8 – 6.2	3	24.535	33	33	0.051	0.019	−0.051	−0.014	0.058	0.024	−0.121	−0.065
C1361 (DEH), CH_4–CO_2–C_3H_8	21	293 – 308	3.8 – 6.1	3	23.115	21	21	0.026	0.120	0.024	−0.120	0.033	0.125	0.058	−0.190
C1461 (DEH), CH_4–C_2H_6–C_3H_8	32	293 – 308	3.8 – 6.6	3	20.318	32	32	0.073	0.091	−0.073	−0.091	0.079	0.097	−0.146	−0.175
C1462 (BUR), CH_4–C_2H_6–C_3H_8	29	320	0.3 – 11.9	3	18.997	29	29	0.011	0.004	0.011	−0.004	0.012	0.005	0.017	−0.016
C1463 (OPT), CH_4–C_2H_6–C_3H_8	347	270 – 350	0.2 – 29.1	3	18.997	347	347	0.020	0.018	0.018	−0.009	0.025	0.024	0.079	−0.074
C1464 (DEH), CH_4–C_2H_6–C_3H_8	14	290 – 300	1.0 – 7.0	3	19.004	14	14	0.032	0.043	−0.028	−0.041	0.034	0.047	−0.059	−0.076
C1465 (DEH), CH_4–C_2H_6–C_3H_8	17	283 – 293	3.1 – 7.7	3	18.998	17	17	0.009	0.015	0.002	−0.006	0.012	0.018	0.031	−0.032
C1466 (DEH), CH_4–C_2H_6–C_3H_8	9	294 – 313	2.0 – 6.0	3	19.005	9	9	0.039	0.056	−0.039	−0.056	0.043	0.058	−0.069	−0.085
C1467 (DEH), CH_4–C_2H_6–C_3H_8	22	290 – 313	2.9 – 7.3	3	18.999	22	22	0.037	0.024	0.035	0.022	0.041	0.028	0.066	0.047
C1468 (ADH), CH_4–C_2H_6–C_3H_8	24	280 – 310	2.0 – 7.0	3	18.998	24	24	0.029	0.020	0.027	0.015	0.036	0.027	0.087	0.069
C1469 (DEH), CH_4–C_2H_6–C_3H_8	12	289 – 300	2.1 – 7.1	3	19.002	12	12	0.034	0.043	−0.023	−0.035	0.041	0.051	−0.069	−0.082
C14610 (BUR), CH_4–C_2H_6–C_3H_8	40	290 – 320	0.2 – 10.7	3	18.999	40	40	0.007	0.011	0.003	−0.011	0.007	0.013	−0.015	−0.031
C14611 (ADH), CH_4–C_2H_6–C_3H_8	30	280 – 310	2.0 – 7.0	3	18.997	30	30	0.026	0.020	0.022	0.011	0.035	0.027	0.087	0.067
C14612 (DEH), CH_4–C_2H_6–C_3H_8	11	290	2.9 – 6.8	3	19.005	11	11	0.017	0.015	0.002	−0.008	0.020	0.021	−0.044	−0.047
C14613 (OPT), CH_4–C_2H_6–C_3H_8	108	280 – 313	0.6 – 13.1	3	18.994	108	108	0.016	0.036	−0.002	−0.032	0.021	0.051	−0.048	−0.128
GERG TM7 [Jaeschke *et al.* (1997)], D-file (synthetic multi-component mixtures)[c,d]															
D1 (BUR), CH_4–N_2–C_2H_6–O_2	24	219 – 273	0.3 – 9.9	4	18.984	24	24	0.051	0.097	0.050	0.096	0.089	0.220	0.281	0.862
D2 (DEH), CH_4–N_2–C_2H_6–C_3H_8	5	283 – 293	3.0 – 7.0	4	17.120	5	5	0.050	0.048	−0.020	−0.019	0.055	0.052	0.077	0.072
D3 (DEH), CH_4–N_2–C_2H_6–C_3H_8	5	283 – 293	3.0 – 7.0	4	17.565	5	5	0.034	0.030	−0.032	−0.030	0.041	0.036	−0.062	−0.057
D4 (DEH), CH_4–N_2–C_2H_6–C_3H_8	6	283 – 293	3.0 – 7.0	4	17.977	6	6	0.040	0.034	0.016	0.016	0.051	0.044	0.080	0.069
D5 (DEH), CH_4–N_2–C_2H_6–C_3H_8	6	283 – 293	3.0 – 7.0	4	18.407	6	6	0.032	0.028	0.017	0.016	0.043	0.035	0.077	0.064

Table A2.2 (continued)

Authors/Mixture	N_P[a]	Covered ranges		N_C[b]	M[m]	Statistical analysis[n]									
		Temperature T/K	Pressure p/MPa		g·mol^{-1}	N_1 %	N_2 %	AAD$_1$ %	AAD$_2$ %	Bias$_1$ %	Bias$_2$ %	RMS$_1$ %	RMS$_2$ %	MaxD$_1$ %	MaxD$_2$ %
***pρT* data (continued)**						**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA
GERG TM7 [Jaeschke *et al.* (1997)], D-file (synthetic multi-component mixtures)[c,d] (continued)															
D6 (DEH), CH_4–N_2–C_2H_6–C_3H_8	6	283 – 293	3.0 – 7.0	4	17.845	6	6	0.048	0.044	−0.009	−0.012	0.053	0.047	−0.067	−0.056
D7 (DEH), CH_4–N_2–C_2H_6–C_3H_8	6	284 – 294	3.0 – 7.0	4	18.559	6	6	0.045	0.037	0.013	0.006	0.053	0.044	0.091	0.073
D8 (DEH), CH_4–N_2–C_2H_6–C_3H_8	6	284 – 293	3.0 – 7.0	4	19.149	6	6	0.167	0.157	0.167	0.157	0.175	0.167	0.263	0.267
D9 (DEH), CH_4–N_2–C_2H_6–C_3H_8	6	283 – 293	3.0 – 7.0	4	20.838	6	6	0.062	0.042	0.062	0.039	0.069	0.056	0.109	0.114
D10 (DEH), CH_4–N_2–C_2H_6–H_2	7	283 – 293	3.0 – 7.0	4	16.597	7	7	0.033	0.042	0.033	0.042	0.035	0.044	0.052	0.068
D11 (DEH), CH_4–N_2–C_2H_6–C_3H_8	6	283 – 293	3.0 – 7.0	4	21.483	6	6	0.065	0.050	0.053	0.020	0.070	0.062	0.112	0.106
D12 (DEH), CH_4–N_2–C_2H_6–C_3H_8	6	283 – 293	3.0 – 7.0	4	18.454	6	6	0.249	0.240	−0.249	−0.240	0.265	0.254	−0.371	−0.346
D13 (DEH), CH_4–N_2–C_2H_6–C_3H_8	6	283 – 293	3.0 – 7.0	4	19.391	6	6	0.033	0.026	0.013	0.020	0.044	0.040	0.091	0.087
D14 (DEH), CH_4–N_2–CO_2–C_2H_6	22	280 – 308	3.8 – 6.4	4	29.531	22	22	0.163	0.151	−0.163	0.151	0.185	0.181	−0.387	0.373
D15 (DEH), CH_4–N_2–C_2H_6–C_3H_8	18	273 – 293	2.0 – 7.0	4	16.754	18	18	0.023	0.025	−0.023	−0.024	0.027	0.029	−0.058	−0.062
D16 (BUR), CH_4–CO_2–C_2H_6–C_3H_8	49	273 – 313	0.4 – 30.2	5	19.232	49	49	0.053	0.064	0.052	0.062	0.068	0.098	0.182	0.277
D17 (OPT), CH_4–CO_2–C_2H_6–C_3H_8	168	273 – 313	0.4 – 28.2	5	19.232	168	168	0.026	0.073	0.021	0.072	0.032	0.087	0.070	0.164
D18 (OPT), CH_4–N_2–CO_2–C_2H_6	274	270 – 350	0.4 – 28.4	4	22.901	274	274	0.032	0.076	0.005	0.074	0.041	0.118	−0.103	0.471
D19 (OPT), CH_4–N_2–C_2H_6–C_3H_8	284	275 – 350	0.3 – 28.4	10	17.991	284	284	0.061	0.047	−0.057	−0.025	0.073	0.053	−0.172	0.109
D20 (OPT), CH_4–N_2–C_2H_6–C_3H_8	153	290 – 350	0.4 – 27.4	10	17.985	153	153	0.041	0.046	−0.028	−0.004	0.051	0.055	−0.127	0.152
D21 (OPT), CH_4–N_2–CO_2–C_2H_6	225	280 – 330	0.5 – 28.4	5	22.072	225	225	0.022	0.058	−0.002	0.052	0.029	0.082	−0.088	0.205
D22 (OPT), GU1	279	275 – 350	0.5 – 28.0	7	18.648	279	279	0.013	0.025	−0.007	0.011	0.019	0.032	−0.049	0.077
D23 (GDM), GU1	13	300	0.5 – 5.0	7	18.648	13	13	0.007	0.010	−0.004	−0.009	0.009	0.011	−0.018	−0.019
D24 (BUR), GU1	78	250 – 325	0.2 – 10.4	7	18.671	78	78	0.013	0.021	−0.005	−0.001	0.019	0.036	−0.100	0.161
D25 (PYC), GU1	91	225 – 350	3.5 – 60.0	7	18.671	91	91	0.075	0.094	−0.045	−0.053	0.097	0.121	0.277	0.359
D26 (BUR), GU1	65	225 – 350	2.0 – 34.6	7	18.671	65	65	0.023	0.038	−0.021	0.006	0.028	0.048	−0.072	0.134
D27 (BUR), GU1	155	273 – 323	0.2 – 33.9	7	18.648	155	155	0.046	0.037	−0.017	−0.014	0.065	0.049	−0.218	−0.121
D28 (IBU), GU1	64	242 – 273	0.6 – 4.1	7	18.648	64	64	0.019	0.020	0.001	−0.003	0.042	0.041	0.248	0.238
D29 (OPT), GU2	269	275 – 350	0.5 – 27.7	7	19.829	269	269	0.019	0.032	0.015	−0.031	0.026	0.048	0.063	−0.136
D30 (GDM), GU2	13	300	0.5 – 8.0	7	19.829	13	13	0.011	0.029	−0.010	−0.029	0.015	0.034	−0.029	−0.058
D31 (BUR), GU2	85	250 – 325	0.2 – 11.2	7	19.831	85	85	0.018	0.017	0.006	−0.007	0.028	0.024	−0.101	0.072

Table A2.2 (continued)

Authors/Mixture	N_P[a]	Covered ranges		N_C[b]	M[m]	Statistical analysis[n]									
		Temperature T/K	Pressure p/MPa		g·mol^{-1}	N_1 %	N_2 %	AAD$_1$ %	AAD$_2$ %	Bias$_1$ %	Bias$_2$ %	RMS$_1$ %	RMS$_2$ %	MaxD$_1$ %	MaxD$_2$ %
***pρT* data (continued)**						**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA
GERG TM7 [Jaeschke *et al.* (1997)], D-file (synthetic multi-component mixtures)[c,d] (continued)															
D32 (PYC), GU2	89	225 – 350	3.4 – 60.0	7	19.831	89	89	0.089	0.234	−0.061	−0.178	0.109	0.269	−0.313	−0.581
D33 (BUR), GU2	70	225 – 350	1.7 – 33.1	7	19.831	70	70	0.025	0.078	−0.022	−0.067	0.039	0.123	−0.217	−0.617
D34 (BUR), GU2	119	273 – 323	0.3 – 35.9	7	19.829	119	119	0.037	0.045	−0.006	−0.034	0.051	0.067	0.154	−0.280
D35 (BUR), RG2	18	300	0.3 – 22.1	9	18.768	18	18	0.011	0.010	0.004	−0.005	0.012	0.011	−0.026	0.020
D36 (OPT), RG2	275	275 – 350	0.5 – 27.9	9	18.768	275	275	0.023	0.009	−0.006	0.000	0.027	0.011	−0.063	0.030
D37 (GDM), RG2	9	300	0.5 – 6.0	9	18.768	9	9	0.009	0.030	−0.008	−0.030	0.011	0.034	−0.018	−0.048
D38 (BUR), RG2	61	275 – 325	0.2 – 10.2	9	18.770	61	61	0.017	0.031	−0.013	−0.031	0.027	0.040	−0.096	−0.112
D39 (PYC), RG2	87	225 – 350	2.8 – 59.6	9	18.770	87	87	0.217	0.177	−0.206	−0.154	0.484	0.351	−2.627	−2.568
D40 (BUR), RG2	65	225 – 350	1.9 – 33.0	9	18.770	65	65	0.065	0.065	−0.060	−0.065	0.101	0.090	−0.495	−0.439
D41 (OPT), NIST1	280	275 – 350	0.5 – 27.6	10	16.799	280	280	0.026	0.012	0.026	0.002	0.030	0.015	0.078	0.036
D42 (GDM), NIST1	15	300	0.5 – 8.0	10	16.799	15	15	0.006	0.015	0.006	−0.015	0.007	0.017	0.011	−0.029
D43 (BUR), NIST1	77	250 – 325	0.2 – 10.3	10	16.781	77	77	0.013	0.015	0.004	−0.015	0.018	0.021	−0.045	−0.078
D44 (PYC), NIST1	82	225 – 350	3.5 – 56.8	10	16.781	82	82	0.107	0.148	−0.101	−0.129	0.153	0.190	−0.951	−0.987
D45 (BUR), NIST1	66	225 – 350	2.0 – 34.3	10	16.781	66	66	0.022	0.026	0.006	−0.014	0.032	0.039	−0.171	0.207
D46 (IBU), NIST1	64	243 – 273	0.5 – 4.1	10	16.799	64	64	0.036	0.018	0.034	0.003	0.050	0.029	0.136	−0.088
D47 (OPT), NIST2	278	275 – 350	0.5 – 28.0	10	17.595	278	278	0.016	0.025	0.013	0.023	0.020	0.032	0.052	0.071
D48 (GDM), NIST2	11	300	0.5 – 3.8	10	17.595	11	11	0.007	0.019	−0.007	−0.019	0.008	0.020	−0.014	−0.032
D49 (BUR), NIST2	78	250 – 325	0.2 – 9.6	10	17.598	78	78	0.021	0.014	0.016	0.003	0.027	0.023	0.069	0.085
D50 (PYC), NIST2	66	225 – 350	3.4 – 58.7	10	17.598	66	66	0.146	0.156	−0.123	−0.124	0.166	0.172	0.438	0.407
D51 (BUR), NIST2	67	225 – 350	1.9 – 34.5	10	17.598	67	67	0.028	0.047	−0.005	0.028	0.051	0.090	−0.313	0.495
D52 (BUR), NIST2	135	273 – 323	0.1 – 39.0	10	17.595	135	135	0.077	0.073	−0.046	−0.050	0.114	0.106	−0.441	−0.449
D53 (IBU), NIST2	40	243 – 273	1.1 – 4.1	10	17.595	40	40	0.051	0.028	0.050	0.024	0.060	0.040	0.137	0.104
D54 (BUR)	33	298 – 323	0.1 – 15.0	6	18.181	33	33	0.023	0.015	−0.013	−0.010	0.033	0.018	−0.091	−0.039
D55 (BUR)	35	290 – 323	0.1 – 16.1	4	20.244	35	35	0.088	0.081	−0.082	−0.078	0.130	0.114	−0.328	−0.350
D56 (BUR), CH_4–N_2–C_2H_6–C_3H_8	133	255 – 315	0.1 – 54.5	4	17.636	133	133	0.092	0.097	−0.009	−0.004	0.128	0.132	−0.657	−0.651
D57 (BUR), CH_4–N_2–C_2H_6–C_3H_8	47	340	0.2 – 52.3	4	17.707	47	47	0.010	0.018	−0.001	−0.005	0.012	0.022	0.029	0.059

Table A2.2 (continued)

Authors/Mixture	N_{P}[a]	Covered ranges		N_{C}[b]	M[m]	Statistical analysis[n]									
		Temperature T/K	Pressure p/MPa		g·mol^{-1}	N_1 %	N_2 %	AAD$_1$ %	AAD$_2$ %	Bias$_1$ %	Bias$_2$ %	RMS$_1$ %	RMS$_2$ %	MaxD$_1$ %	MaxD$_2$ %
***pρT* data (continued)**						**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA
GERG TM7 [Jaeschke *et al.* (1997)], D-file (synthetic multi-component mixtures)[c,d] (continued)															
D58 (DEH)	13	300	1.1 – 5.3	10	16.864	13	13	0.012	0.041	−0.012	−0.041	0.015	0.042	−0.028	−0.054
D59 (DEH)	32	289 – 300	1.1 – 6.3	11	17.558	32	32	0.028	0.018	0.027	0.014	0.033	0.024	0.082	0.073
GERG TM7 [Jaeschke *et al.* (1997)], N-file (natural gases and other multi-component mixtures)[c]															
N1[e] (DEH)	18	273 – 293	2.0 – 7.0	15	19.323	18	18	0.058	0.089	−0.027	−0.076	0.067	0.095	0.136	−0.153
N2 (DEH)	18	273 – 293	2.0 – 7.0	12	16.837	18	18	0.024	0.030	−0.004	−0.012	0.029	0.035	0.077	0.082
N3 (DEH)	18	273 – 293	2.0 – 7.0	12	18.672	18	18	0.050	0.072	−0.049	−0.072	0.057	0.079	−0.085	−0.114
N4 (DEH)	18	273 – 293	2.0 – 7.0	12	19.081	18	18	0.044	0.050	0.032	−0.015	0.065	0.058	0.188	0.130
N5[e] (DEH)	24	273 – 303	2.0 – 7.0	17	18.225	24	24	0.033	0.053	−0.013	−0.046	0.040	0.061	−0.088	−0.109
N6[e] (DEH)	24	273 – 303	2.0 – 7.0	17	18.503	24	24	0.019	0.022	0.011	−0.016	0.023	0.028	0.054	−0.064
N7[e] (DEH)	24	273 – 303	2.0 – 7.0	16	17.309	24	24	0.039	0.065	−0.035	−0.064	0.045	0.070	−0.089	−0.111
N8[e] (DEH)	23	273 – 303	2.0 – 7.0	17	18.029	23	23	0.044	0.049	−0.025	−0.037	0.053	0.059	−0.100	−0.123
N9 (BUR)	67	273 – 293	0.1 – 8.6	12	16.841	67	67	0.031	0.029	0.019	0.014	0.042	0.041	0.125	0.148
N10 (BUR)	68	273 – 293	0.2 – 8.7	12	19.298	68	68	0.021	0.022	0.018	−0.013	0.028	0.028	0.094	0.087
N11 (BUR)	69	273 – 293	0.1 – 8.6	12	18.669	69	69	0.019	0.018	0.013	−0.003	0.024	0.022	−0.059	0.073
N12 (BUR)	69	273 – 293	0.2 – 8.6	12	19.081	69	69	0.032	0.022	0.031	0.002	0.043	0.028	0.112	0.086
N13 (OPT)	74	273 – 293	0.1 – 7.7	12	16.841	74	74	0.022	0.020	0.020	0.013	0.030	0.028	0.066	0.076
N14 (OPT)	74	273 – 293	0.1 – 7.7	12	19.298	74	74	0.072	0.036	0.072	0.035	0.083	0.048	0.148	0.125
N15 (OPT)	73	273 – 293	0.1 – 7.7	12	18.669	73	73	0.052	0.056	0.038	0.020	0.080	0.072	0.166	0.140
N16 (OPT)	74	273 – 293	0.1 – 7.7	12	19.081	74	74	0.053	0.030	0.050	0.015	0.061	0.042	0.167	0.147
N17 (OPT)	76	273 – 293	0.1 – 7.8	12	16.833	76	76	0.045	0.042	0.032	0.026	0.058	0.055	−0.136	−0.139
N18 (OPT)	68	273 – 293	0.1 – 7.9	12	19.308	68	68	0.041	0.036	0.030	−0.010	0.054	0.049	0.154	0.140
N19 (OPT)	73	273 – 293	0.1 – 7.7	12	18.665	73	73	0.040	0.047	−0.009	−0.026	0.053	0.059	−0.152	−0.159
N20 (OPT)	77	273 – 293	0.1 – 7.9	12	19.087	77	77	0.043	0.034	0.042	0.008	0.059	0.052	0.258	0.252
N21 (BUR)	12	274 – 291	0.4 – 7.0	13	17.446	12	12	0.124	0.140	−0.124	−0.140	0.163	0.177	−0.360	−0.368
N22 (BUR)	15	273 – 294	0.2 – 10.2	14	17.248	15	15	0.078	0.081	−0.078	−0.081	0.120	0.111	−0.337	−0.262
N23 (DEH)	18	279 – 298	2.0 – 7.0	12	18.661	18	18	0.068	0.058	−0.050	−0.043	0.074	0.063	−0.129	−0.103

Table A2.2 (continued)

Authors/Mixture	N_P[a]	Covered ranges		N_C[b]	M[m]	Statistical analysis[n]									
		Temperature T/K	Pressure p/MPa		g·mol^{-1}	N_1 %	N_2 %	AAD$_1$ %	AAD$_2$ %	Bias$_1$ %	Bias$_2$ %	RMS$_1$ %	RMS$_2$ %	MaxD$_1$ %	MaxD$_2$ %
***pρT* data (continued)**						**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA
GERG TM7 [Jaeschke *et al.* (1997)], N-file (natural gases and other multi-component mixtures)[c] (continued)															
N24 (DEH)	12	278 – 298	2.0 – 7.0	11	17.624	12	12	0.060	0.062	−0.038	−0.047	0.065	0.070	−0.095	−0.100
N25 (DEH)	10	288 – 293	1.0 – 4.5	12	19.422	10	10	0.058	0.045	0.054	0.012	0.083	0.072	0.223	0.198
N26 (DEH)	5	284	1.0 – 4.5	12	19.435	5	5	0.101	0.110	0.055	0.009	0.136	0.136	0.273	0.247
N27 (DEH)	5	279	1.0 – 4.5	12	19.443	5	5	0.119	0.123	0.060	0.013	0.153	0.152	0.282	0.254
N28 (DEH)	64	280 – 300	3.7 – 6.4	12	18.298	64	64	0.026	0.032	0.014	−0.023	0.034	0.037	0.078	−0.072
N29 (DEH)	53	281 – 300	3.7 – 6.4	13	20.282	53	53	0.022	0.022	−0.015	−0.011	0.028	0.027	−0.060	−0.055
N30 (DEH)	52	281 – 300	3.7 – 6.4	13	18.169	52	52	0.020	0.033	−0.012	−0.032	0.025	0.039	−0.058	−0.079
N31 (DEH)	53	280 – 300	3.7 – 6.4	12	17.431	53	53	0.037	0.050	−0.037	−0.050	0.041	0.053	−0.077	−0.092
N32 (DEH)	54	280 – 300	3.7 – 6.5	13	17.865	54	54	0.024	0.034	−0.018	−0.031	0.030	0.039	−0.062	−0.077
N33 (DEH)	64	279 – 300	3.7 – 6.5	13	24.135	64	64	0.034	0.020	0.027	−0.001	0.039	0.028	0.077	−0.083
N34 (DEH)	52	280 – 300	3.7 – 6.4	13	20.476	52	52	0.040	0.032	0.030	−0.009	0.050	0.039	0.098	−0.090
N35 (DEH)	55	281 – 300	3.8 – 6.4	13	25.056	55	55	0.080	0.064	0.080	0.064	0.089	0.075	0.152	0.137
N36 (DEH)	55	281 – 300	3.8 – 6.4	13	18.407	55	55	0.020	0.029	−0.003	−0.025	0.023	0.033	0.048	−0.056
N37 (DEH)	64	280 – 300	3.7 – 6.5	11	19.490	64	64	0.044	0.065	0.007	−0.057	0.054	0.077	−0.135	−0.209
N38 (DEH)	65	280 – 300	3.7 – 6.6	12	18.807	65	65	0.069	0.062	−0.068	−0.062	0.078	0.071	−0.161	−0.138
N39 (DEH)	55	280 – 300	3.7 – 6.4	13	18.371	55	55	0.047	0.022	0.047	0.016	0.054	0.030	0.103	0.072
N40 (DEH)	54	281 – 300	3.7 – 6.5	13	19.015	54	54	0.060	0.061	−0.059	−0.060	0.065	0.064	−0.103	−0.097
N41 (DEH)	16	279 – 294	3.8 – 5.5	13	18.625	16	16	0.077	0.074	−0.077	−0.074	0.079	0.075	−0.111	−0.098
N42 (DEH)	44	280 – 300	3.8 – 6.5	13	18.637	44	44	0.085	0.079	−0.084	−0.078	0.103	0.095	−0.205	−0.181
N43 (DEH)	66	280 – 300	3.7 – 6.5	13	18.388	66	66	0.045	0.030	0.044	0.026	0.051	0.037	0.101	0.088
N44 (DEH)	66	280 – 300	3.8 – 6.5	13	17.402	66	66	0.036	0.041	−0.027	−0.038	0.054	0.060	−0.149	−0.152
N45 (DEH)	66	280 – 300	3.7 – 6.4	13	17.662	66	66	0.048	0.040	0.033	0.020	0.051	0.044	0.100	0.093
N46 (DEH)	65	280 – 300	3.7 – 6.5	12	19.065	65	65	0.094	0.080	−0.093	−0.080	0.107	0.094	−0.198	−0.189
N47 (DEH)	65	280 – 300	3.7 – 6.4	12	19.635	65	65	0.083	0.074	−0.083	−0.074	0.091	0.081	−0.143	−0.125
N48 (DEH)	65	280 – 300	3.7 – 6.5	12	22.617	65	65	0.055	0.060	−0.038	−0.052	0.066	0.074	−0.120	−0.133
N49 (DEH)	33	280 – 286	3.8 – 6.4	13	18.492	33	33	0.114	0.068	0.114	0.068	0.115	0.070	0.138	0.095

Table A2.2 (continued)

Authors/Mixture	N_P[a]	Covered ranges		N_C[b]	M[m]	Statistical analysis[n]									
		Temperature T/K	Pressure p/MPa		g·mol^{-1}	N_1 %	N_2 %	AAD$_1$ %	AAD$_2$ %	Bias$_1$ %	Bias$_2$ %	RMS$_1$ %	RMS$_2$ %	MaxD$_1$ %	MaxD$_2$ %
***pρT* data (continued)**						**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA
GERG TM7 [Jaeschke *et al.* (1997)], N-file (natural gases and other multi-component mixtures)[c] (continued)															
N50 (DEH)	22	280 – 283	3.7 – 6.4	13	18.619	22	22	0.070	0.061	−0.070	−0.061	0.071	0.062	−0.085	−0.077
N51 (BUR)	31	273 – 313	0.6 – 30.1	12	19.081	31	31	0.083	0.064	0.083	0.064	0.101	0.093	0.218	0.249
N52 (OPT)	54	313	0.3 – 27.0	12	19.081	54	54	0.064	0.079	0.064	0.079	0.066	0.089	0.087	0.130
N53 (BUR)	47	273 – 353	0.4 – 30.2	12	19.087	47	47	0.042	0.033	0.042	0.025	0.057	0.054	0.160	0.176
N54 (OPT)	113	273 – 353	0.3 – 28.1	12	19.087	113	113	0.037	0.038	0.036	0.032	0.046	0.050	0.114	0.108
N55 (BUR)	98	275 – 330	0.3 – 27.3	13	19.104	98	98	0.035	0.023	0.035	0.017	0.044	0.038	0.116	0.122
N56 (OPT)	175	270 – 330	0.4 – 29.6	13	19.104	175	175	0.054	0.058	0.053	0.056	0.062	0.068	0.131	0.118
N57 (BUR)	30	290	0.4 – 25.1	13	16.819	30	30	0.010	0.011	0.010	0.010	0.014	0.017	0.031	0.049
N58 (OPT)	116	280 – 290	0.5 – 29.0	13	16.819	116	116	0.028	0.031	0.028	0.031	0.031	0.034	0.062	0.057
N59 (BUR)	34	310	0.3 – 26.0	13	18.627	34	34	0.025	0.033	0.023	0.029	0.030	0.048	0.051	0.111
N60 (OPT)	342	270 – 350	0.4 – 29.4	13	18.627	342	342	0.044	0.083	0.044	0.082	0.047	0.102	0.103	0.223
N61 (BUR)	36	310	0.2 – 26.0	13	16.323	36	36	0.010	0.005	0.009	0.002	0.012	0.006	0.024	0.013
N62 (OPT)	311	270 – 350	0.4 – 28.8	13	16.323	311	311	0.024	0.012	0.024	0.010	0.027	0.014	0.065	0.031
N63 (BUR)	62	310 – 330	0.3 – 26.8	12	18.080	62	62	0.012	0.022	−0.009	−0.021	0.018	0.031	0.093	−0.100
N64 (OPT)	336	270 – 350	0.5 – 28.0	12	18.080	336	336	0.020	0.049	−0.016	−0.048	0.026	0.062	−0.147	−0.254
N65[e] (BUR)	60	275 – 280	0.4 – 26.8	15	19.049	60	60	0.042	0.022	0.042	0.016	0.048	0.036	0.093	0.111
N66[e] (OPT)	333	270 – 350	0.3 – 28.1	15	19.049	333	333	0.035	0.032	0.016	0.025	0.041	0.042	−0.090	0.100
N67[e] (BUR)	68	273 – 303	0.4 – 9.2	17	18.503	68	68	0.046	0.032	0.046	0.027	0.054	0.045	0.098	0.146
N68[e] (BUR)	69	273 – 303	0.4 – 9.2	17	18.225	69	69	0.020	0.011	0.019	−0.003	0.024	0.015	0.064	0.066
N69[e] (BUR)	70	273 – 303	0.4 – 9.2	16	17.309	70	70	0.010	0.020	0.001	−0.019	0.012	0.023	−0.041	−0.045
N70[e] (BUR)	68	273 – 303	0.4 – 9.2	17	18.498	68	68	0.046	0.031	0.046	0.028	0.059	0.052	0.144	0.195
N71[e] (BUR)	70	273 – 303	0.3 – 9.2	17	18.227	70	70	0.016	0.014	0.012	−0.011	0.020	0.017	0.049	−0.049
N72[e] (BUR)	67	273 – 303	0.4 – 9.2	16	17.300	67	67	0.013	0.021	0.004	−0.017	0.016	0.025	0.047	−0.054
N73[e] (BUR)	31	310	0.5 – 26.1	16	17.300	31	31	0.012	0.008	0.009	0.005	0.013	0.012	0.021	0.028
N74[e] (OPT)	341	270 – 350	0.4 – 28.5	16	17.300	341	341	0.023	0.032	0.010	0.024	0.029	0.045	0.077	0.132
N75 (OPT)	331	270 – 350	0.4 – 28.3	12	18.793	331	331	0.040	0.026	−0.031	−0.012	0.057	0.032	−0.175	−0.086

Table A2.2 (continued)

Authors/Mixture	N_P[a]	Covered ranges Temperature T/K	 Pressure p/MPa	N_C[b]	M[m] g·mol^{-1}	Statistical analysis[n] N_1 %	 N_2 %	 AAD$_1$ %	 AAD$_2$ %	 Bias$_1$ %	 Bias$_2$ %	 RMS$_1$ %	 RMS$_2$ %	 MaxD$_1$ %	 MaxD$_2$ %
***pρT* data (continued)**						**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA
GERG TM7 [Jaeschke *et al.* (1997)], N-file (natural gases and other multi-component mixtures)[c] (continued)															
N76[e] (DMA)	135	273 – 323	0.1 – 8.0	16	19.318	135	135	0.022	0.023	0.020	−0.020	0.026	0.027	0.073	−0.076
N77 (DEH)	11	296 – 297	3.7 – 7.2	13	18.646	11	11	0.059	0.057	−0.004	0.003	0.070	0.065	−0.109	0.101
N78 (DEH)	19	295 – 297	3.6 – 6.5	14	18.415	19	19	0.082	0.054	0.082	0.053	0.088	0.061	0.131	0.101
N79[e,f] (DEH)	21	296 – 297	3.0 – 5.4	18	19.516	21	21	0.036	0.069	−0.024	−0.069	0.051	0.082	−0.121	−0.166
N80 (DEH)	44	280 – 294	3.7 – 6.4	13	25.056	44	44	0.083	0.067	0.083	0.066	0.099	0.084	0.188	0.158
N81 (DEH)	42	280 – 294	3.8 – 6.4	13	20.480	42	42	0.058	0.031	0.058	0.020	0.069	0.041	0.141	0.100
N82 (BUR)	57	310 – 330	0.6 – 26.2	12	18.716	57	57	0.012	0.013	0.009	0.010	0.014	0.022	−0.026	0.061
N83 (OPT)	353	270 – 350	0.3 – 28.8	12	18.716	353	353	0.022	0.034	−0.004	0.032	0.030	0.043	−0.089	0.108
N84 (DEH)	37	283 – 313	1.0 – 8.0	12	12.501	37	37	0.058	0.061	−0.058	−0.061	0.068	0.067	−0.143	−0.140
N85 (DEH)	48	280 – 298	2.9 – 7.4	10	18.788	48	48	0.045	0.036	0.042	−0.013	0.058	0.043	0.143	−0.123
N86 (EXP)	10	303	1.0 – 15.0	8	18.754	10	10	0.079	0.089	−0.079	−0.089	0.085	0.092	−0.134	−0.131
N87 (DEH)	7	289	4.9 – 5.3	8	16.864	7	7	0.036	0.023	0.036	−0.021	0.042	0.030	0.068	−0.052
N88 (DEH)	40	283 – 313	1.0 – 6.0	11	16.935	40	40	0.047	0.057	−0.045	−0.055	0.050	0.060	−0.076	−0.089
N89 (DEH)	42	284 – 313	1.5 – 6.5	11	17.660	42	42	0.022	0.018	−0.021	−0.017	0.024	0.022	−0.047	−0.050
N90 (DEH)	35	284 – 313	1.5 – 5.5	11	17.159	35	35	0.043	0.056	−0.043	−0.056	0.047	0.060	−0.087	−0.102
N91 (DEH)	32	283 – 313	1.0 – 5.1	11	18.429	32	32	0.041	0.069	−0.035	−0.066	0.047	0.075	−0.083	−0.122
N92 (DEH)	26	283 – 313	1.0 – 4.0	11	16.718	26	26	0.025	0.026	−0.017	−0.021	0.029	0.031	−0.050	−0.053
N93 (DEH)	8	303	1.0 – 5.2	6	16.956	8	8	0.041	0.037	0.041	0.037	0.043	0.038	0.057	0.053
N94 (DEH)	26	286	3.0 – 7.8	10	18.788	26	26	0.015	0.043	0.014	−0.043	0.017	0.045	0.035	−0.067
N95 (DEH)	44	280 – 298	2.9 – 7.2	10	18.863	44	44	0.040	0.028	0.033	0.015	0.053	0.037	0.148	0.115
N96 (DEH)	48	280 – 298	2.8 – 7.7	10	19.054	48	48	0.063	0.052	−0.063	−0.052	0.066	0.054	−0.118	−0.089
N97[e,f] (BUR)	33	310	0.4 – 25.7	16	22.954	33	33	0.016	0.030	−0.001	0.005	0.024	0.041	0.094	0.102
N98[e,f] (OPT)	306	270 – 350	0.5 – 28.4	16	22.954	306	306	0.055	0.067	−0.005	0.045	0.087	0.093	−0.394	0.279
N99[e,f] (BUR)	15	290	0.6 – 26.9	16	21.363	15	15	0.018	0.013	−0.015	−0.009	0.027	0.015	−0.069	−0.025
N100[e,f] (OPT)	285	270 – 350	0.4 – 28.0	16	21.363	285	285	0.042	0.026	−0.041	−0.022	0.057	0.030	−0.151	−0.058
N101[e,f] (OPT)	338	270 – 350	0.5 – 28.5	16	22.678	338	338	0.019	0.024	−0.016	−0.021	0.025	0.029	−0.076	−0.058

Table A2.2 (continued)

Authors/Mixture	N_P[a]	Covered ranges		N_C[b]	M[m]	Statistical analysis[n]									
		Temperature T/K	Pressure p/MPa		g·mol^{-1}	N_1 %	N_2 %	AAD$_1$ %	AAD$_2$ %	Bias$_1$ %	Bias$_2$ %	RMS$_1$ %	RMS$_2$ %	MaxD$_1$ %	MaxD$_2$ %
***pρT* data (continued)**						**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA
GERG TM7 [Jaeschke *et al.* (1997)], N-file (natural gases and other multi-component mixtures)[c] (continued)															
N102[e,f] (BUR)	33	290	0.4 – 26.1	16	19.405	33	33	0.023	0.041	0.023	0.034	0.025	0.071	0.042	0.211
N103[e,f] (OPT)	336	270 – 350	0.5 – 28.6	16	19.405	336	336	0.056	0.100	0.032	0.093	0.068	0.120	−0.238	0.266
N104 (OPT)	223	270 – 350	0.5 – 28.0	14	20.061	223	223	0.084	0.039	−0.083	−0.022	0.105	0.048	−0.256	0.149
N105[e,f] (BUR)	33	330	0.4 – 26.3	15	24.749	33	33	0.060	0.055	0.057	0.049	0.082	0.081	0.184	0.194
N106[e,f] (OPT)	220	270 – 350	0.5 – 28.6	15	24.749	220	220	0.114	0.118	0.114	0.117	0.130	0.157	0.219	0.471
N107[e,f] (OPT)	460	265 – 350	0.5 – 29.3	15	18.639	460	460	0.030	0.017	−0.028	−0.004	0.035	0.021	−0.077	0.063
N108[e] (OPT)	187	270 – 350	0.5 – 20.0	15	19.319	187	187	0.023	0.055	0.020	0.054	0.026	0.077	0.057	0.201
N109[e,f] (OPT)	322	265 – 350	0.5 – 30.0	16	20.961	322	322	0.056	0.036	0.052	−0.003	0.064	0.052	0.105	−0.197
N110 (OPT)	360	270 – 350	0.5 – 30.0	15	15.743	360	360	0.066	0.060	0.063	−0.052	0.084	0.078	0.153	−0.212
N111[e] (OPT)	90	270 – 350	0.4 – 4.9	15	22.028	90	90	0.043	0.012	0.043	−0.011	0.048	0.015	0.097	−0.035
N112[e,f] (OPT)	100	270 – 350	0.4 – 6.8	15	19.674	100	100	0.047	0.067	−0.046	−0.067	0.067	0.088	−0.196	−0.255
N113[e,f] (OPT)	173	270 – 350	0.4 – 14.0	15	19.706	173	173	0.015	0.030	−0.002	−0.030	0.019	0.036	−0.063	−0.085
N114[e,f] (OPT)	125	270 – 350	0.4 – 8.5	15	20.569	125	125	0.042	0.010	0.041	−0.005	0.048	0.014	0.090	−0.054
N115 (OPT)	342	270 – 350	0.5 – 28.4	12	18.779	342	342	0.018	0.097	0.003	−0.097	0.022	0.106	−0.066	−0.187
N116 (OPT)	345	270 – 350	0.5 – 28.5	12	17.941	345	345	0.020	0.259	0.012	−0.258	0.029	0.313	0.076	−0.675
Natural gases and other multi-component mixtures															
Assael *et al.* (2001b)	40	241 – 455	0.2 – 14.0	5	18.216	40	40	0.045	0.033	0.001	0.004	0.079	0.071	−0.322	−0.291
Capla *et al.* (2002), M1	28	253 – 323	1.0 – 15.0	11	16.313	28	28	0.024	0.011	0.023	0.010	0.029	0.013	0.062	0.021
Capla *et al.* (2002), M2	28	253 – 323	1.0 – 15.0	14	17.841	28	28	0.092	0.016	−0.053	0.001	0.141	0.016	−0.433	−0.023
Capla *et al.* (2002), M3	28	253 – 323	1.0 – 15.0	10	17.085	28	28	0.020	0.017	0.009	0.017	0.028	0.025	0.087	0.095
Duschek *et al.* (1989)[e,f]	135	273 – 323	0.1 – 8.0	17	19.319	135	135	0.023	0.022	0.021	−0.019	0.026	0.026	0.065	−0.070
Robinson & Jacoby (1965), M1[g]	6	344	1.7 – 10.4	6	26.236	–	6		0.137		−0.137		0.137		−0.148
Robinson & Jacoby (1965), M2	5	311	2.4 – 10.7	5	16.404	5	5	0.030	0.024	0.030	0.024	0.034	0.028	0.044	0.038
Robinson & Jacoby (1965), M3	5	311	2.4 – 10.3	5	17.876	5	5	0.019	0.016	0.007	−0.016	0.021	0.018	0.031	−0.032
Robinson & Jacoby (1965), M4	6	311	1.8 – 11.1	5	19.569	6	6	0.050	0.027	0.021	−0.009	0.058	0.042	−0.088	−0.098
Robinson & Jacoby (1965), M5	6	311	1.7 – 10.8	5	21.830	6	6	0.021	0.020	0.019	−0.007	0.024	0.025	0.037	−0.048

Table A2.2 (continued)

Authors/Mixture	N_P[a]	Covered ranges		N_C[b]	M[m]	Statistical analysis[n]									
		Temperature T/K	Pressure p/MPa		g·mol^{-1}	N_1 %	N_2 %	AAD$_1$ %	AAD$_2$ %	Bias$_1$ %	Bias$_2$ %	RMS$_1$ %	RMS$_2$ %	MaxD$_1$ %	MaxD$_2$ %
***pρT* data (continued)**						**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA
Natural gases and other multi-component mixtures (continued)															
Robinson & Jacoby (1965), M6	8	311	1.1 – 11.7	4	31.400	8	8	0.307	0.437	0.307	0.437	0.395	0.596	0.845	1.326
Robinson & Jacoby (1965), M7	6	339	1.7 – 11.2	5	22.594	6	6	0.095	0.081	0.095	0.081	0.098	0.082	0.129	0.098
Robinson & Jacoby (1965), M8	6	366	1.6 – 10.8	5	24.173	6	6	0.142	0.155	0.142	0.155	0.153	0.168	0.236	0.260
Robinson & Jacoby (1965), M9[g]	6	311	1.6 – 10.1	6	17.875	–	6		0.061		0.021		0.070		−0.119
Robinson & Jacoby (1965), M10[g]	6	311	1.8 – 10.7	6	19.827	–	6		0.093		0.007		0.109		−0.209
Robinson & Jacoby (1965), M11[g]	7	311	1.4 – 11.1	6	21.856	–	7		0.279		0.279		0.376		0.822
Robinson & Jacoby (1965), M12[g]	6	339	1.8 – 11.1	6	20.210	–	6		0.076		0.076		0.095		0.162
Robinson & Jacoby (1965), M13[g]	6	366	1.7 – 11.2	6	20.442	–	6		0.041		0.041		0.042		0.061
Robinson & Jacoby (1965), M14[g]	6	311	1.7 – 10.7	6	19.748	–	6		0.233		0.233		0.261		0.431
Robinson & Jacoby (1965), M15[g]	7	311	1.3 – 11.3	6	23.314	–	7		0.292		0.292		0.346		0.690
Five-component synthetic natural gas mixture															
Ruhrgas (1999), Bu	18	310	0.3 – 28.8	5	19.338	18	18	0.013	0.003	0.008	0.001	0.014	0.004	−0.027	0.011
Ruhrgas (1999), Op	172	270 – 310	0.5 – 28.5	5	19.338	172	172	0.021	0.021	−0.005	0.020	0.026	0.032	−0.060	0.090
RG-GDMA natural gas mixtures[r]															
Guo *et al.* (1990a), M1	8	300	0.5 – 3.8	8	17.595	8	8	0.008	0.007	0.008	−0.003	0.009	0.009	0.017	−0.015
Guo *et al.* (1990a), M2	40	273 – 293	0.1 – 12.0	14	18.819	40	40	0.033	0.051	−0.033	−0.051	0.035	0.052	−0.068	−0.068
Guo *et al.* (1990a), M3	14	300	0.5 – 8.0	6	19.829	14	14	0.013	0.026	−0.012	−0.026	0.017	0.031	−0.033	−0.054
Guo *et al.* (1990a), M4	15	300	0.5 – 8.0	8	16.799	15	15	0.005	0.012	0.005	−0.012	0.006	0.014	0.009	−0.023
Guo *et al.* (1990a), M5[e,f]	57	273 – 293	0.1 – 12.0	15	18.676	57	57	0.086	0.076	−0.086	−0.076	0.090	0.077	−0.166	−0.097
Guo *et al.* (1990b), M1	10	300	0.5 – 5.0	6	18.648	10	10	0.006	0.009	−0.005	−0.009	0.008	0.009	−0.018	−0.015
Guo *et al.* (1990b), M2	9	300	0.5 – 6.0	7	18.768	9	9	0.011	0.024	−0.010	−0.024	0.014	0.026	−0.023	−0.039
Guo *et al.* (1993), M1[e]	8	283	2.7 – 9.6	16	16.586	8	8	0.026	0.018	0.026	0.018	0.031	0.019	0.047	0.028
Guo *et al.* (1993), M2[e,f]	8	283	2.3 – 7.8	17	19.550	8	8	0.085	0.056	0.085	0.056	0.085	0.057	0.094	0.070
Guo *et al.* (1993), M3[e,f]	17	273 – 293	2.3 – 10.4	18	18.503	17	17	0.089	0.102	0.089	0.102	0.090	0.104	0.098	0.150
Guo *et al.* (1993), M4[e]	16	273 – 293	2.2 – 8.2	16	18.910	16	16	0.010	0.035	−0.007	−0.035	0.014	0.037	−0.037	−0.054

Table A2.2 (continued)

Authors/Mixture	N_P[a]	Covered ranges Temperature T/K	 Pressure p/MPa	N_C[b]	M[m] g·mol^{-1}	Statistical analysis[n] N_1 %	 N_2 %	 AAD$_1$ %	 AAD$_2$ %	 Bias$_1$ %	 Bias$_2$ %	 RMS$_1$ %	 RMS$_2$ %	 MaxD$_1$ %	 MaxD$_2$ %
***pρT* data (continued)**						**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA
RG-GDMA natural gas mixtures[r] (continued)															
Guo *et al.* (1993), M5[e]	17	273 – 293	2.3 – 10.0	15	18.217	17	17	0.199	0.184	0.199	0.184	0.200	0.188	0.243	0.254
Guo *et al.* (1993), M6	8	283	2.7 – 9.5	14	16.294	8	8	0.017	0.010	0.017	0.010	0.017	0.010	0.019	0.015
Kleinrahm *et al.* (1996), M1[e]	31	273 – 293	0.6 – 8.2	15	19.001	31	31	0.052	0.024	0.052	0.024	0.052	0.028	0.072	0.057
Kleinrahm *et al.* (1996), M2[e,f]	14	283	2.4 – 8.6	16	18.379	14	14	0.095	0.100	0.095	0.100	0.095	0.101	0.097	0.129
Rich natural gases															
Jaeschke & Schley (1998), RNG1	268	280 – 350	0.2 – 28.5	6	26.171	268	268	0.122	0.395	0.113	−0.395	0.148	0.511	0.324	−0.990
Jaeschke & Schley (1998), RNG2	327	280 – 350	0.2 – 30.0	6	25.336	327	327	0.082	0.124	0.063	−0.037	0.099	0.160	0.174	−0.484
Jaeschke & Schley (1998), RNG3	247	280 – 350	0.2 – 28.0	8	24.903	247	247	0.038	0.112	0.007	0.028	0.050	0.139	0.137	0.355
Jaeschke & Schley (1998), RNG4	249	280 – 350	0.2 – 28.0	8	25.318	249	249	0.047	0.187	−0.002	−0.187	0.074	0.241	−0.275	−0.576
Jaeschke & Schley (1998), RNG5	256	280 – 350	0.2 – 28.0	8	24.828	256	256	0.063	0.274	0.053	−0.274	0.080	0.332	0.159	−0.659
Jaeschke & Schley (1998), RNG6	251	280 – 350	0.2 – 28.0	8	26.498	251	251	0.181	0.346	0.171	−0.346	0.215	0.406	0.356	−0.795
Jaeschke & Schley (1998), RNG7	250	280 – 350	0.2 – 28.0	8	28.170	250	250	0.260	0.416	0.249	−0.416	0.313	0.486	0.481	−0.977
Watson & Millington (1998), RNG1	39	318 – 353	10.0 – 17.7	6	26.171	39	39	0.155	0.481	0.155	−0.481	0.157	0.528	0.217	−0.910
Watson & Millington (1998), RNG2	48	315 – 353	7.9 – 17.8	6	25.328	48	48	0.094	0.149	0.094	0.148	0.098	0.164	0.139	0.223
Watson & Millington (1998), RNG3	48	313 – 348	7.8 – 17.8	8	24.900	48	48	0.024	0.200	0.014	0.196	0.028	0.228	0.065	0.388
Watson & Millington (1998), RNG4	48	313 – 348	7.9 – 17.7	8	25.317	48	48	0.056	0.055	0.051	−0.021	0.063	0.068	0.147	−0.211
Watson & Millington (1998), RNG5	48	313 – 348	7.9 – 17.6	8	24.818	48	48	0.086	0.243	0.086	−0.243	0.090	0.259	0.125	−0.442
Watson & Millington (1998), RNG6	48	313 – 348	7.8 – 17.8	8	26.498	48	48	0.211	0.341	0.211	−0.341	0.219	0.356	0.309	−0.584
Watson & Millington (1998), RNG7-A	48	313 – 348	7.8 – 17.7	8	28.176	48	48	0.263	0.463	0.263	−0.463	0.285	0.475	0.438	−0.723
Watson & Millington (1998), RNG7-B	48	313 – 348	7.9 – 18.0	8	28.167	48	48	0.326	0.404	0.326	−0.404	0.348	0.420	0.482	−0.689
Speed of sound						**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA
Natural gases and other multi-component mixtures															
Blanke & Weiß (1986), M1	24	273 – 303	0.001 – 6.0	12	17.928	24	24	0.194	0.180	−0.194	−0.180	0.203	0.187	−0.290	−0.262
Blanke & Weiß (1986), M2	24	273 – 303	0.001 – 6.0	12	18.041	24	24	0.152	0.137	−0.152	−0.137	0.174	0.157	−0.383	−0.354
Blanke & Weiß (1986), M3	24	273 – 303	0.001 – 6.0	11	18.072	24	24	0.503	0.488	−0.503	−0.488	0.509	0.493	−0.708	−0.684

Table A2.2 (continued)

Authors/Mixture	N_P[a]	Covered ranges		N_C[b]	M[m]	Statistical analysis[n]									
		Temperature T/K	Pressure p/MPa		g·mol^{-1}	N_1 %	N_2 %	AAD$_1$ %	AAD$_2$ %	Bias$_1$ %	Bias$_2$ %	RMS$_1$ %	RMS$_2$ %	MaxD$_1$ %	MaxD$_2$ %
Speed of sound (continued)						**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA
Natural gases and other multi-component mixtures (continued)															
Blanke & Weiß (1986), M4	24	273 – 303	0.001 – 6.0	12	18.392	24	24	0.025	0.029	−0.016	−0.001	0.031	0.035	−0.083	−0.082
Blanke & Weiß (1986), M5	24	273 – 303	0.001 – 6.0	9	18.604	24	24	0.096	0.081	−0.096	−0.081	0.099	0.086	−0.131	−0.125
Blanke & Weiß (1986), M6	24	273 – 303	0.001 – 6.0	9	18.598	24	24	0.260	0.253	−0.245	−0.236	0.278	0.269	−0.364	−0.362
Blanke & Weiß (1986), M7	24	273 – 303	0.001 – 6.0	13	18.798	24	24	0.044	0.054	0.001	0.016	0.052	0.061	0.104	0.118
Blanke & Weiß (1986), M8	24	273 – 303	0.001 – 6.0	9	18.894	24	24	0.195	0.186	−0.195	−0.186	0.196	0.188	−0.257	−0.281
Blanke & Weiß (1986), M9	24	273 – 303	0.001 – 6.0	10	19.532	24	24	0.324	0.327	−0.324	−0.327	0.327	0.336	−0.489	−0.618
Blanke & Weiß (1986), M10	24	273 – 303	0.001 – 6.0	10	20.087	24	24	0.677	0.660	−0.677	−0.660	0.687	0.669	−0.889	−0.853
Ewing & Goodwin (1993)	11	255	0.06 – 6.1	10	17.011	11	11	0.047	0.048	0.018	0.020	0.050	0.051	0.070	0.064
Fawcett (1995)	42	293 – 303	0.4 – 10.1	9	18.663	42	42	0.031	0.053	0.026	0.051	0.037	0.063	0.065	0.116
Ingrain *et al.* (1993), M1	58	213 – 346	0.2 – 17.1	13	18.184	58	57	0.305	0.646	−0.195	−0.499	0.542	1.656	−2.197	−9.119
Ingrain *et al.* (1993), M2	75	213 – 346	0.2 – 17.1	7	17.775	75	75	0.191	0.328	−0.049	−0.205	0.437	0.694	−3.308	−3.832
Labes *et al.* (1994), M1	240	262 – 354	12.0 – 70.0	13	18.184	240	240	0.358	0.365	0.298	0.357	0.506	0.450	1.347	1.275
Labes *et al.* (1994), M2	286	273 – 414	20.0 – 70.0	7	17.775	286	286	0.532	0.621	0.532	0.621	0.648	0.699	2.537	2.356
Younglove *et al.* (1993), M1 (Gulf Coast)	83	250 – 350	0.5 – 10.7	10	16.786	83	83	0.027	0.055	0.019	0.046	0.032	0.062	−0.082	0.147
Younglove *et al.* (1993), M2 (Amarillo)	82	250 – 350	0.6 – 23.4	10	17.593	82	82	0.021	0.047	0.004	0.026	0.032	0.059	−0.142	−0.194
Younglove *et al.* (1993), M3 (Statoil Dry)	91	250 – 350	0.5 – 10.4	9	18.551	91	91	0.036	0.094	0.031	0.001	0.044	0.153	0.103	−0.579
Younglove *et al.* (1993), M4 (Statfjord)	44	300 – 350	0.4 – 10.4	8	22.150	44	44	0.065	0.123	−0.019	−0.064	0.124	0.231	−0.474	−0.793
Five-component synthetic natural gas mixture															
Costa Gomes & Trusler (1998)	39	250 – 350	0.00 – 20.2	5	19.337	39	39	0.064	0.124	−0.058	−0.064	0.123	0.239	−0.370	−0.853
Le Noë & Desentfant (1996), M1	12	225 – 350	2.5 – 5.0	5	19.353	10	10	0.105	0.091	0.105	0.091	0.113	0.095	0.173	0.119
Le Noë & Desentfant (1996), M2	6	225 – 350	7.5	5	19.432	5	5	0.051	0.119	0.051	0.046	0.055	0.124	0.074	−0.183
Le Noë & Desentfant (1996), M3	12	225 – 350	10.0 – 12.5	5	19.340	10	10	0.068	0.171	−0.037	−0.006	0.124	0.221	−0.359	−0.498
Le Noë & Desentfant (1996), M4	6	225 – 350	15.0	5	19.366	5	5	0.105	0.168	−0.105	−0.048	0.157	0.254	−0.331	−0.540
Le Noë & Desentfant (1996), M5	5	250 – 350	17.5	5	19.333	5	5	0.143	0.260	−0.121	−0.108	0.226	0.391	−0.464	−0.843
Le Noë & Desentfant (1996), M6	5	250 – 350	20.0	5	19.337	5	5	0.231	0.258	−0.231	−0.251	0.280	0.475	−0.507	−1.045

Table A2.2 (continued)

Authors/Mixture	N_P[a]	Covered ranges Temperature T/K	Covered ranges Pressure p/MPa	N_C[b]	M^m g·mol^{-1}	Statistical analysis[n] N_1 %	N_2 %	AAD$_1$ %	AAD$_2$ %	Bias$_1$ %	Bias$_2$ %	RMS$_1$ %	RMS$_2$ %	MaxD$_1$ %	MaxD$_2$ %
Isobaric heat capacity						**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA
Natural gases and other multi-component mixtures															
Trappehl (1987), M1	69	205 – 300	2.0 – 12.0	3	24.628	69	69	0.585	0.838	0.243	0.433	0.825	1.265	2.944	4.904
Trappehl (1987), M2	51	200 – 300	2.0 – 8.0	3	21.036	51	51	0.801	0.801	−0.591	−0.198	0.944	1.031	−2.955	3.411
Trappehl (1987), M3	36	240 – 300	2.0 – 12.0	3	22.439	34	34	3.097	3.259	3.097	3.259	3.226	3.456	5.268	6.126
Trappehl (1987), M4	42	240 – 300	2.0 – 12.0	3	29.023	42	42	1.078	1.285	1.078	1.284	1.170	1.504	2.257	3.479
Trappehl (1987), M5	44	235 – 300	2.0 – 12.0	4	22.542	44	44	1.041	1.384	−0.849	−0.148	1.277	1.709	−2.836	4.556
van Kasteren & Zeldenrust (1979), M1	11	115 – 265	5.1	8	18.309	11	–	0.803		0.796		1.096		2.687	
van Kasteren & Zeldenrust (1979), M2	18	105 – 250	5.1	4	16.984	18	–	4.670		−0.619		5.470		−11.142	
Five-component synthetic natural gas mixture															
Wirbser *et al.* (1996)	54	250 – 350	0.5 – 30.0	5	19.364	54	54	1.271	1.554	1.266	1.551	1.737	1.948	6.408	6.376
Enthalpy differences						**EqG**	EqA	**EqG**[u]	EqA[u]	**EqG**[u]	EqA[u]	**EqG**[u]	EqA[u]	**EqG**[u]	EqA[u]
Natural gases and other multi-component mixtures															
Ashton & Haselden (1980), M1[p]	22	129 – 367	1.3 – 4.5	6	17.253	11	–	2.235		−2.235		2.753		−6.736	
Ashton & Haselden (1980), M2[p]	22	154 – 362	1.5 – 5.7	6	19.838	8	–	3.984		−3.984		4.574		−9.066	
Ashton & Haselden (1980), M3[p]	19	153 – 363	1.4 – 5.6	6	19.151	6	–	2.359		−2.122		2.997		−5.742	
Ashton & Haselden (1980), M4[p]	19	158 – 362	1.4 – 5.6	6	18.614	7	–	5.039		−5.039		6.449		−11.983	
Banks & Haselden (1969)[p]	10	220 – 374	2.8 – 3.9	5	17.523	10	10	1.326	1.318	−0.397	−0.441	2.158	2.161	−6.235	−6.279
Gregory *et al.* (1973)	14	296 – 297	0.2 – 12.4	10	16.756	14	14	2.844	2.848	−0.900	−0.814	3.418	3.400	7.544	7.647
Gregory *et al.* (1973)[p]	75	144 – 367	0.4 – 8.3	10	16.756	48	–	1.864		0.428		2.326		−6.586	
Grini *et al.* (1998)[h]	72	197 – 344	0.2 – 14.1	3	21.448	54	–	*8.401*		*−5.124*		*11.158*		*−28.370*	
Grini *et al.* (1998)[p]	72	179 – 344	0.9 – 14.1	3	21.448	72	–	4.239		−3.861		5.616		−13.712	
Lammers *et al.* (1978), M1[p]	11	110 – 270	5.1	8	18.309	5	–	0.948		0.948		0.966		1.083	
Lammers *et al.* (1978), M2[p]	8	110 – 270	0.3	4	26.298	2	–	1.762		−1.762		1.865		−2.373	
Laverman & Selculkoglu (1968)[p]	9	184 – 298	3.0	5	16.915	4	–	9.524		9.524		10.080		14.681	
Ng & Mather (1976), M1	16	273 – 363	3.0 – 13.7	2	32.179	16	16	0.460	0.593	0.179	−0.136	0.540	0.794	−1.005	−1.770
Ng & Mather (1976), M2	16	293 – 363	3.0 – 13.7	2	39.954	16	16	0.546	0.690	−0.385	−0.215	0.654	0.852	−1.330	−1.663

Table A2.2 (continued)

Authors/Mixture	N_P[a]	Covered ranges		N_C[b]	M[m]	Statistical analysis[n]									
		Temperature T/K	Pressure p/MPa		g·mol^{-1}	N_1 %	N_2 %	AAD$_1$ %	AAD$_2$ %	Bias$_1$ %	Bias$_2$ %	RMS$_1$ %	RMS$_2$ %	MaxD$_1$ %	MaxD$_2$ %
Enthalpy differences (continued)						**EqG**	EqA	**EqG**[u]	EqA[u]	**EqG**[u]	EqA[u]	**EqG**[u]	EqA[u]	**EqG**[u]	EqA[u]
Natural gases and other multi-component mixtures (continued)															
Ng & Mather (1977), M1	33	243 – 283	3.0 – 13.7	3	29.370	33	33	0.315	0.999	−0.135	0.907	0.412	1.149	−0.960	2.217
Ng & Mather (1977), M2	44	263 – 333	3.0 – 13.7	4	29.493	44	44	0.308	2.400	0.043	2.400	0.349	2.702	0.627	5.067
Ng & Mather (1978), M1	20	273 – 363	3.0 – 13.7	3	29.970	20	20	0.795	2.915	−0.389	2.915	1.137	3.256	−3.188	5.823
Ng & Mather (1978), M2	24	263 – 363	3.0 – 13.7	3	26.261	24	24	0.725	2.203	0.315	2.203	0.824	2.412	−1.513	4.389
Powers *et al.* (1979)[p]	155	122 – 422	1.7 – 13.8	3	18.904	122	–	1.195		0.340		2.347		11.746	
Sood & Haselden (1972)[p]	29	174 – 373	1.8 – 5.7	6	16.743	21	–	1.409		−0.590		1.840		−4.792	
Trappehl (1987), M1[h]	72	149 – 300	0.3 – 12.0	3	24.628	70	70	*10.118*	*10.060*	*−2.095*	*0.208*	*12.623*	*12.105*	*−29.712*	*−28.066*
Trappehl (1987), M1[p]	35	205 – 300	2.0 – 12.0	3	24.628	34	34	2.459	2.613	0.446	0.664	3.085	3.204	−7.974	−7.033
Trappehl (1987), M2[h]	51	168 – 300	0.3 – 8.0	3	21.036	40	41	*14.851*	*15.022*	*12.974*	*13.136*	*17.169*	*17.123*	*29.717*	*29.720*
Trappehl (1987), M2[p]	24	200 – 295	2.0 – 8.0	3	21.036	24	24	2.292	2.280	−1.294	−0.869	3.527	3.297	−10.183	−10.156
Trappehl (1987), M3[h]	36	211 – 300	0.3 – 12.0	3	22.439	12	21	*13.562*	*17.379*	*−13.562*	*−17.379*	*13.589*	*19.746*	*−14.626*	*−29.357*
Trappehl (1987), M3[p]	17	240 – 300	2.0 – 12.0	3	22.439	15	15	3.559	3.707	3.501	3.626	4.104	4.261	9.317	9.721
Trappehl (1987), M4[h]	42	209 – 300	0.3 – 12.0	3	29.023	42	42	*10.521*	*7.742*	*−10.521*	*−7.128*	*11.908*	*11.183*	*−19.520*	*−27.010*
Trappehl (1987), M4[p]	19	240 – 295	2.0 – 12.0	3	29.023	19	19	0.999	1.239	0.999	1.239	1.079	1.344	1.577	2.214
Trappehl (1987), M5[h]	44	161 – 300	0.3 – 12.0	4	22.542	18	17	*16.747*	*17.012*	*4.065*	*5.957*	*18.579*	*19.314*	*−28.832*	*−29.619*
Trappehl (1987), M5[p]	21	235 – 300	2.0 – 12.0	4	22.542	21	21	3.683	4.047	0.729	1.439	4.635	5.181	13.987	15.416
van Kasteren & Zeldenrust (1979), M1[p]	19	105 – 270	5.1	8	18.309	12	–	0.573		0.573		0.588		0.987	
van Kasteren & Zeldenrust (1979), M2[p]	17	105 – 250	5.1	4	16.984	16	–	1.838		−0.016		2.182		4.871	
Wilson & Barton (1967)[p]	15	150 – 301	1.4 – 3.4	9	18.256	6	–	1.028		1.028		1.146		1.519	
Five-component synthetic natural gas mixture															
Owren *et al.* (1996)[h]	32	238 – 348	0.8 – 16.5	5	19.350	32a	32	0.879	2.086	0.069	0.517	1.254	2.695	−4.516	−8.576
Owren *et al.* (1996)[p]	32	243 – 348	2.5 – 16.5	5	19.350	32	32	0.211	0.559	0.202	0.559	0.272	0.779	0.773	1.672
Saturated liquid density						**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP
LNG-like and other multi-component mixtures															
Haynes (1982), M1	4	110 – 125	0.2 – 0.5	3	18.856	4	4	0.356	11.432	0.356	−11.432	0.356	11.432	0.371	−11.547

Table A2.2 (continued)

Authors/Mixture	N_P[a]	Covered ranges		N_C[b]	M[m]	Statistical analysis[n]									
		Temperature	Pressure		g·mol^{-1}	N_1	N_2	AAD$_1$	AAD$_2$	Bias$_1$	Bias$_2$	RMS$_1$	RMS$_2$	MaxD$_1$	MaxD$_2$
		T/K	p/MPa			%	%	%	%	%	%	%	%	%	%
Saturated liquid density (continued)						**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP
LNG-like and other multi-component mixtures (continued)															
Haynes (1982), M2	5	115 – 135	0.1 – 0.4	4	20.008	5	5	0.305	10.315	0.305	−10.315	0.308	10.315	0.364	−10.434
Haynes (1982), M3	4	115 – 130	0.1 – 0.3	4	19.604	4	4	0.206	10.626	0.206	−10.626	0.210	10.626	0.262	−10.707
Haynes (1982), M4	5	115 – 135	0.1 – 0.4	4	19.954	5	5	0.024	10.356	0.019	−10.356	0.028	10.356	0.049	−10.478
Haynes (1982), M5	4	115 – 130	0.1 – 0.3	4	20.083	4	4	0.006	10.379	−0.002	−10.379	0.007	10.379	0.009	−10.433
Haynes (1982), M6	4	115 – 130	0.1 – 0.3	5	18.556	4	4	0.089	11.225	0.089	−11.225	0.091	11.225	0.113	−11.312
Haynes (1982), M7	4	115 – 130	0.1 – 0.3	5	19.583	4	4	0.164	10.607	0.164	−10.607	0.166	10.607	0.202	−10.696
Haynes (1982), M8	4	115 – 130	0.2 – 0.5	5	20.070	4	4	0.164	10.741	0.164	−10.741	0.165	10.741	0.180	−10.772
Haynes (1982), M9	4	115 – 130	0.3 – 0.6	5	20.635	4	4	0.011	10.605	−0.003	−10.605	0.014	10.605	−0.023	−10.667
Haynes (1982), M10	4	115 – 130	0.1 – 0.4	6	17.819	4	4	0.133	11.410	0.133	−11.410	0.135	11.412	0.162	−11.642
Haynes (1982), M11	3	115 – 125	0.2 – 0.3	6	18.309	3	3	0.135	11.339	0.135	−11.339	0.137	11.340	0.167	−11.393
Haynes (1982), M12	4	115 – 130	0.2 – 0.4	6	18.749	4	4	0.221	11.057	0.221	−11.057	0.222	11.057	0.252	−11.216
Haynes (1982), M13	5	110 – 130	0.08 – 0.3	7	19.358	5	5	0.230	10.763	0.230	−10.763	0.231	10.763	0.254	−10.843
Haynes (1982), M14	4	110 – 125	0.07 – 0.2	7	21.105	4	4	0.142	10.092	0.142	−10.092	0.144	10.092	0.161	−10.162
Haynes (1982), M15	5	110 – 130	0.1 – 0.4	8	21.309	5	5	0.361	9.968	0.361	−9.968	0.363	9.968	0.408	−10.011
Haynes (1982), M16	4	110 – 125	0.1 – 0.3	8	21.097	4	4	0.086	10.234	0.086	−10.234	0.088	10.234	0.115	−10.305
Haynes (1982), M17	4	115 – 130	0.1 – 0.4	8	17.902	4	4	0.141	11.394	0.141	−11.394	0.142	11.395	0.166	−11.585
Hiza & Haynes (1980), M1	4	105 – 120	0.05 – 0.2	3	20.185	4	4	0.053	10.442	0.053	−10.442	0.060	10.443	0.098	−10.497
Hiza & Haynes (1980), M2	5	110 – 120	0.04 – 0.1	3	30.089	5	5	0.127	6.710	−0.127	−6.710	0.131	6.711	−0.164	−6.837
Hiza & Haynes (1980), M3	4	105 – 120	0.4 – 0.8	3	20.330	4	4	0.233	12.017	0.233	−12.017	0.234	12.017	0.253	−12.046
Hiza & Haynes (1980), M4	3	105 – 115	0.7 – 1.2	3	24.586	3	3	0.487	11.582	0.487	−11.582	0.491	11.582	0.556	−11.737
Hiza & Haynes (1980), M5	4	105 – 120	0.3 – 0.6	3	20.117	4	4	0.151	11.304	0.151	−11.304	0.154	11.304	0.193	−11.379
Hiza & Haynes (1980), M6	4	105 – 120	0.2 – 0.4	4	18.722	4	4	0.062	11.650	0.062	−11.650	0.064	11.651	0.088	−11.711
Hiza & Haynes (1980), M7	4	105 – 120	0.05 – 0.2	5	20.188	4	4	0.285	10.158	0.285	−10.158	0.286	10.158	0.328	−10.231
Hiza & Haynes (1980), M8	2	105 – 110	0.2 – 0.3	5	20.901	2	2	0.267	10.521	0.267	−10.521	0.268	10.521	0.292	−10.588
Hiza & Haynes (1980), M9	4	105 – 120	0.2 – 0.4	5	20.742	4	4	0.035	10.564	0.025	−10.564	0.039	10.564	0.058	−10.619
Hiza & Haynes (1980), M10	4	105 – 120	0.2 – 0.4	6	20.616	4	4	0.199	10.502	0.199	−10.502	0.202	10.502	0.257	−10.567

Table A2.2 (continued)

Authors/Mixture	N_P[a]	Covered ranges		N_C[b]	M[m]	Statistical analysis[n]									
		Temperature T/K	Pressure p/MPa		g·mol^{-1}	N_1 %	N_2 %	AAD$_1$ %	AAD$_2$ %	Bias$_1$ %	Bias$_2$ %	RMS$_1$ %	RMS$_2$ %	MaxD$_1$ %	MaxD$_2$ %
Saturated liquid density (continued)						**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP
LNG-like and other multi-component mixtures (continued)															
Vrabec & Fischer (1997)[z]	15	233 – 251	1.9 – 3.2	3	n/a[v]	15	15	0.568	2.890	0.557	−2.890	0.762	3.295	1.951	−5.439

[a] Number of data points.

[b] Number of components.

[c] Abbreviations for methods of measurement:

- ADH: Automatic Desgranges et Huot apparatus.
- BUR: Burnett apparatus.
- DEH: Desgranges et Huot Z-meter.
- DMA: Two-sinker method, Ruhr-Universität Bochum.
- EXP: Dantest expansion apparatus.
- GDM: Two-sinker method, Ruhrgas.
- IBU: Isochoric Burnett apparatus.
- OPT: Optical interferometry method.
- PYC: Pycnometer method.

[d] Abbreviations for mixtures of round-robin measurements [see Magee *et al.* (1997)]:

- GU1: Simulated NAM high-N_2 natural gas.
- GU2: Simulated high-CO_2 natural gas.
- RG2: Simulated Ekofisk natural gas.
- NIST1: Simulated Gulf Coast natural gas.
- NIST2: Simulated Amarillo natural gas.

[e] Mixture contains small fractions of n-nonane.

[f] Mixture contains small fractions of n-decane.

[g] Mixture contains high fractions of hydrogen sulphide.

[h] Isenthalpic measurements.

[m] Molar mass. Values were calculated from the mixture compositions using the atomic weights according to Wieser (2006).

[n] Nomenclature of the statistical analysis:

- N: Number of data points used for the statistical analysis.

Table A2.2 (continued)

- AAD: Average absolute deviation.
- Bias: Average deviation.
- RMS: Root-mean-squared deviation.
- MaxD: Maximum deviation.
- EqG: GERG-2004 equation of state.
- EqA: AGA8-DC92 equation of state of Starling and Savidge (1992) (used for comparison with GERG-2004 for properties in the homogeneous gas phase only).
- EqP: Cubic equation of state of Peng and Robinson (1976) (used for comparison with GERG-2004 for liquid and saturated liquid densities and VLE properties).

Subscripts:

- 1: GERG-2004 equation of state (EqG).
- 2: AGA8-DC92 equation of state of Starling and Savidge (1992) (EqA) or cubic equation of state of Peng and Robinson (1976) (EqP).

Notes:

- The AGA8-DC92 equation of state of Starling and Savidge (1992) is not valid for the liquid phase and saturated/VLE properties.
- Density deviations are tabulated for $p\rho T$ data.

[p] Isobaric measurements.

[r] Data were measured at Ruhrgas using a two-sinker densimeter.

[u] Values printed in italics indicate deviations in $\mathrm{J \cdot mol^{-1}}$.

[v] No explicit molar mass due to a varying composition.

[z] Calculated data.

Table A2.3 Mixture compositions of the data sets for thermal and caloric properties of natural gases and other multi-component mixtures listed in Table A2.2

Authors/Mixture	Composition (mole per cent)												
	CH_4	N_2	CO_2	C_2H_6	C_3H_8	n-C_4H_{10}	i-C_4H_{10}	n-C_5H_{12}	i-C_5H_{12}	n-C_6H_{14}	H_2[a]	CO[b]	Rest[s]
***pρT* data**													
GERG TM7 [Jaeschke *et al.* (1997)], C-file (ternary mixtures)[c]													
C1231 (DEH), CH_4–N_2–CO_2	50.2100	24.9740	24.8160	–	–	–	–	–	–	–	–	–	–
C1241 (DEH), CH_4–N_2–C_2H_6	49.9680	24.8980	–	25.1340	–	–	–	–	–	–	–	–	–
C1242 (BUR), CH_4–N_2–C_2H_6	62.6500	12.0900	–	25.2600	–	–	–	–	–	–	–	–	–
C1341 (DEH), CH_4–CO_2–C_2H_6	50.3940	–	24.7680	24.8370	0.0010	–	–	–	–	–	–	–	–
C1342 (DEH), CH_4–CO_2–C_2H_6	59.5950	–	20.2650	20.1400	–	–	–	–	–	–	–	–	–
C1361 (DEH), CH_4–CO_2–C_3H_8	74.7260	–	20.1900	–	5.0840	–	–	–	–	–	–	–	–
C1461 (DEH), CH_4–C_2H_6–C_3H_8	74.7000	–	–	20.1200	5.1800	–	–	–	–	–	–	–	–
C1462 (BUR), CH_4–C_2H_6–C_3H_8	81.2000	–	–	16.5400	2.2600	–	–	–	–	–	–	–	–
C1463 (OPT), CH_4–C_2H_6–C_3H_8	81.2000	–	–	16.5400	2.2600	–	–	–	–	–	–	–	–
C1464 (DEH), CH_4–C_2H_6–C_3H_8	81.1500	–	–	16.5900	2.2600	–	–	–	–	–	–	–	–
C1465 (DEH), CH_4–C_2H_6–C_3H_8	81.1900	–	–	16.5500	2.2600	–	–	–	–	–	–	–	–
C1466 (DEH), CH_4–C_2H_6–C_3H_8	81.3200	–	–	16.2400	2.4400	–	–	–	–	–	–	–	–
C1467 (DEH), CH_4–C_2H_6–C_3H_8	81.3600	–	–	16.2000	2.4400	–	–	–	–	–	–	–	–
C1468 (ADH), CH_4–C_2H_6–C_3H_8	81.3700	–	–	16.1900	2.4400	–	–	–	–	–	–	–	–
C1469 (DEH), CH_4–C_2H_6–C_3H_8	81.3400	–	–	16.2200	2.4400	–	–	–	–	–	–	–	–
C14610 (BUR), CH_4–C_2H_6–C_3H_8	81.1800	–	–	16.5600	2.2600	–	–	–	–	–	–	–	–
C14611 (ADH), CH_4–C_2H_6–C_3H_8	81.2000	–	–	16.5400	2.2600	–	–	–	–	–	–	–	–
C14612 (DEH), CH_4–C_2H_6–C_3H_8	81.1300	–	–	16.6200	2.2500	–	–	–	–	–	–	–	–
C14613 (OPT), CH_4–C_2H_6–C_3H_8	81.4000	–	–	16.1600	2.4400	–	–	–	–	–	–	–	–
GERG TM7 [Jaeschke *et al.* (1997)], D-file (synthetic multi-component mixtures)[c,d]													
D1 (BUR), CH_4–N_2–C_2H_6–O_2	76.8000	15.6000	–	7.2000	–	–	–	–	–	–	–	–	0.4000
D2 (DEH), CH_4–N_2–C_2H_6–C_3H_8	92.9300	3.0100	–	3.0100	1.0500	–	–	–	–	–	–	–	–
D3 (DEH), CH_4–N_2–C_2H_6–C_3H_8	89.7100	3.1150	–	6.1550	1.0200	–	–	–	–	–	–	–	–
D4 (DEH), CH_4–N_2–C_2H_6–C_3H_8	86.8000	3.0400	–	9.1200	1.0400	–	–	–	–	–	–	–	–
D5 (DEH), CH_4–N_2–C_2H_6–C_3H_8	83.7200	3.1500	–	12.0900	1.0400	–	–	–	–	–	–	–	–
D6 (DEH), CH_4–N_2–C_2H_6–C_3H_8	88.8400	2.9400	–	6.1000	2.1200	–	–	–	–	–	–	–	–
D7 (DEH), CH_4–N_2–C_2H_6–C_3H_8	84.7700	2.8500	–	9.2500	3.1300	–	–	–	–	–	–	–	–

Table A2.3 (continued)

Authors/Mixture	Composition (mole per cent)												
	CH_4	N_2	CO_2	C_2H_6	C_3H_8	n-C_4H_{10}	i-C_4H_{10}	n-C_5H_{12}	i-C_5H_{12}	n-C_6H_{14}	H_2[a]	CO[b]	Rest[s]
pρT **data (continued)**													
GERG TM7 [Jaeschke *et al.* (1997)], D-file (synthetic multi-component mixtures)[c,d] (continued)													
D8 (DEH), CH_4–N_2–C_2H_6–C_3H_8	81.3200	2.9500	–	11.8300	3.9000	–	–	–	–	–	–	–	–
D9 (DEH), CH_4–N_2–C_2H_6–C_3H_8	66.9300	17.8700	–	11.4600	3.7400	–	–	–	–	–	–	–	–
D10 (DEH), CH_4–N_2–C_2H_6–H_2	90.1000	1.0000	–	6.0000	–	–	–	–	–	–	2.9000	–	–
D11 (DEH), CH_4–N_2–C_2H_6–C_3H_8	61.8000	22.6000	–	11.7000	3.9000	–	–	–	–	–	–	–	–
D12 (DEH), CH_4–N_2–C_2H_6–C_3H_8	81.9000	13.7000	–	3.3000	1.1000	–	–	–	–	–	–	–	–
D13 (DEH), CH_4–N_2–C_2H_6–C_3H_8	73.9000	22.0000	–	3.1000	1.0000	–	–	–	–	–	–	–	–
D14 (DEH), CH_4–N_2–CO_2–C_2H_6	25.1800	25.0000	25.1600	24.6600	–	–	–	–	–	–	–	–	–
D15 (DEH), CH_4–N_2–C_2H_6–C_3H_8	95.4432	1.8589	–	1.9099	0.7880	–	–	–	–	–	–	–	–
D16 (BUR), CH_4–CO_2–C_2H_6–C_3H_8	84.7831	–	2.0052	8.9208	3.0535	1.2374	–	–	–	–	–	–	–
D17 (OPT), CH_4–CO_2–C_2H_6–C_3H_8	84.7831	–	2.0052	8.9208	3.0535	1.2374	–	–	–	–	–	–	–
D18 (OPT), CH_4–N_2–CO_2–C_2H_6	61.7700	12.6600	12.6000	12.9700	–	–	–	–	–	–	–	–	–
D19 (OPT), CH_4–N_2–C_2H_6–C_3H_8	88.6020	0.6520	–	8.6860	1.5110	0.3000	0.1940	0.0050	0.0210	–	–	–	0.0290
D20 (OPT), CH_4–N_2–C_2H_6–C_3H_8	88.6520	0.5980	–	8.6960	1.5150	0.3000	0.1940	0.0050	0.0210	–	–	–	0.0190
D21 (OPT), CH_4–N_2–CO_2–C_2H_6	66.0860	13.1300	11.0600	9.7100	–	–	–	–	–	–	–	–	0.0140
D22 (OPT), GU1	81.4410	13.4650	0.9850	3.3000	0.6050	0.1040	0.1000	–	–	–	–	–	–
D23 (GDM), GU1	81.4410	13.4650	0.9850	3.3000	0.6050	0.1040	0.1000	–	–	–	–	–	–
D24 (BUR), GU1	81.2990	13.5750	0.9940	3.2940	0.6370	0.1000	0.1010	–	–	–	–	–	–
D25 (PYC), GU1	81.2990	13.5750	0.9940	3.2940	0.6370	0.1000	0.1010	–	–	–	–	–	–
D26 (BUR), GU1	81.2990	13.5750	0.9940	3.2940	0.6370	0.1000	0.1010	–	–	–	–	–	–
D27 (BUR), GU1	81.4410	13.4650	0.9850	3.3000	0.6050	0.1040	0.1000	–	–	–	–	–	–
D28 (IBU), GU1	81.4410	13.4650	0.9850	3.3000	0.6050	0.1040	0.1000	–	–	–	–	–	–
D29 (OPT), GU2	81.2120	5.7020	7.5850	4.3030	0.8950	0.1520	0.1510	–	–	–	–	–	–
D30 (GDM), GU2	81.2120	5.7020	7.5850	4.3030	0.8950	0.1520	0.1510	–	–	–	–	–	–
D31 (BUR), GU2	81.2020	5.7030	7.5920	4.3060	0.8940	0.1550	0.1480	–	–	–	–	–	–
D32 (PYC), GU2	81.2020	5.7030	7.5920	4.3060	0.8940	0.1550	0.1480	–	–	–	–	–	–
D33 (BUR), GU2	81.2020	5.7030	7.5920	4.3060	0.8940	0.1550	0.1480	–	–	–	–	–	–
D34 (BUR), GU2	81.2120	5.7020	7.5850	4.3030	0.8950	0.1520	0.1510	–	–	–	–	–	–

Table A2.3 (continued)

Authors/Mixture	Composition (mole per cent)												
	CH_4	N_2	CO_2	C_2H_6	C_3H_8	n-C_4H_{10}	i-C_4H_{10}	n-C_5H_{12}	i-C_5H_{12}	n-C_6H_{14}	H_2[a]	CO[b]	Rest[s]
***pρT* data (continued)**													
GERG TM7 [Jaeschke *et al.* (1997)], D-file (synthetic multi-component mixtures)[c,d] (continued)													
D35 (BUR), RG2	85.9063	1.0068	1.4954	8.4919	2.3015	0.3506	0.3486	0.0480	0.0509	–	–	–	–
D36 (OPT), RG2	85.9063	1.0068	1.4954	8.4919	2.3015	0.3506	0.3486	0.0480	0.0509	–	–	–	–
D37 (GDM), RG2	85.9063	1.0068	1.4954	8.4919	2.3015	0.3506	0.3486	0.0480	0.0509	–	–	–	–
D38 (BUR), RG2	85.8980	1.0070	1.4980	8.4990	2.2960	0.3470	0.3510	0.0530	0.0510	–	–	–	–
D39 (PYC), RG2	85.8980	1.0070	1.4980	8.4990	2.2960	0.3470	0.3510	0.0530	0.0510	–	–	–	–
D40 (BUR), RG2	85.8980	1.0070	1.4980	8.4990	2.2960	0.3470	0.3510	0.0530	0.0510	–	–	–	–
D41 (OPT), NIST1	96.5222	0.2595	0.5956	1.8186	0.4596	0.1007	0.0977	0.0324	0.0473	0.0664	–	–	–
D42 (GDM), NIST1	96.5222	0.2595	0.5956	1.8186	0.4596	0.1007	0.0977	0.0324	0.0473	0.0664	–	–	–
D43 (BUR), NIST1	96.5790	0.2690	0.5890	1.8150	0.4050	0.1020	0.0990	0.0320	0.0470	0.0630	–	–	–
D44 (PYC), NIST1	96.5790	0.2690	0.5890	1.8150	0.4050	0.1020	0.0990	0.0320	0.0470	0.0630	–	–	–
D45 (BUR), NIST1	96.5790	0.2690	0.5890	1.8150	0.4050	0.1020	0.0990	0.0320	0.0470	0.0630	–	–	–
D46 (IBU), NIST1	96.5222	0.2595	0.5956	1.8186	0.4596	0.1007	0.0977	0.0324	0.0473	0.0664	–	–	–
D47 (OPT), NIST2	90.6724	3.1284	0.4676	4.5279	0.8280	0.1563	0.1037	0.0443	0.0321	0.0393	–	–	–
D48 (GDM), NIST2	90.6724	3.1284	0.4676	4.5279	0.8280	0.1563	0.1037	0.0443	0.0321	0.0393	–	–	–
D49 (BUR), NIST2	90.6430	3.1340	0.4660	4.5530	0.8330	0.1560	0.1000	0.0450	0.0300	0.0400	–	–	–
D50 (PYC), NIST2	90.6430	3.1340	0.4660	4.5530	0.8330	0.1560	0.1000	0.0450	0.0300	0.0400	–	–	–
D51 (BUR), NIST2	90.6430	3.1340	0.4660	4.5530	0.8330	0.1560	0.1000	0.0450	0.0300	0.0400	–	–	–
D52 (BUR), NIST2	90.6724	3.1284	0.4676	4.5279	0.8280	0.1563	0.1037	0.0443	0.0321	0.0393	–	–	–
D53 (IBU), NIST2	90.6724	3.1284	0.4676	4.5279	0.8280	0.1563	0.1037	0.0443	0.0321	0.0393	–	–	–
D54 (BUR)	88.2690	2.6930	0.9360	6.1150	0.9980	0.9890	–	–	–	–	–	–	–
D55 (BUR)	80.0790	–	–	11.6410	6.5300	1.7500	–	–	–	–	–	–	–
D56 (BUR), CH_4–N_2–C_2H_6–C_3H_8	89.9200	2.2000	–	6.2800	1.6000	–	–	–	–	–	–	–	–
D57 (BUR), CH_4–N_2–C_2H_6–C_3H_8	90.3500	2.1500	–	4.9700	2.5300	–	–	–	–	–	–	–	–
D58 (DEH)	96.5000	0.2500	0.6000	1.7500	0.4000	0.1000	0.1000	0.1000	0.1000	0.1000	–	–	–
D59 (DEH)	90.6600	3.2200	0.4200	4.5900	0.7800	0.1400	0.1000	0.0200	0.0300	0.0300	–	–	0.0100
GERG TM7 [Jaeschke *et al.* (1997)], N-file (natural gases and other multi-component mixtures)[c]													
N1[e] (DEH)	84.3346	0.4390	1.9285	8.8946	3.1919	0.6463	0.3381	0.0903	0.0922	0.0325	0.0015	–	0.0105

Table A2.3 (continued)

Authors/Mixture	Composition (mole per cent)												
	CH_4	N_2	CO_2	C_2H_6	C_3H_8	$n\text{-}C_4H_{10}$	$i\text{-}C_4H_{10}$	$n\text{-}C_5H_{12}$	$i\text{-}C_5H_{12}$	$n\text{-}C_6H_{14}$	H_2[a]	CO[b]	Rest[s]
***pρT* data (continued)**													
GERG TM7 [Jaeschke *et al.* (1997)], N-file (natural gases and other multi-component mixtures)[c] (continued)													
N2 (DEH)	95.5340	1.6004	0.2331	1.8790	0.4926	0.0892	0.0619	0.0276	0.0311	0.0309	–	–	0.0202
N3 (DEH)	85.1473	5.6769	1.4546	5.4174	1.5968	0.3232	0.1841	0.0801	0.0648	0.0391	–	–	0.0157
N4 (DEH)	85.4814	0.6224	1.8643	8.0607	2.8624	0.5668	0.3027	0.0986	0.0905	0.0398	–	–	0.0104
N5[e] (DEH)	80.1984	5.3899	1.7006	5.6317	1.6910	0.3454	0.2003	0.0618	0.0539	0.0293	4.1947	0.3826	0.1204
N6[e] (DEH)	82.1692	5.2846	1.7126	5.7439	1.7778	0.3586	0.2081	0.0621	0.0554	0.0304	2.3094	0.2019	0.0860
N7[e] (DEH)	73.6405	9.9108	1.3360	3.5915	0.7661	0.1482	0.0974	0.0451	0.0293	0.0230	9.3919	0.9067	0.1135
N8[e] (DEH)	78.7092	10.3008	1.2641	3.7212	0.8272	0.1631	0.1073	0.0464	0.0315	0.0245	4.2885	0.4137	0.1025
N9 (BUR)	95.5192	1.6052	0.2339	1.8835	0.4933	0.0896	0.0622	0.0283	0.0308	0.0326	–	–	0.0214
N10 (BUR)	84.4678	0.4278	1.8497	8.8604	3.1831	0.6304	0.3364	0.1005	0.0994	0.0369	–	–	0.0076
N11 (BUR)	85.1666	5.6760	1.4579	5.4022	1.5922	0.3216	0.1845	0.0804	0.0647	0.0385	–	–	0.0154
N12 (BUR)	85.4915	0.6122	1.8630	8.0626	2.8576	0.5683	0.3026	0.0995	0.0907	0.0404	–	–	0.0116
N13 (OPT)	95.5192	1.6052	0.2339	1.8835	0.4933	0.0896	0.0622	0.0283	0.0308	0.0326	–	–	0.0214
N14 (OPT)	84.4678	0.4278	1.8497	8.8604	3.1831	0.6304	0.3364	0.1005	0.0994	0.0369	–	–	0.0076
N15 (OPT)	85.1666	5.6760	1.4579	5.4022	1.5922	0.3216	0.1845	0.0804	0.0647	0.0385	–	–	0.0154
N16 (OPT)	85.4915	0.6122	1.8630	8.0626	2.8576	0.5683	0.3026	0.0995	0.0907	0.0404	–	–	0.0116
N17 (OPT)	95.5480	1.6032	0.2299	1.8724	0.4883	0.0885	0.0612	0.0269	0.0308	0.0312	–	–	0.0196
N18 (OPT)	84.4333	0.4293	1.8647	8.8669	3.1897	0.6311	0.3386	0.1015	0.0996	0.0377	–	–	0.0076
N19 (OPT)	85.1784	5.6680	1.4349	5.4163	1.5962	0.3226	0.1845	0.0804	0.0647	0.0387	–	–	0.0153
N20 (OPT)	85.4620	0.6137	1.8710	8.0768	2.8634	0.5688	0.3024	0.0990	0.0912	0.0405	–	–	0.0112
N21 (BUR)	92.2794	2.2937	0.0401	3.7252	0.9170	0.2498	0.1863	0.0792	0.0691	0.0654	–	–	0.0948
N22 (BUR)	93.0357	2.3939	0.0402	3.1217	0.6420	0.1468	0.1348	0.0729	0.0426	0.0436	–	–	0.3258
N23 (DEH)	81.2125	14.3770	0.9940	2.8090	0.3800	0.0670	0.0622	0.0321	0.0233	0.0237	–	–	0.0192
N24 (DEH)	90.8251	2.4630	1.5280	4.4050	0.6420	0.0610	0.0519	0.0027	0.0204	0.0003	–	–	0.0006
N25 (DEH)	83.9520	0.4040	1.9870	9.1380	3.2590	0.6270	0.3620	0.1050	0.1040	0.0473	–	–	0.0147
N26 (DEH)	83.8681	0.4050	2.0270	9.1800	3.2790	0.6190	0.3570	0.1029	0.1020	0.0459	–	–	0.0141
N27 (DEH)	83.7500	0.3940	1.9730	9.3490	3.3080	0.6130	0.3550	0.0996	0.1000	0.0447	–	–	0.0137
N28 (DEH)	88.9650	1.2330	1.9820	5.4550	1.6160	0.3300	0.1830	0.1050	0.0580	0.0310	–	–	0.0420

Table A2.3 (continued)

Authors/Mixture	Composition (mole per cent)												
	CH_4	N_2	CO_2	C_2H_6	C_3H_8	n-C_4H_{10}	i-C_4H_{10}	n-C_5H_{12}	i-C_5H_{12}	n-C_6H_{14}	H_2[a]	CO[b]	Rest[s]
***pρT* data (continued)**													
GERG TM7 [Jaeschke *et al.* (1997)], N-file (natural gases and other multi-component mixtures)[c] (continued)													
N29 (DEH)	75.7200	13.7510	7.1770	2.5220	0.4110	0.0850	0.0580	0.0470	0.0260	0.0230	–	–	0.1800
N30 (DEH)	87.9810	4.1240	1.5730	4.8020	0.9080	0.1700	0.1440	0.1030	0.0520	0.0450	–	–	0.0980
N31 (DEH)	92.7220	1.8580	1.9860	2.7990	0.3430	0.0560	0.0470	0.0860	0.0210	0.0150	–	–	0.0670
N32 (DEH)	88.8020	5.0460	0.5810	4.1500	0.8580	0.1690	0.1300	0.0720	0.0500	0.0400	–	–	0.1020
N33 (DEH)	68.7140	2.0650	25.4370	2.8070	0.5540	0.1170	0.0850	0.0560	0.0430	0.0390	–	–	0.0830
N34 (DEH)	80.8760	2.9080	11.2480	3.7680	0.7040	0.1450	0.0940	0.0730	0.0480	0.0430	–	–	0.0930
N35 (DEH)	65.6860	1.8580	28.9430	2.5520	0.5360	0.1150	0.0860	0.0570	0.0450	0.0410	–	–	0.0810
N36 (DEH)	86.6460	4.9040	1.6030	4.9600	1.2440	0.2450	0.1580	0.0900	0.0540	0.0340	–	–	0.0620
N37 (DEH)	84.0050	0.4230	2.1250	8.7790	3.2380	0.7030	0.3760	0.1470	0.1320	0.0590	–	–	0.0130
N38 (DEH)	79.3180	16.8100	0.5550	2.6710	0.4050	0.0770	0.0510	0.0260	0.0280	0.0230	–	–	0.0360
N39 (DEH)	87.9700	2.4340	1.7790	5.5520	1.5120	0.3060	0.1860	0.1020	0.0620	0.0360	–	–	0.0610
N40 (DEH)	79.6150	14.7670	1.4720	3.0380	0.6150	0.1370	0.0960	0.0650	0.0390	0.0380	–	–	0.1180
N41 (DEH)	81.5920	13.7870	0.9780	2.9160	0.4120	0.0800	0.0700	0.0440	0.0270	0.0250	–	–	0.0690
N42 (DEH)	81.4780	13.9310	0.9800	2.8990	0.3960	0.0790	0.0690	0.0400	0.0280	0.0280	–	–	0.0720
N43 (DEH)	86.4450	5.4550	1.7960	4.7560	0.9140	0.1790	0.1520	0.0890	0.0540	0.0460	–	–	0.1140
N44 (DEH)	92.3210	2.4480	0.9750	3.2850	0.5690	0.1130	0.0720	0.0660	0.0340	0.0350	–	–	0.0820
N45 (DEH)	90.4400	4.0710	0.7040	3.5110	0.7500	0.1580	0.1260	0.0680	0.0510	0.0410	–	–	0.0800
N46 (DEH)	75.1050	23.7320	0.1180	0.8670	0.0580	0.0140	0.0050	0.0030	0.0090	0.0070	–	–	0.0820
N47 (DEH)	70.3170	28.5000	0.1080	0.8940	0.0560	0.0140	0.0050	0.0030	0.0080	0.0070	–	–	0.0880
N48 (DEH)	45.2360	53.5570	0.0590	0.9510	0.0480	0.0110	0.0020	0.0010	0.0070	0.0050	–	–	0.1230
N49 (DEH)	88.0480	1.0140	2.0360	6.2390	1.8390	0.3000	0.3130	0.0760	0.0760	0.0260	–	–	0.0330
N50 (DEH)	81.5500	13.9300	0.9580	2.8630	0.4030	0.0720	0.0720	0.0325	0.0325	0.0220	–	–	0.0650
N51 (BUR)	85.4915	0.6122	1.8630	8.0626	2.8576	0.5683	0.3026	0.0995	0.0907	0.0404	–	–	0.0116
N52 (OPT)	85.4915	0.6122	1.8630	8.0626	2.8576	0.5683	0.3026	0.0995	0.0907	0.0404	–	–	0.0116
N53 (BUR)	85.4620	0.6137	1.8710	8.0768	2.8634	0.5688	0.3024	0.0990	0.0912	0.0405	–	–	0.0112
N54 (OPT)	85.4620	0.6137	1.8710	8.0768	2.8634	0.5688	0.3024	0.0990	0.0912	0.0405	–	–	0.0112
N55 (BUR)	85.3453	0.6039	1.9051	8.1433	2.8692	0.5864	0.3111	0.0902	0.0843	0.0345	–	–	0.0267

Table A2.3 (continued)

Authors/Mixture	Composition (mole per cent)												
	CH_4	N_2	CO_2	C_2H_6	C_3H_8	n-C_4H_{10}	i-C_4H_{10}	n-C_5H_{12}	i-C_5H_{12}	n-C_6H_{14}	H_2[a]	CO[b]	Rest[s]
***pρT* data (continued)**													
GERG TM7 [Jaeschke *et al.* (1997)], N-file (natural gases and other multi-component mixtures)[c] (continued)													
N56 (OPT)	85.3453	0.6039	1.9051	8.1433	2.8692	0.5864	0.3111	0.0902	0.0843	0.0345	–	–	0.0267
N57 (BUR)	94.6077	3.7581	0.2609	1.0118	0.2128	0.0422	0.0340	0.0122	0.0122	0.0086	–	–	0.0395
N58 (OPT)	94.6077	3.7581	0.2609	1.0118	0.2128	0.0422	0.0340	0.0122	0.0122	0.0086	–	–	0.0395
N59 (BUR)	82.5198	11.7266	1.1093	3.4611	0.7645	0.1543	0.0996	0.0413	0.0333	0.0225	–	–	0.0677
N60 (OPT)	82.5198	11.7266	1.1093	3.4611	0.7645	0.1543	0.0996	0.0413	0.0333	0.0225	–	–	0.0677
N61 (BUR)	98.2722	0.8858	0.0668	0.5159	0.1607	0.0334	0.0258	0.0068	0.0089	0.0055	–	–	0.0182
N62 (OPT)	98.2722	0.8858	0.0668	0.5159	0.1607	0.0334	0.0258	0.0068	0.0089	0.0055	–	–	0.0182
N63 (BUR)	89.4525	5.3701	4.8625	0.2353	0.0163	0.0043	0.0021	0.0011	0.0009	0.0003	–	–	0.0546
N64 (OPT)	89.4525	5.3701	4.8625	0.2353	0.0163	0.0043	0.0021	0.0011	0.0009	0.0003	–	–	0.0546
N65[e] (BUR)	85.4541	0.4275	1.7708	8.4983	2.7421	0.5947	0.3004	0.0848	0.0825	0.0315	0.0019	–	0.0114
N66[e] (OPT)	85.4541	0.4275	1.7708	8.4983	2.7421	0.5947	0.3004	0.0848	0.0825	0.0315	0.0019	–	0.0114
N67[e] (BUR)	82.1692	5.2846	1.7126	5.7439	1.7778	0.3586	0.2081	0.0621	0.0554	0.0304	2.3094	0.2019	0.0860
N68[e] (BUR)	80.1984	5.3899	1.7006	5.6317	1.6910	0.3454	0.2003	0.0618	0.0539	0.0293	4.1947	0.3826	0.1204
N69[e] (BUR)	73.6405	9.9108	1.3360	3.5915	0.7661	0.1482	0.0974	0.0451	0.0293	0.0230	9.3919	0.9067	0.1135
N70[e] (BUR)	82.2373	5.2736	1.7080	5.7536	1.7596	0.3530	0.2067	0.0620	0.0554	0.0304	2.2770	0.1960	0.0874
N71[e] (BUR)	80.1543	5.3907	1.7022	5.6228	1.7111	0.3468	0.2012	0.0613	0.0538	0.0290	4.2203	0.3863	0.1202
N72[e] (BUR)	73.5015	9.9289	1.3390	3.6007	0.7657	0.1483	0.0975	0.0447	0.0293	0.0230	9.4918	0.9142	0.1154
N73[e] (BUR)	73.5015	9.9289	1.3390	3.6007	0.7657	0.1483	0.0975	0.0447	0.0293	0.0230	9.4918	0.9142	0.1154
N74[e] (OPT)	73.5015	9.9289	1.3390	3.6007	0.7657	0.1483	0.0975	0.0447	0.0293	0.0230	9.4918	0.9142	0.1154
N75 (OPT)	85.9284	0.9617	1.5021	8.4563	2.3022	0.4604	0.2381	0.0630	0.0588	0.0228	–	–	0.0062
N76[e] (DMA)	84.3769	0.4198	1.9201	8.8749	3.1776	0.6574	0.3448	0.0896	0.0916	0.0307	0.0020	–	0.0146
N77 (DEH)	81.3140	14.1790	0.9890	2.8290	0.3910	0.0750	0.0650	0.0380	0.0240	0.0248	–	–	0.0712
N78 (DEH)	88.2210	1.1660	1.8560	6.1190	1.8840	0.3770	0.2120	0.0340	0.0590	0.0230	–	–	0.0490
N79[e,f] (DEH)	83.4177	0.3350	1.8816	9.5284	3.5694	0.6588	0.3777	0.0895	0.0933	0.0326	0.0010	–	0.0150
N80 (DEH)	65.6961	1.8530	28.9263	2.5547	0.5395	0.1185	0.0860	0.0571	0.0424	0.0425	–	–	0.0839
N81 (DEH)	80.8753	2.9080	11.2419	3.7681	0.7038	0.1457	0.0943	0.0733	0.0488	0.0448	–	–	0.0960
N82 (BUR)	84.4872	5.9990	1.3984	5.9271	1.5364	0.3287	0.1802	0.0555	0.0502	0.0251	–	–	0.0122

Table A2.3 (continued)

Authors/Mixture	Composition (mole per cent)												
	CH_4	N_2	CO_2	C_2H_6	C_3H_8	n-C_4H_{10}	i-C_4H_{10}	n-C_5H_{12}	i-C_5H_{12}	n-C_6H_{14}	H_2[a]	CO[b]	Rest[s]
***pρT* data (continued)**													
GERG TM7 [Jaeschke *et al.* (1997)], N-file (natural gases and other multi-component mixtures)[c] (continued)													
N83 (OPT)	84.4872	5.9990	1.3984	5.9271	1.5364	0.3287	0.1802	0.0555	0.0502	0.0251	–	–	0.0122
N84 (DEH)	57.6930	1.2800	0.0330	1.7800	3.2000	0.0720	0.0730	0.0180	0.0240	0.0560	35.6310	–	0.1400
N85 (DEH)	85.9610	0.6370	1.4550	8.7390	2.3870	–	0.6680	–	0.1220	0.0210	–	–	0.0100
N86 (EXP)	82.7100	0.6200	0.7900	14.7000	1.0400	–	0.1200	–	0.0100	0.0100	–	–	–
N87 (DEH)	96.5016	0.2501	0.5990	1.7490	0.4003	–	0.1999	–	0.2000	0.1001	–	–	–
N88 (DEH)	95.0220	1.1200	0.0600	2.9190	0.4900	–	0.1900	–	0.0920	0.0410	–	–	0.0660
N89 (DEH)	87.4320	11.1140	0.2100	0.9100	0.1600	–	0.0500	–	0.0280	0.0170	–	–	0.0790
N90 (DEH)	93.6200	2.1390	0.3200	2.9390	0.5500	–	0.2100	–	0.0950	0.0470	–	–	0.0800
N91 (DEH)	85.2970	7.7470	0.6000	4.5080	1.0600	–	0.5000	–	0.1720	0.0620	–	–	0.0540
N92 (DEH)	95.6160	0.5100	0.3000	3.4800	0.0440	–	0.0140	–	0.0060	0.0100	–	–	0.0200
N93 (DEH)	94.2320	1.6100	0.8500	3.1500	0.1500	–	–	–	–	–	–	–	0.0080
N94 (DEH)	85.9230	0.6640	1.4400	8.7770	2.3800	–	0.6640	–	0.1210	0.0210	–	–	0.0100
N95 (DEH)	85.9030	0.5890	1.4380	8.7660	2.3870	–	0.6690	–	0.1220	0.0210	–	–	0.1050
N96 (DEH)	75.2030	23.6960	0.1320	0.7830	0.0590	–	0.0180	–	0.0130	0.0080	–	–	0.0880
N97[e,f] (BUR)	64.8023	10.5646	12.3737	9.7844	1.7735	0.3716	0.1885	0.0541	0.0501	0.0227	0.0010	–	0.0135
N98[e,f] (OPT)	64.8023	10.5646	12.3737	9.7844	1.7735	0.3716	0.1885	0.0541	0.0501	0.0227	0.0010	–	0.0135
N99[e,f] (BUR)	59.0265	36.2145	0.8961	2.9194	0.6048	0.1229	0.0768	0.0346	0.0266	0.0258	0.0040	–	0.0480
N100[e,f] (OPT)	59.0265	36.2145	0.8961	2.9194	0.6048	0.1229	0.0768	0.0346	0.0266	0.0258	0.0040	–	0.0480
N101[e,f] (OPT)	47.2554	48.9495	0.7105	2.3419	0.4785	0.0980	0.0612	0.0262	0.0203	0.0202	0.0030	–	0.0353
N102[e,f] (BUR)	82.4733	0.5698	1.6892	11.6708	2.5719	0.5448	0.2775	0.0772	0.0752	0.0324	0.0030	–	0.0149
N103[e,f] (OPT)	82.4733	0.5698	1.6892	11.6708	2.5719	0.5448	0.2775	0.0772	0.0752	0.0324	0.0030	–	0.0149
N104 (OPT)	76.3370	0.5048	1.4003	18.9473	2.0863	0.3974	0.2033	0.0486	0.0472	0.0186	0.0009	–	0.0083
N105[e,f] (BUR)	65.8470	2.2860	26.6276	3.9360	0.8770	0.1710	0.1070	0.0442	0.0318	0.0281	–	–	0.0443
N106[e,f] (OPT)	65.8470	2.2860	26.6276	3.9360	0.8770	0.1710	0.1070	0.0442	0.0318	0.0281	–	–	0.0443
N107[e,f] (OPT)	79.3693	18.9654	0.5039	0.9616	0.0919	0.0179	0.0135	0.0104	0.0062	0.0053	–	–	0.0546
N108[e] (OPT)	79.9500	1.1265	1.0216	16.0145	1.3992	0.2598	0.1345	0.0348	0.0324	0.0152	0.0008	–	0.0107
N109[e,f] (OPT)	80.0420	3.0448	15.0437	1.4115	0.2997	0.0564	0.0356	0.0140	0.0110	0.0098	–	–	0.0315

Table A2.3 (continued)

Authors/Mixture	Composition (mole per cent)											
	CH_4	N_2	CO_2	C_2H_6	C_3H_8	n-C_4H_{10}	i-C_4H_{10}	n-C_5H_{12}	i-C_5H_{12}	n-C_6H_{14}	H_2[a]	CO[b]	Rest[s]
***pρT* data (continued)**													
GERG TM7 [Jaeschke *et al.* (1997)], N-file (natural gases and other multi-component mixtures)[c] (continued)													
N110 (OPT)	27.9285	29.8385	3.6880	0.4970	0.0676	0.0150	0.0020	0.0073	0.0007	0.0040	36.7585	1.0250	0.1679
N111[e] (OPT)	70.7555	13.1240	4.9420	0.9770	9.9210	0.1034	0.1320	0.0078	0.0083	0.0061	0.0019	–	0.0210
N112[e,f] (OPT)	81.0253	10.5126	1.1871	3.3305	0.6060	3.0997	0.0866	0.0367	0.0289	0.0277	–	–	0.0589
N113[e,f] (OPT)	79.5699	10.2928	1.1705	3.2772	5.3338	0.1202	0.0849	0.0357	0.0293	0.0267	–	–	0.0590
N114[e,f] (OPT)	76.8450	9.9330	1.1030	2.9580	8.8360	0.1040	0.0770	0.0333	0.0267	0.0259	–	–	0.0581
N115 (OPT)	81.5264	11.8050	1.1940	2.8280	0.6220	0.2080	0.0001	0.0720	0.0004	0.0220	–	–	1.7221
N116 (OPT)	28.8898	28.0000	2.0180	0.8380	0.1550	0.0710	–	0.0271	0.0003	0.0087	26.9920	13.0000	0.0001
Natural gases and other multi-component mixtures													
Assael *et al.* (2001b)	84.8400	5.6000	0.6600	8.4000	0.5000	–	–	–	–	–	–	–	–
Capla *et al.* (2002), M1	98.3520	0.8410	0.0660	0.5110	0.1530	0.0310	0.0210	0.0110	0.0080	0.0050	–	–	0.0010
Capla *et al.* (2002), M2	90.3620	1.4740	0.6470	5.7080	1.1240	0.1690	0.3010	0.0290	0.0590	0.0580	–	–	0.0690
Capla *et al.* (2002), M3	92.4360	5.7510	0.0520	1.2850	0.3480	0.0460	0.0410	0.0140	0.0150	0.0120	–	–	–
Duschek *et al.* (1989)[e,f]	84.3820	0.4161	1.9190	8.8710	3.1790	0.6589	0.3466	0.0910	0.0897	0.0317	0.0020	–	0.0130
Robinson & Jacoby (1965), M1[g]	49.0600	10.6600	10.1800	9.5500	10.2200	–	–	–	–	–	–	–	10.33[j]
Robinson & Jacoby (1965), M2	97.4000	0.9500	0.0400	1.5300	0.0800	–	–	–	–	–	–	–	–
Robinson & Jacoby (1965), M3	92.2200	0.8400	5.3600	1.4900	0.0900	–	–	–	–	–	–	–	–
Robinson & Jacoby (1965), M4	86.1600	0.8800	11.4600	1.4600	0.0400	–	–	–	–	–	–	–	–
Robinson & Jacoby (1965), M5	78.3000	0.5500	19.7200	1.3900	0.0400	–	–	–	–	–	–	–	–
Robinson & Jacoby (1965), M6	44.6000	0.2600	54.4600	0.6800	–	–	–	–	–	–	–	–	–
Robinson & Jacoby (1965), M7	75.5900	0.5000	22.3000	1.4000	0.2100	–	–	–	–	–	–	–	–
Robinson & Jacoby (1965), M8	69.9300	0.8200	28.1400	1.0600	0.0500	–	–	–	–	–	–	–	–
Robinson & Jacoby (1965), M9[g]	89.2600	0.9600	0.0800	1.5400	0.0700	–	–	–	–	–	–	–	8.09[j]
Robinson & Jacoby (1965), M10[g]	79.4800	0.7700	1.4400	1.5300	0.4800	–	–	–	–	–	–	–	16.30[j]
Robinson & Jacoby (1965), M11[g]	68.6800	0.6800	2.1000	1.1500	0.4300	–	–	–	–	–	–	–	26.96[j]
Robinson & Jacoby (1965), M12[g]	77.2600	0.7700	1.2700	1.3200	0.3900	–	–	–	–	–	–	–	18.99[j]
Robinson & Jacoby (1965), M13[g]	76.3000	0.2300	1.1800	1.2900	0.7300	–	–	–	–	–	–	–	20.27[j]
Robinson & Jacoby (1965), M14[g]	83.0300	0.8100	7.4400	1.3000	0.0700	–	–	–	–	–	–	–	7.35[j]

Table A2.3 (continued)

Authors/Mixture	Composition (mole per cent)												
	CH_4	N_2	CO_2	C_2H_6	C_3H_8	n-C_4H_{10}	i-C_4H_{10}	n-C_5H_{12}	i-C_5H_{12}	n-C_6H_{14}	H_2[a]	CO[b]	Rest[s]
***pρT* data (continued)**													
Natural gases and other multi-component mixtures (continued)													
Robinson & Jacoby (1965), M15[g]	67.9200	0.4100	15.5500	1.1100	0.1000	–	–	–	–	–	–	–	14.91[j]
Five-component synthetic natural gas mixture													
Ruhrgas (1999), Bu	80.0430	9.9500	1.9880	4.9980	3.0210	–	–	–	–	–	–	–	–
Ruhrgas (1999), Op	80.0430	9.9500	1.9880	4.9980	3.0210	–	–	–	–	–	–	–	–
RG-GDMA natural gas mixtures[r]													
Guo *et al.* (1990a), M1	90.6720	3.1280	0.4680	4.5290	0.8280	0.2600	–	0.0760	–	0.0390	–	–	–
Guo *et al.* (1990a), M2	85.8933	0.5898	1.6008	8.6968	2.4039	0.4483	0.2300	0.0531	0.0519	0.0214	0.0011	–	0.0096
Guo *et al.* (1990a), M3	81.2120	5.7020	7.5850	4.3030	0.8950	0.3030	–	–	–	–	–	–	–
Guo *et al.* (1990a), M4	96.5222	0.2595	0.5956	1.8186	0.4596	0.1984	–	0.0797	–	0.0664	–	–	–
Guo *et al.* (1990a), M5[e,f]	82.1255	12.0316	1.0869	3.6615	0.7067	0.1434	0.0968	0.0354	0.0307	0.0247	–	–	0.0568
Guo *et al.* (1990b), M1	81.4410	13.4650	0.9850	3.3000	0.6050	0.2040	–	–	–	–	–	–	–
Guo *et al.* (1990b), M2	85.8988	1.0293	1.4937	8.4873	2.2830	0.7119	–	0.0960	–	–	–	–	–
Guo *et al.* (1993), M1[e]	81.7329	3.7700	0.8010	3.5000	0.9150	0.1830	0.0970	0.0286	0.0260	0.0150	8.1100	0.8010	0.0205
Guo *et al.* (1993), M2[e,f]	83.3243	2.7520	7.3370	5.4910	0.7550	0.1460	0.0870	0.0285	0.0245	0.0175	0.0013	–	0.0359
Guo *et al.* (1993), M3[e,f]	83.1821	11.4800	1.1832	3.2393	0.5632	0.1092	0.0804	0.0339	0.0282	0.0272	0.0012	–	0.0721
Guo *et al.* (1993), M4[e]	85.4917	0.6535	1.6127	8.9402	2.3936	0.4817	0.2410	0.0700	0.0638	0.0342	0.0012	–	0.0164
Guo *et al.* (1993), M5[e]	88.0605	3.3697	1.5609	5.1911	1.2024	0.2515	0.1568	0.0636	0.0479	0.0386	0.0006	–	0.0564
Guo *et al.* (1993), M6	98.4435	0.8021	0.0340	0.4661	0.1631	0.0358	0.0281	0.0046	0.0064	0.0027	0.0003	–	0.0133
Kleinrahm *et al.* (1996), M1[e]	84.8802	0.7580	1.6632	9.3062	2.5296	0.4632	0.2342	0.0636	0.0604	0.0258	0.0027	–	0.0129
Kleinrahm *et al.* (1996), M2[e,f]	84.4668	10.1514	1.3018	3.1392	0.5539	0.1291	0.0868	0.0392	0.0338	0.0314	0.0004	–	0.0662
Rich natural gases													
Jaeschke & Schley (1998), RNG1	59.0129	4.9964	6.0059	9.9959	13.9931	5.9958	–	–	–	–	–	–	–
Jaeschke & Schley (1998), RNG2	58.9863	4.9985	5.9983	14.9991	10.0200	4.9978	–	–	–	–	–	–	–
Jaeschke & Schley (1998), RNG3	58.9976	4.9867	5.9920	18.0010	8.0180	3.2996	–	0.4947	–	0.2104	–	–	–
Jaeschke & Schley (1998), RNG4	60.0063	5.0134	5.9864	13.9839	10.0111	4.2898	–	0.5058	–	0.2033	–	–	–

Table A2.3 (continued)

Authors/Mixture	Composition (mole per cent)												
	CH_4	N_2	CO_2	C_2H_6	C_3H_8	n-C_4H_{10}	i-C_4H_{10}	n-C_5H_{12}	i-C_5H_{12}	n-C_6H_{14}	H_2^a	CO^b	Rest^s
***pρT* data (continued)**													
Rich natural gases (continued)													
Jaeschke & Schley (1998), RNG5	63.9757	2.0246	7.9923	11.9742	10.0102	3.3144	–	0.5074	–	0.2012	–	–	–
Jaeschke & Schley (1998), RNG6	57.9945	2.0178	13.9977	11.9898	9.9957	3.2983	–	0.4994	–	0.2068	–	–	–
Jaeschke & Schley (1998), RNG7	51.9810	2.0562	19.9859	11.9785	10.0038	3.3027	–	0.4948	–	0.1971	–	–	–
Watson & Millington (1998), RNG1	59.0013	5.0006	5.9924	9.9969	14.0265	5.9822	–	–	–	–	–	–	–
Watson & Millington (1998), RNG2	59.0055	4.9979	6.0177	15.0051	9.9949	4.9790	–	–	–	–	–	–	–
Watson & Millington (1998), RNG3	58.9899	5.0154	5.9757	18.0115	8.0037	3.2963	–	0.4919	–	0.2157	–	–	–
Watson & Millington (1998), RNG4	59.9917	4.9971	5.9955	14.0162	10.0007	4.3049	–	0.5018	–	0.1921	–	–	–
Watson & Millington (1998), RNG5	64.0068	1.9841	7.9953	12.0099	9.9945	3.3037	–	0.5065	–	0.1991	–	–	–
Watson & Millington (1998), RNG6	57.9937	2.0151	13.9975	11.9846	10.0054	3.2971	–	0.5057	–	0.2009	–	–	–
Watson & Millington (1998), RNG7-A	51.9924	1.9953	20.0098	12.0105	9.9855	3.3033	–	0.5016	–	0.2014	–	–	–
Watson & Millington (1998), RNG7-B	52.0035	2.0116	20.0028	11.9990	9.9881	3.3053	–	0.4980	–	0.1917	–	–	–

Authors/Mixture	Composition (mole per cent)												
	CH_4	N_2	CO_2	C_2H_6	C_3H_8	n-C_4H_{10}	i-C_4H_{10}	n-C_5H_{12}	i-C_5H_{12}	n-C_6H_{14}	n-C_7H_{16}	n-C_8H_{18}	Rest^s
Speed of sound													
Natural gases and other multi-component mixtures													
Blanke & Weiß (1986), M1	89.6788	3.3292	1.0398	4.0490	1.3097	0.2849	0.1410	0.0527	0.0466	0.0265	0.0127	–	0.0291
Blanke & Weiß (1986), M2	84.5038	13.3006	0.5920	1.4601	0.0613	0.0118	0.0129	0.0073	0.0038	0.0062	0.0022	–	0.0380
Blanke & Weiß (1986), M3	86.4160	8.0215	1.1102	3.6607	0.5161	0.0981	0.0590	0.0296	0.0228	0.0160	–	–	0.0500
Blanke & Weiß (1986), M4	81.2158	17.1033	0.4931	1.0502	0.0392	0.0075	0.0087	0.0055	0.0024	0.0032	0.0010	–	0.0700
Blanke & Weiß (1986), M5	82.6909	11.7235	1.0767	3.4252	0.7326	0.2522	–	0.0516	–	0.0303	0.0169	–	–
Blanke & Weiß (1986), M6	85.4207	5.6287	1.4847	5.3138	1.5294	0.4812	–	0.0909	–	0.0276	0.0230	–	–
Blanke & Weiß (1986), M7	81.8371	11.6507	1.3602	3.7926	0.8971	0.1898	0.1156	0.0353	0.0304	0.0259	0.0131	0.0078	0.0443
Blanke & Weiß (1986), M8	83.8939	6.0111	1.7374	5.8864	1.7645	0.5624	–	0.1023	–	0.0248	0.0171	–	–
Blanke & Weiß (1986), M9	83.3283	0.7387	1.9367	9.2044	3.5939	0.5990	0.2795	0.2596	–	0.0399	0.0200	–	–
Blanke & Weiß (1986), M10	80.0880	7.9088	3.5295	3.8194	3.0395	0.9019	0.4349	0.1270	0.1250	0.0260	–	–	–
Ewing & Goodwin (1993)	93.9610	0.7600	0.5480	4.4030	0.2630	0.0240	0.0170	0.0010	0.0060	0.0170	–	–	–

Table A2.3 (continued)

Authors/Mixture	Composition (mole per cent)												
	CH_4	N_2	CO_2	C_2H_6	C_3H_8	n-C_4H_{10}	i-C_4H_{10}	n-C_5H_{12}	i-C_5H_{12}	n-C_6H_{14}	n-C_7H_{16}	n-C_8H_{18}	Rest^s
Speed of sound (continued)													
Natural gases and other multi-component mixtures (continued)													
Fawcett (1995)	87.6450	1.2100	2.8700	5.4300	2.0500	0.4840	0.2970	0.0030	0.0110	–	–	–	–
Ingrain *et al.* (1993), M1	88.4050	3.1870	1.4900	5.1660	1.1760	0.2260	0.1490	0.0490	0.0560	0.0689	0.0223	0.0037	0.0011
Ingrain *et al.* (1993), M2	89.5690	0.4960	–	8.3480	1.1970	0.2260	0.1490	–	0.0150	–	–	–	–
Labes *et al.* (1994), M1	88.4050	3.1870	1.4900	5.1660	1.1760	0.2260	0.1490	0.0490	0.0560	0.0689	0.0223	0.0037	0.0011
Labes *et al.* (1994), M2	89.5690	0.4960	–	8.3480	1.1970	0.2260	0.1490	–	0.0150	–	–	–	–
Younglove *et al.* (1993), M1 (Gulf Coast)	96.5610	0.2620	0.5970	1.8290	0.4100	0.0980	0.0980	0.0320	0.0460	0.0670	–	–	–
Younglove *et al.* (1993), M2 (Amarillo)	90.7080	3.1130	0.5000	4.4910	0.8150	0.1410	0.1060	0.0650	0.0270	0.0340	–	–	–
Younglove *et al.* (1993), M3 (Statoil Dry)	83.9800	0.7180	0.7560	13.4750	0.9430	0.0670	0.0400	0.0080	0.0130	–	–	–	–
Younglove *et al.* (1993), M4 (Statfjord)	74.3480	0.5370	1.0280	12.0050	8.2510	3.0260	–	0.5750	–	0.2300	–	–	–
Five-component synthetic natural gas mixture													
Costa Gomes & Trusler (1998)	80.0510	9.9220	2.0000	5.0230	3.0040	–	–	–	–	–	–	–	–
Le Noë & Desentfant (1996), M1	80.0300	9.9530	2.0360	4.9990	3.0090	–	–	–	–	–	–	–	–
Le Noë & Desentfant (1996), M2	79.5120	10.0930	2.1890	5.2280	2.9780	–	–	–	–	–	–	–	–
Le Noë & Desentfant (1996), M3	80.0440	9.9350	2.0330	5.0000	2.9880	–	–	–	–	–	–	–	–
Le Noë & Desentfant (1996), M4	79.8950	9.9580	2.1040	5.0270	2.9870	–	–	–	–	–	–	–	–
Le Noë & Desentfant (1996), M5	80.0700	9.9200	1.9780	5.0170	3.0150	–	–	–	–	–	–	–	–
Le Noë & Desentfant (1996), M6	80.0660	9.9440	2.0370	4.9700	2.9830	–	–	–	–	–	–	–	–
Isobaric heat capacity													
Natural gases and other multi-component mixtures													
Trappehl (1987), M1	30.0000	60.0000	–	10.0000	–	–	–	–	–	–	–	–	–
Trappehl (1987), M2	60.0000	30.0000	–	10.0000	–	–	–	–	–	–	–	–	–
Trappehl (1987), M3	60.0000	30.0000	–	–	10.0000	–	–	–	–	–	–	–	–
Trappehl (1987), M4	–	85.0000	–	10.0000	5.0000	–	–	–	–	–	–	–	–
Trappehl (1987), M5	55.0000	25.0000	–	15.0000	5.0000	–	–	–	–	–	–	–	–
van Kasteren & Zeldenrust (1979), M1	89.9400	0.7800	–	4.5200	3.3500	0.6300	0.7400	0.0300	0.0100	–	–	–	–
van Kasteren & Zeldenrust (1979), M2	93.8000	0.3000	–	4.4000	1.2000	–	–	–	–	–	–	–	–

Table A2.3 (continued)

Authors/Mixture	Composition (mole per cent)												
	CH_4	N_2	CO_2	C_2H_6	C_3H_8	n-C_4H_{10}	i-C_4H_{10}	n-C_5H_{12}	i-C_5H_{12}	n-C_6H_{14}	n-C_7H_{16}	n-C_8H_{18}	Rest[s]
Isobaric heat capacity (continued)													
Five-component synthetic natural gas mixture													
Wirbser *et al.* (1996)	79.9420	9.9390	2.0900	5.0290	3.0000	–	–	–	–	–	–	–	–
Enthalpy differences													
Natural gases and other multi-component mixtures													
Ashton & Haselden (1980), M1[p]	91.0200	6.1600	–	2.3200	0.4200	0.0400	0.0300	–	–	–	–	–	–
Ashton & Haselden (1980), M2[p]	69.9900	27.2100	–	2.0300	0.5000	0.1400	0.1300	–	–	–	–	–	–
Ashton & Haselden (1980), M3[p]	75.6800	20.9400	–	2.5900	0.6100	0.0900	0.0700	–	–	–	–	–	–
Ashton & Haselden (1980), M4[p]	80.5000	15.5400	–	3.0400	0.7000	0.1100	0.1000	–	–	–	–	–	–
Banks & Haselden (1969)[p]	90.6900	3.9700	–	3.8600	1.1300	–	0.3500	–	–	–	–	–	–
Gregory *et al.* (1973)	95.7900	0.6000	–	3.0000	0.3900	0.0700	0.0700	0.0100	0.0300	0.0250	0.0150	–	–
Gregory *et al.* (1973)[p]	95.7900	0.6000	–	3.0000	0.3900	0.0700	0.0700	0.0100	0.0300	0.0250	0.0150	–	–
Grini *et al.* (1998)[h]	59.9910	10.0170	–	29.9920	–	–	–	–	–	–	–	–	–
Grini *et al.* (1998)[p]	59.9910	10.0170	–	29.9920	–	–	–	–	–	–	–	–	–
Lammers *et al.* (1978), M1[p]	89.9400	0.7800	–	4.5200	3.3500	0.6300	0.7400	0.0300	0.0100	–	–	–	–
Lammers *et al.* (1978), M2[p]	40.1000	10.8000	–	34.3000	14.8000	–	–	–	–	–	–	–	–
Laverman & Selculkoglu (1968)[p]	94.0000	1.7100	–	3.8600	0.3900	–	0.0400	–	–	–	–	–	–
Ng & Mather (1976), M1	42.3000	–	57.7000	–	–	–	–	–	–	–	–	–	–
Ng & Mather (1976), M2	14.5000	–	85.5000	–	–	–	–	–	–	–	–	–	–
Ng & Mather (1977), M1	33.3000	33.3000	33.4000	–	–	–	–	–	–	–	–	–	–
Ng & Mather (1977), M2	25.3000	25.4000	25.5000	23.6000	–	–	–	–	–	–	–	–	–
Ng & Mather (1978), M1	34.0000	–	33.5000	32.5000	–	–	–	–	–	–	–	–	–
Ng & Mather (1978), M2	51.4000	–	24.4000	24.2000	–	–	–	–	–	–	–	–	–
Powers *et al.* (1979)[p]	85.3000	–	–	9.0000	5.7000	–	–	–	–	–	–	–	–
Sood & Haselden (1972)[p]	95.4700	1.4200	–	2.5600	0.4600	0.0600	0.0400	–	–	–	–	–	–
Trappehl (1987), M1[h]	30.0000	60.0000	–	10.0000	–	–	–	–	–	–	–	–	–
Trappehl (1987), M1[p]	30.0000	60.0000	–	10.0000	–	–	–	–	–	–	–	–	–
Trappehl (1987), M2[h]	60.0000	30.0000	–	10.0000	–	–	–	–	–	–	–	–	–

Table A2.3 (continued)

Authors/Mixture	Composition (mole per cent)												
	CH_4	N_2	CO_2	C_2H_6	C_3H_8	n-C_4H_{10}	i-C_4H_{10}	n-C_5H_{12}	i-C_5H_{12}	n-C_6H_{14}	n-C_7H_{16}	n-C_8H_{18}	Rest^{s}
Enthalpy differences (continued)													
Natural gases and other multi-component mixtures (continued)													
Trappehl (1987), M2^{p}	60.0000	30.0000	–	10.0000	–	–	–	–	–	–	–	–	–
Trappehl (1987), M3^{h}	60.0000	30.0000	–	–	10.0000	–	–	–	–	–	–	–	–
Trappehl (1987), M3^{p}	60.0000	30.0000	–	–	10.0000	–	–	–	–	–	–	–	–
Trappehl (1987), M4^{h}	–	85.0000	–	10.0000	5.0000	–	–	–	–	–	–	–	–
Trappehl (1987), M4^{p}	–	85.0000	–	10.0000	5.0000	–	–	–	–	–	–	–	–
Trappehl (1987), M5^{h}	55.0000	25.0000	–	15.0000	5.0000	–	–	–	–	–	–	–	–
Trappehl (1987), M5^{p}	55.0000	25.0000	–	15.0000	5.0000	–	–	–	–	–	–	–	–
van Kasteren & Zeldenrust (1979), M1^{p}	89.9400	0.7800	–	4.5200	3.3500	0.6300	0.7400	0.0300	0.0100	–	–	–	–
van Kasteren & Zeldenrust (1979), M2^{p}	93.8000	0.3000	–	4.4000	1.2000	–	–	–	–	–	–	–	–
Wilson & Barton (1967)^{p}	91.3600	–	–	4.6700	2.0400	0.6400	0.5900	0.1200	0.2100	0.2000	0.1700	–	–
Five-component synthetic natural gas mixture													
Owren *et al.* (1996)^{h}	79.9690	9.9460	2.0130	5.0650	3.0070								
Owren *et al.* (1996)^{p}	79.9690	9.9460	2.0130	5.0650	3.0070	–	–	–	–	–	–	–	–
Saturated liquid density													
LNG-like and other multi-component mixtures													
Haynes (1982), M1	89.0710	5.9310	–	–	–	4.9980	–	–	–	–	–	–	–
Haynes (1982), M2	85.1330	–	–	5.7590	4.8080	4.3000	–	–	–	–	–	–	–
Haynes (1982), M3	84.5660	–	–	7.9240	5.0600	2.4500	–	–	–	–	–	–	–
Haynes (1982), M4	86.0400	–	–	4.6000	4.7900	–	4.5700	–	–	–	–	–	–
Haynes (1982), M5	85.3780	–	–	5.1780	4.7030	–	4.7410	–	–	–	–	–	–
Haynes (1982), M6	85.8920	–	–	11.5320	1.3410	0.7050	0.5300	–	–	–	–	–	–
Haynes (1982), M7	84.5580	–	–	8.1530	4.7780	1.2520	1.2590	–	–	–	–	–	–
Haynes (1982), M8	81.2490	2.6280	–	8.4840	4.9310	2.7080	–	–	–	–	–	–	–
Haynes (1982), M9	80.9400	4.8010	–	4.5420	5.0500	–	4.6670	–	–	–	–	–	–
Haynes (1982), M10	90.6130	0.6010	–	6.0260	2.1540	0.3060	0.3000	–	–	–	–	–	–
Haynes (1982), M11	88.2250	0.9730	–	7.2590	2.5610	0.4920	0.4900	–	–	–	–	–	–

Table A2.3 (continued)

Authors/Mixture	Composition (mole per cent)												
	CH_4	N_2	CO_2	C_2H_6	C_3H_8	$n\text{-}C_4H_{10}$	$i\text{-}C_4H_{10}$	$n\text{-}C_5H_{12}$	$i\text{-}C_5H_{12}$	$n\text{-}C_6H_{14}$	$n\text{-}C_7H_{16}$	$n\text{-}C_8H_{18}$	Rest[s]
Saturated liquid density (continued)													
LNG-like and other multi-component mixtures (continued)													
Haynes (1982), M12	85.9340	1.3830	–	8.4770	2.9800	0.7070	0.5190	–	–	–	–	–	–
Haynes (1982), M13	85.3410	–	–	7.8980	4.7290	0.9920	0.8540	0.0890	0.0970	–	–	–	–
Haynes (1982), M14	75.4420	–	–	15.4010	6.9500	1.0570	0.9780	0.0830	0.0890	–	–	–	–
Haynes (1982), M15	75.7130	0.8590	–	13.5850	6.7420	1.3260	1.3360	0.2160	0.2230	–	–	–	–
Haynes (1982), M16	74.2750	0.8010	–	16.5050	6.5470	0.8930	0.8430	0.0670	0.0690	–	–	–	–
Haynes (1982), M17	90.0680	0.5990	–	6.5370	2.2000	0.2840	0.2910	0.0110	0.0100	–	–	–	–
Hiza & Haynes (1980), M1	80.2840	–	–	9.9020	9.8140	–	–	–	–	–	–	–	–
Hiza & Haynes (1980), M2	34.2420	–	–	31.3720	34.3860	–	–	–	–	–	–	–	–
Hiza & Haynes (1980), M3	67.0400	16.3500	–	16.6100	–	–	–	–	–	–	–	–	–
Hiza & Haynes (1980), M4	34.1400	33.8000	–	32.0600	–	–	–	–	–	–	–	–	–
Hiza & Haynes (1980), M5	79.7700	9.9500	–	–	10.2800	–	–	–	–	–	–	–	–
Hiza & Haynes (1980), M6	85.2600	4.8400	–	4.8300	5.0700	–	–	–	–	–	–	–	–
Hiza & Haynes (1980), M7	85.4420	–	–	5.0420	4.0380	2.9010	2.5770	–	–	–	–	–	–
Hiza & Haynes (1980), M8	79.0900	5.5400	–	5.6000	5.0000	4.7700	–	–	–	–	–	–	–
Hiza & Haynes (1980), M9	80.6000	4.9000	–	4.6800	4.8200	–	5.0000	–	–	–	–	–	–
Hiza & Haynes (1980), M10	81.3000	4.2500	–	4.7500	4.8700	2.4200	2.4100	–	–	–	–	–	–
Vrabec & Fischer (1997)[v,z]	n/a	–	n/a	n/a	–	–	–	–	–	–	–	–	–

[a] Column H_2 only exists for $p\rho T$ data. For all other data types this column corresponds to n-C_7H_{16}.

[b] Column CO only exists for $p\rho T$ data. For all other data types this column corresponds to n-C_8H_{18}.

[c] Abbreviations for methods of measurement:

- ADH: Automatic Desgranges et Huot apparatus.
- BUR: Burnett apparatus.
- DEH: Desgranges et Huot Z-meter.
- DMA: Two-sinker method, Ruhr-Universität Bochum.
- EXP: Dantest expansion apparatus.
- GDM: Two-sinker method, Ruhrgas.
- IBU: Isochoric Burnett apparatus.

Table A2.3 (continued)

- OPT: Optical interferometry method.
- PYC: Pycnometer method.

[d] Abbreviations for mixtures of round-robin measurements [see Magee *et al.* (1997)]:

- GU1: Simulated NAM high-N_2 natural gas.
- GU2: Simulated high-CO_2 natural gas.
- RG2: Simulated Ekofisk natural gas.
- NIST1: Simulated Gulf Coast natural gas.
- NIST2: Simulated Amarillo natural gas.

[e] Mixture contains small fractions of n-nonane.

[f] Mixture contains small fractions of n-decane.

[g] Mixture contains high fractions of hydrogen sulphide.

[h] Isenthalpic measurements.

[j] Hydrogen sulphide.

[p] Isobaric measurements.

[r] Data were measured at Ruhrgas using a two-sinker densimeter.

[s] Sum of components not explicitly listed in the table (n-C_7H_{16}, n-C_8H_{18}, H_2O, O_2, Ar, He, n-nonane, n-decane, and hydrogen sulphide), unless otherwise stated.

[v] Various compositions.

[z] Calculated data.

Table A2.4 Supplementary data sets for thermal properties of ternary and quaternary mixtures used for the evaluation of the new equation of state (GERG-2004), Eqs. (7.1) – (7.10), and statistical analysis

Authors	N_P[a]	Covered ranges Temperature T/K	Pressure p/MPa	N_C[b]	M[m] g·mol^{-1}	Statistical analysis[n] N_1 %	N_2 %	AAD$_1$ %	AAD$_2$ %	Bias$_1$ %	Bias$_2$ %	RMS$_1$ %	RMS$_2$ %	MaxD$_1$ %	MaxD$_2$ %
***pρT* data**															
CH_4–N_2–CO_2						**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA
Seitz *et al.* (1996b), M1	16	323 – 573	19.9 – 99.9	3	28.416	16	16	0.367	0.363	0.334	0.043	0.442	0.428	1.089	1.005
Seitz *et al.* (1996b), M2	13	323 – 573	19.9 – 99.9	3	26.022	13	13	0.414	0.331	0.409	0.153	0.469	0.422	0.789	0.797
Seitz *et al.* (1996b), M3	14	323 – 573	19.9 – 99.9	3	22.430	14	14	0.711	0.619	0.711	0.559	0.797	0.734	1.446	1.433
Seitz *et al.* (1996b), M4	14	323 – 573	19.9 – 99.9	3	20.036	14	14	0.823	0.756	0.817	0.717	0.920	0.869	1.513	1.475
Seitz *et al.* (1996b), M5	16	323 – 573	19.9 – 99.9	3	28.818	16	16	0.405	0.389	0.386	0.057	0.453	0.468	0.769	−0.839
Seitz *et al.* (1996b), M6	16	323 – 573	19.9 – 99.9	3	26.424	16	16	0.452	0.522	0.363	0.160	0.521	0.573	0.900	0.980
Seitz *et al.* (1996b), M7	15	323 – 573	19.9 – 99.9	3	24.030	15	15	0.524	0.563	0.492	0.361	0.625	0.658	1.094	1.172
Seitz *et al.* (1996b), M8	14	323 – 573	19.9 – 99.9	3	31.615	14	14	0.280	0.455	0.218	−0.274	0.349	0.576	0.654	−1.185
Seitz *et al.* (1996b), M9	16	323 – 573	19.9 – 99.9	3	29.221	16	16	0.321	0.410	0.319	0.086	0.372	0.476	0.650	−0.894
Seitz *et al.* (1996b), M10	16	323 – 573	19.9 – 99.9	3	28.024	16	16	0.391	0.534	0.357	0.197	0.485	0.615	1.147	1.323
Seitz *et al.* (1996b), M11	14	323 – 573	19.9 – 99.9	3	25.630	14	14	0.420	0.554	0.350	0.223	0.550	0.655	1.370	1.536
Seitz *et al.* (1996b), M12	16	323 – 573	19.9 – 99.9	3	32.018	16	16	0.279	0.518	0.192	−0.103	0.335	0.635	0.645	−1.270
Seitz *et al.* (1996b), M13	15	323 – 573	19.9 – 99.9	3	30.821	15	15	0.317	0.577	0.055	−0.157	0.365	0.658	0.705	−1.043
Seitz *et al.* (1996b), M14	16	323 – 573	19.9 – 99.9	3	29.624	16	16	0.228	0.457	0.139	0.031	0.278	0.511	0.559	0.792
Seitz *et al.* (1996b), M15	14	323 – 573	19.9 – 99.9	3	36.414	14	14	0.228	0.667	−0.028	−0.523	0.260	0.858	−0.465	−1.600
Seitz *et al.* (1996b), M16	16	323 – 573	19.9 – 99.9	3	35.217	16	16	0.278	0.598	−0.120	−0.328	0.315	0.755	−0.489	−1.341
Seitz *et al.* (1996b), M17	15	323 – 573	19.9 – 99.9	3	34.020	15	15	0.167	0.506	−0.068	−0.198	0.202	0.597	−0.386	−1.015
Seitz *et al.* (1996b), M18	15	323 – 573	19.9 – 99.9	3	39.613	15	15	0.220	0.573	−0.175	−0.500	0.272	0.711	−0.563	−1.502
CH_4–N_2–C_2H_6						**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA
Boomer *et al.* (1938b)	6	298	0.1 – 17.1	3	17.216	6	6	0.562	0.571	0.089	0.100	0.673	0.680	−1.088	−1.087
						EqG	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP
Pan *et al.* (1975)	4	91.0 – 115	0.05 – 0.2	3	17.816	4	4	0.209	11.979	0.209	−11.979	0.260	11.981	0.475	−12.138
Rodosevich & Miller (1973)	4	91.0 – 115	0.07 – 0.3	3	18.170	4	4	0.076	12.046	0.076	−12.046	0.078	12.046	0.093	−12.099

Table A2.4 (continued)

Authors	N_P[a]	Covered ranges		N_C[b]	M[m]	Statistical analysis[n]									
		Temperature T/K	Pressure p/MPa		g·mol^{-1}	N_1 %	N_2 %	AAD$_1$ %	AAD$_2$ %	Bias$_1$ %	Bias$_2$ %	RMS$_1$ %	RMS$_2$ %	MaxD$_1$ %	MaxD$_2$ %
***pρT* data (continued)**															
CH_4–N_2–C_3H_8						**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP
Rodosevich & Miller (1973)	2	91.0 – 108	0.07 – 0.2	3	17.972	2	2	0.077	11.896	0.077	−11.896	0.079	11.896	0.097	−11.932
CH_4–N_2–n-C_6H_{14}						**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA
Jaeschke *et al.* (1997)	158	270 – 350	0.5 – 12.8	3	16.108	158	158	0.028	0.027	0.024	0.011	0.037	0.041	0.107	0.177
Watson & Millington (1998)	46	314 – 353	7.9 – 17.8	3	17.823	46	46	0.031	0.127	−0.031	−0.117	0.035	0.142	−0.083	−0.253
CH_4–N_2–H_2						**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA
Kritschewsky & Levchenko (1941), M1	35	273 – 473	10.1 – 70.9	3	16.208	35	35	1.061	1.005	0.523	0.605	1.285	1.240	3.043	2.989
Kritschewsky & Levchenko (1941), M2	35	273 – 473	10.1 – 70.9	3	15.878	35	35	0.788	0.722	−0.619	−0.504	0.956	0.824	−2.089	−1.627
Kritschewsky & Levchenko (1941), M3	35	273 – 473	10.1 – 70.9	3	19.222	35	35	0.678	0.629	0.407	0.476	0.820	0.765	−2.010	−1.952
Mueller *et al.* (1961), M1	75	144 – 283	0.4 – 49.6	3	13.242	75	75	0.614	0.649	−0.351	−0.430	1.111	1.180	−3.658	−3.315
Mueller *et al.* (1961), M2	83	144 – 283	0.6 – 49.6	3	11.150	83	83	0.608	0.630	−0.365	−0.499	0.855	0.926	4.708	4.139
Mueller *et al.* (1961), M3	85	144 – 283	0.7 – 48.3	3	8.126	85	85	0.959	0.948	−0.958	−0.948	1.846	1.708	−7.492	−6.543
Mueller *et al.* (1961), M4	189	144 – 283	0.7 – 48.3	3	5.115	189	189	0.948	0.938	−0.948	−0.938	1.766	1.688	−8.692	−8.853
CH_4–CO_2–C_2H_6						**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA
Hou *et al.* (1996), M1	43	300 – 320	0.1 – 6.4	3	30.272	43	43	0.335	0.291	−0.335	−0.291	0.563	0.457	−2.071	−1.523
Hou *et al.* (1996), M2	43	300 – 320	0.1 – 6.4	3	29.278	43	43	0.081	0.053	−0.081	−0.053	0.145	0.083	−0.470	−0.360
McElroy *et al.* (2001), M1	10	283	0.7 – 5.8	3	30.742	10	10	0.902	0.551	−0.902	−0.551	1.002	0.563	−1.803	−0.743
McElroy *et al.* (2001), M2	10	293	0.7 – 6.1	3	30.473	10	10	0.352	0.210	−0.323	−0.110	0.476	0.248	−1.079	−0.385
McElroy *et al.* (2001), M3	10	303	1.0 – 6.5	3	30.192	10	10	0.629	0.476	−0.629	−0.476	0.691	0.512	−1.121	−0.757
McElroy *et al.* (2001), M4	11	313	0.8 – 8.6	3	31.370	10	10	0.966	0.853	−0.966	−0.853	0.998	0.867	−1.320	−1.045
McElroy *et al.* (2001), M5	11	323	0.8 – 7.5	3	30.243	11	11	2.184	2.139	−2.184	−2.139	2.219	2.181	−3.302	−3.312
McElroy *et al.* (2001), M6	9	333	1.1 – 7.0	3	29.928	9	9	0.402	0.412	−0.402	−0.412	0.427	0.434	−0.606	−0.579
CH_4–C_2H_6–C_3H_8						**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP
Pan *et al.* (1975)	4	91.0 – 115	0.03 – 0.1	3	18.893	4	4	0.010	11.066	0.010	−11.066	0.015	11.067	0.029	−11.210
Rodosevich & Miller (1973)	4	100 – 115	0.05 – 0.1	3	18.908	4	4	0.048	11.109	0.048	−11.109	0.050	11.109	0.069	−11.144

Table A2.4 (continued)

Authors	N_P[a]	Covered ranges		N_C[b]	M[m]	Statistical analysis[n]									
		Temperature T/K	Pressure p/MPa		g·mol^{-1}	N_1 %	N_2 %	AAD$_1$ %	AAD$_2$ %	Bias$_1$ %	Bias$_2$ %	RMS$_1$ %	RMS$_2$ %	MaxD$_1$ %	MaxD$_2$ %
***pρT* data (continued)**															
CH_4–C_2H_6–C_3H_8 (continued)						**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP
Shana'a & Canfield (1968), M1	1	108	0.04	3	28.689	1	1	0.225	6.958	−0.225	−6.958	0.225	6.958	−0.225	−6.958
Shana'a & Canfield (1968), M2	1	108	0.06	3	21.451	1	1	0.161	9.655	0.161	−9.655	0.161	9.655	0.161	−9.655
CH_4–C_3H_8–n-C_6H_{14}						**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA
May *et al.* (2001), M1	22	281 – 313	2.1 – 10.2	3	18.680	22	22	0.316	0.487	−0.309	−0.487	0.359	0.522	−0.629	−0.810
May *et al.* (2001), M2	10	289 – 298	1.9 – 10.1	3	18.062	10	10	0.348	0.540	−0.332	−0.540	0.485	0.632	−1.314	−1.425
May *et al.* (2002), M1	21	294 – 313	2.1 – 10.2	3	18.680	21	21	0.309	0.475	−0.297	−0.471	0.354	0.512	−0.631	−0.812
May *et al.* (2002), M2	9	298	1.9 – 10.1	3	18.062	9	9	0.382	0.568	−0.365	−0.568	0.519	0.665	−1.324	−1.435
N_2–CO_2–H_2						**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA	**EqG**	EqA
Kritschewsky & Markov (1940), M1	30	273 – 473	5.1 – 50.7	3	25.151	30	30	2.321	1.739	2.321	1.625	2.519	2.133	5.264	5.105
Kritschewsky & Markov (1940), M2	30	273 – 473	5.1 – 50.7	3	17.406	29	29	2.084	1.580	2.084	1.580	2.204	1.775	3.692	3.253
Kritschewsky & Markov (1940), M3	30	273 – 473	5.1 – 50.7	3	23.859	30	30	1.914	1.571	1.914	1.571	1.993	1.669	2.672	2.661
CO_2–C_3H_8–n-C_5H_{12}–n-C_8H_{18}						**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP
Barrufet & Rahman (1997)	30	311 – 394	3.1 – 6.4	4	n/a[v]	27	30	5.246	4.785	3.834	1.895	5.657	5.993	8.652	−15.365
C_3H_8–n-C_4H_{10}–i-C_4H_{10}						**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP
Kayukawa *et al.* (2005a), M1	101	240 – 380	0.5 – 7.1	3	55.317	101	101	0.131	4.481	0.119	−4.267	0.138	4.808	−0.241	−6.065
Kayukawa *et al.* (2005a), M2	100	240 – 380	0.5 – 7.1	3	53.353	100	100	0.060	4.761	−0.045	−4.443	0.132	5.133	−0.781	−6.557
Kayukawa *et al.* (2005a), M3	94	240 – 380	0.2 – 7.1	3	49.706	94	94	0.110	4.850	−0.073	−4.277	0.255	5.221	−1.602	−6.756
Kayukawa *et al.* (2005a), M1[s]	8	240 – 380	0.1 – 2.3	3	55.317	8	8	0.100	4.041	0.044	−2.932	0.116	4.419	−0.223	−5.748
Kayukawa *et al.* (2005a), M2[s]	8	240 – 380	0.1 – 2.8	3	53.353	8	8	0.154	4.490	−0.153	−2.729	0.272	4.858	−0.734	−6.185
Kayukawa *et al.* (2005a), M3[s]	8	240 – 380	0.1 – 3.5	3	49.706	8	8	0.217	4.953	−0.204	−1.712	0.359	5.602	−0.849	9.807
C_3H_8–n-C_5H_{12}–n-C_8H_{18}						**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP
Barrufet & Rahman (1997)	4	297 – 394	2.0 – 2.7	3	67.778	4	4	2.559	2.299	2.559	−0.608	2.714	2.490	3.970	3.382

Table A2.4 (continued)

Authors	N_P[a]	Covered ranges		N_C[b]	M[m]	Statistical analysis[n]									
		Temperature T/K	Pressure p/MPa		g·mol^{-1}	N_1 %	N_2 %	AAD$_1$ %	AAD$_2$ %	Bias$_1$ %	Bias$_2$ %	RMS$_1$ %	RMS$_2$ %	MaxD$_1$ %	MaxD$_2$ %
***pρT* data (continued)**															
n-C_5H_{12}–n-C_6H_{14}–n-C_7H_{16}						**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP
Pecar & Dolecek (2003), M1	15	298 – 348	0.1 – 40.0	3	91.506	15	15	0.103	0.929	0.097	−0.929	0.121	1.103	0.221	−1.911
Pecar & Dolecek (2003), M2	15	298 – 348	0.1 – 40.0	3	93.133	15	15	0.105	0.693	0.105	−0.671	0.121	0.892	0.208	−1.631
Pecar & Dolecek (2003), M3	15	298 – 348	0.1 – 40.0	3	87.971	15	15	0.093	1.479	0.069	−1.479	0.111	1.598	0.244	−2.481
Pecar & Dolecek (2003), M4	15	298 – 348	0.1 – 40.0	3	86.161	15	15	0.073	1.771	0.027	−1.771	0.090	1.869	0.178	−2.777
Pecar & Dolecek (2003), M5	15	298 – 348	0.1 – 40.0	3	89.668	15	15	0.120	1.185	0.117	−1.185	0.144	1.331	0.292	−2.179
Pecar & Dolecek (2003), M6	15	298 – 348	0.1 – 40.0	3	94.633	15	15	0.106	0.567	0.106	−0.434	0.117	0.725	0.201	−1.374
Pecar & Dolecek (2003), M7	15	298 – 348	0.1 – 40.0	3	87.817	15	15	0.176	1.428	0.176	−1.428	0.194	1.550	0.350	−2.421
Pecar & Dolecek (2003), M8	15	298 – 348	0.1 – 40.0	3	91.520	15	15	0.243	0.802	0.243	−0.796	0.253	0.996	0.373	−1.785
Pecar & Dolecek (2003), M9	15	298 – 348	0.1 – 40.0	3	84.464	15	15	0.106	1.997	0.097	−1.997	0.129	2.086	0.258	−3.028
Pecar & Dolecek (2003), M10	15	298 – 348	0.1 – 40.0	3	89.626	15	15	0.242	1.094	0.242	−1.094	0.258	1.255	0.434	−2.104
Pecar & Dolecek (2003), M11	15	298 – 348	0.1 – 40.0	3	86.105	15	15	0.123	1.743	0.121	−1.743	0.143	1.841	0.251	−2.745
Pecar & Dolecek (2003), M12	15	298 – 348	0.1 – 40.0	3	85.965	15	15	0.306	1.607	0.306	−1.607	0.311	1.702	0.415	−2.535
Pecar & Dolecek (2003), M13	15	298 – 348	0.1 – 40.0	3	84.422	15	15	0.288	1.856	0.288	−1.856	0.308	1.954	0.482	−2.907
Pecar & Dolecek (2003), M14	15	298 – 348	0.1 – 40.0	3	82.669	15	15	0.184	2.214	0.184	−2.214	0.199	2.295	0.338	−3.246
Pecar & Dolecek (2003), M15	15	298 – 348	0.1 – 40.0	3	87.929	15	15	0.302	1.307	0.302	−1.307	0.311	1.439	0.427	−2.320
Pecar & Dolecek (2003), M16	15	298 – 348	0.1 – 40.0	3	80.958	15	15	0.211	2.472	0.211	−2.472	0.227	2.551	0.376	−3.558
Pecar & Dolecek (2003), M17	15	298 – 348	0.1 – 40.0	3	82.711	15	15	0.313	2.110	0.313	−2.110	0.323	2.199	0.477	−3.167
Pecar & Dolecek (2003), M18	15	298 – 348	0.1 – 40.0	3	84.394	15	15	0.344	1.821	0.344	−1.821	0.352	1.918	0.462	−2.856
Pecar & Dolecek (2003), M19	15	298 – 348	0.1 – 40.0	3	79.176	14	15	0.243	2.616	0.243	−2.616	0.259	2.770	0.414	−3.853
Pecar & Dolecek (2003), M20	15	298 – 348	0.1 – 40.0	3	80.887	15	15	0.334	2.378	0.334	−2.378	0.343	2.461	0.459	−3.473
Pecar & Dolecek (2003), M21	15	298 – 348	0.1 – 40.0	3	77.493	15	15	0.272	2.967	0.272	−2.967	0.279	3.040	0.409	−4.080

Table A2.4 (continued)

Authors	N_P[a]	Covered ranges Temperature T/K	 Pressure p/MPa	N_C[b]	M[m] g·mol^{-1}	 N_1 %	 N_2 %	 AAD$_1$ %	 AAD$_2$ %	Statistical analysis[n] Bias$_1$ %	 Bias$_2$ %	 RMS$_1$ %	 RMS$_2$ %	 MaxD$_1$ %	 MaxD$_2$ %
VLE data						**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP
CH_4–N_2–CO_2															
Xu *et al.* (1992)	53	293	6.0 – 8.3	3		52	50	1.473	0.911	−1.423	0.105	1.823	1.200	−4.328	2.660
CH_4–N_2–Ar															
Jin *et al.* (1993)	9	123	0.7 – 2.4	3		9	9	1.309	0.635	1.309	0.530	1.456	1.037	2.863	2.892
Miller *et al.* (1973)[c,d]	28	112	0.2 – 1.3	3		27	27	0.544	0.993	−0.242	−0.814	0.819	1.150	−2.603	−2.597
CH_4–CO_2–C_2H_6															
Davalos *et al.* (1976)[d]	21	250	2.1 – 3.0	3		21	21	1.444	1.781	1.216	1.492	2.145	2.394	6.397	7.108
Wei *et al.* (1995)	84	230	1.2 – 6.6	3		83	78	1.362	2.154	−0.307	2.122	1.621	2.418	−3.861	6.132
CH_4–CO_2–C_3H_8															
Webster & Kidnay (2001)[c,d]	63	230 – 270	0.8 – 8.0	3		62	61	1.671	1.460	−1.353	0.767	2.166	1.853	−5.687	4.428
N_2–CO_2–C_3H_8															
Yucelen & Kidnay (1999)[c,d]	47	240 – 330	2.0 – 13.0	3		44	43	5.010	5.574	−0.250	−1.582	7.026	8.825	−18.458	−25.271
N_2–CO_2–n-C_4H_{10}															
Brown *et al.* (1994)[d]	76	250 – 270	1.5 – 14.0	3		75	74	8.814	3.041	8.132	1.707	10.412	3.850	19.332	9.803
Shibata & Sandler (1989)	45	311 – 411	3.4 – 27.6	3		40	38	6.545	3.883	6.545	1.972	7.323	4.562	14.274	−10.508
N_2–O_2–Ar															
Fastovskii & Petrovskii (1957b)	14	81.2 – 88.2	0.12	3		14	14	0.586	1.118	0.352	−0.995	0.842	1.344	2.507	−2.542
Funada *et al.* (1982)	60	90.0 – 90.2	0.10	3		60	60	0.302	0.308	−0.109	−0.124	0.398	0.402	1.234	1.192
Narinskii (1969)	115	81.5 – 120	0.1 – 2.2	3		115	114	0.545	1.142	−0.377	−1.105	0.871	1.328	−4.747	−4.149
Weishaupt (1948)	41	80.5 – 91.8	0.13	3		41	39	1.634	2.378	−1.634	−2.378	1.880	2.555	−4.925	−4.332
Wilson *et al.* (1965)	999	77.8 – 130	0.1 – 1.8	3		996	975	0.901	1.376	−0.871	−1.351	1.185	1.640	−4.637	−4.976
Wilson *et al.* (1965)[d]	428	114 – 136	1.8 – 2.6	3		428	428	0.451	1.022	−0.366	−1.008	0.556	1.100	−2.487	−2.860

Table A2.4 (continued)

Authors	N_P[a]	Covered ranges		N_C[b]	M[m]	Statistical analysis[n]									
		Temperature T/K	Pressure p/MPa		g·mol^{-1}	N_1 %	N_2 %	AAD$_1$ %	AAD$_2$ %	Bias$_1$ %	Bias$_2$ %	RMS$_1$ %	RMS$_2$ %	MaxD$_1$ %	MaxD$_2$ %
VLE data (continued)						**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP	**EqG**	EqP
CO_2–C_3H_8–n-C_5H_{12}–n-C_8H_{18}															
Barrufet & Rahman (1997)	15	311 – 394	3.1 – 6.4	4		15	15	4.509	12.754	−4.271	12.754	5.543	13.316	−10.622	18.213
C_2H_6–C_3H_8–n-C_4H_{10}															
Lhoták & Wichterle (1983)	59	305 – 306	0.7 – 4.9	3		52	40	1.278	1.916	−0.218	−1.110	2.098	2.770	9.417	8.511
C_2H_6–n-C_4H_{10}–n-C_7H_{16}															
Mehra & Thodos (1966)[c,d]	73	339 – 394	3.1 – 8.2	3		73	71	3.356	3.359	−1.744	1.577	4.711	4.038	14.521	−10.888
Mehra & Thodos (1968)[c,d]	54	422 – 450	3.5 – 8.3	3		50	52	2.684	4.476	−0.450	3.053	4.019	5.031	−13.292	−10.976

[a] Number of data points.

[b] Number of components.

[c] VLE data set also contains pTx data.

[d] VLE data set also contains pTy data.

[m] Molar mass. Values were calculated from the mixture compositions using the atomic weights according to Wieser (2006).

[n] Nomenclature of the statistical analysis:

- N: Number of data points used for the statistical analysis.
- AAD: Average absolute deviation.
- Bias: Average deviation.
- RMS: Root-mean-squared deviation.
- MaxD: Maximum deviation.
- EqG: GERG-2004 equation of state.
- EqA: AGA8-DC92 equation of state of Starling and Savidge (1992) (used for comparison with GERG-2004 for properties in the homogeneous gas phase only).
- EqP: Cubic equation of state of Peng and Robinson (1976) (used for comparison with GERG-2004 for liquid and saturated liquid densities and VLE properties).

Subscripts:

- 1: GERG-2004 equation of state (EqG).
- 2: AGA8-DC92 equation of state of Starling and Savidge (1992) (EqA) or cubic equation of state of Peng and Robinson (1976) (EqP).

Notes:

- The AGA8-DC92 equation of state of Starling and Savidge (1992) is not valid for the liquid phase and saturated/VLE properties.

Table A2.4 (continued)

- Density deviations are tabulated for $p\rho T$ data.
- Vapour pressure deviations are tabulated for VLE data.

[s] Saturated liquid densities.

[v] No explicit molar mass due to a varying composition.

Note

The tabulated VLE data sets contain $pTxy$ data only, unless otherwise stated.

Table A2.5 Mixture compositions of the supplementary $p\rho T$ data sets for ternary and quaternary mixtures listed in Table A2.4

Authors	Composition (mole per cent)												
	CH_4	N_2	CO_2	C_2H_6	C_3H_8	$n\text{-}C_4H_{10}$	$i\text{-}C_4H_{10}$	$n\text{-}C_5H_{12}$	$i\text{-}C_5H_{12}$	$n\text{-}C_6H_{14}$	$n\text{-}C_7H_{16}$	$n\text{-}C_8H_{18}$	H_2
***pρT* data**													
CH_4–N_2–CO_2													
Seitz *et al.* (1996b), M1	10.0000	80.0000	10.0000	–	–	–	–	–	–	–	–	–	–
Seitz *et al.* (1996b), M2	30.0000	60.0000	10.0000	–	–	–	–	–	–	–	–	–	–
Seitz *et al.* (1996b), M3	60.0000	30.0000	10.0000	–	–	–	–	–	–	–	–	–	–
Seitz *et al.* (1996b), M4	80.0000	10.0000	10.0000	–	–	–	–	–	–	–	–	–	–
Seitz *et al.* (1996b), M5	20.0000	60.0000	20.0000	–	–	–	–	–	–	–	–	–	–
Seitz *et al.* (1996b), M6	40.0000	40.0000	20.0000	–	–	–	–	–	–	–	–	–	–
Seitz *et al.* (1996b), M7	60.0000	20.0000	20.0000	–	–	–	–	–	–	–	–	–	–
Seitz *et al.* (1996b), M8	10.0000	60.0000	30.0000	–	–	–	–	–	–	–	–	–	–
Seitz *et al.* (1996b), M9	30.0000	40.0000	30.0000	–	–	–	–	–	–	–	–	–	–
Seitz *et al.* (1996b), M10	40.0000	30.0000	30.0000	–	–	–	–	–	–	–	–	–	–
Seitz *et al.* (1996b), M11	60.0000	10.0000	30.0000	–	–	–	–	–	–	–	–	–	–
Seitz *et al.* (1996b), M12	20.0000	40.0000	40.0000	–	–	–	–	–	–	–	–	–	–
Seitz *et al.* (1996b), M13	30.0000	30.0000	40.0000	–	–	–	–	–	–	–	–	–	–
Seitz *et al.* (1996b), M14	40.0000	20.0000	40.0000	–	–	–	–	–	–	–	–	–	–
Seitz *et al.* (1996b), M15	10.0000	30.0000	60.0000	–	–	–	–	–	–	–	–	–	–
Seitz *et al.* (1996b), M16	20.0000	20.0000	60.0000	–	–	–	–	–	–	–	–	–	–
Seitz *et al.* (1996b), M17	30.0000	10.0000	60.0000	–	–	–	–	–	–	–	–	–	–
Seitz *et al.* (1996b), M18	10.0000	10.0000	80.0000	–	–	–	–	–	–	–	–	–	–
CH_4–N_2–C_2H_6													
Boomer *et al.* (1938b)	90.8000	5.7000	–	3.5000	–	–	–	–	–	–	–	–	–
Pan *et al.* (1975)	86.7500	4.1600	–	9.0900	–	–	–	–	–	–	–	–	–
Rodosevich & Miller (1973)	84.0900	5.0500	–	10.8600	–	–	–	–	–	–	–	–	–
CH_4–N_2–C_3H_8													
Rodosevich & Miller (1973)	90.5591	4.4704	–	–	4.9705	–	–	–	–	–	–	–	–

Table A2.5 (continued)

Authors	Composition (mole per cent)												
	CH_4	N_2	CO_2	C_2H_6	C_3H_8	n-C_4H_{10}	i-C_4H_{10}	n-C_5H_{12}	i-C_5H_{12}	n-C_6H_{14}	n-C_7H_{16}	n-C_8H_{18}	H_2
***pρT* data (continued)**													
CH_4–N_2–n-C_6H_{14}													
Jaeschke *et al.* (1997)	99.9026	0.0050	–	–	–	–	–	–	–	0.0924	–	–	–
Watson & Millington (1998)	89.9886	9.0110	–	–	–	–	–	–	–	1.0004	–	–	–
CH_4–N_2–H_2													
Kritschewsky & Levchenko (1941), M1	52.6600	26.1800	–	–	–	–	–	–	–	–	–	–	21.1600
Kritschewsky & Levchenko (1941), M2	39.7000	31.9000	–	–	–	–	–	–	–	–	–	–	28.4000
Kritschewsky & Levchenko (1941), M3	19.8000	55.5000	–	–	–	–	–	–	–	–	–	–	24.7000
Mueller *et al.* (1961), M1	79.4795	0.3003	–	–	–	–	–	–	–	–	–	–	20.2202
Mueller *et al.* (1961), M2	64.5646	0.3003	–	–	–	–	–	–	–	–	–	–	35.1351
Mueller *et al.* (1961), M3	43.1864	0.2004	–	–	–	–	–	–	–	–	–	–	56.6132
Mueller *et al.* (1961), M4	21.7217	0.2002	–	–	–	–	–	–	–	–	–	–	78.0781
CH_4–CO_2–C_2H_6													
Hou *et al.* (1996), M1	32.1250	–	33.7760	34.0990	–	–	–	–	–	–	–	–	–
Hou *et al.* (1996), M2	24.7560	–	19.2310	56.0130	–	–	–	–	–	–	–	–	–
McElroy *et al.* (2001), M1	32.3800	–	37.4100	30.2100	–	–	–	–	–	–	–	–	–
McElroy *et al.* (2001), M2	33.0900	–	36.1900	30.7200	–	–	–	–	–	–	–	–	–
McElroy *et al.* (2001), M3	33.6700	–	34.7600	31.5700	–	–	–	–	–	–	–	–	–
McElroy *et al.* (2001), M4	30.6400	–	40.1600	29.2000	–	–	–	–	–	–	–	–	–
McElroy *et al.* (2001), M5	33.2400	–	34.6900	32.0700	–	–	–	–	–	–	–	–	–
McElroy *et al.* (2001), M6	32.7400	–	31.9300	35.3300	–	–	–	–	–	–	–	–	–
CH_4–C_2H_6–C_3H_8													
Pan *et al.* (1975)	84.8000	–	–	10.0800	5.1200	–	–	–	–	–	–	–	–
Rodosevich & Miller (1973)	84.6600	–	–	10.2500	5.0900	–	–	–	–	–	–	–	–
Shana'a & Canfield (1968), M1	38.8400	–	–	32.1600	29.0000	–	–	–	–	–	–	–	–
Shana'a & Canfield (1968), M2	72.3800	–	–	16.6800	10.9400	–	–	–	–	–	–	–	–

Table A2.5 (continued)

Authors	Composition (mole per cent)												
	CH_4	N_2	CO_2	C_2H_6	C_3H_8	n-C_4H_{10}	i-C_4H_{10}	n-C_5H_{12}	i-C_5H_{12}	n-C_6H_{14}	n-C_7H_{16}	n-C_8H_{18}	H_2
pρT **data (continued)**													
CH_4–C_3H_8–n-C_6H_{14}													
May *et al.* (2001), M1	91.5000	–	–	–	7.9000	–	–	–	–	0.6000	–	–	–
May *et al.* (2001), M2	93.9700	–	–	–	5.2500	–	–	–	–	0.7800	–	–	–
May *et al.* (2002), M1	91.5000	–	–	–	7.9000	–	–	–	–	0.6000	–	–	–
May *et al.* (2002), M2	93.9700	–	–	–	5.2500	–	–	–	–	0.7800	–	–	–
N_2–CO_2–H_2													
Kritschewsky & Markov (1940), M1	–	35.2000	33.3000	–	–	–	–	–	–	–	–	–	31.5000
Kritschewsky & Markov (1940), M2	–	23.5000	22.1000	–	–	–	–	–	–	–	–	–	54.4000
Kritschewsky & Markov (1940), M3	–	54.7548	18.1181	–	–	–	–	–	–	–	–	–	27.1271
CO_2–C_3H_8–n-C_5H_{12}–n-C_8H_{18}													
Barrufet & Rahman (1997)^{v}	–	–	n/a	–	n/a	–	–	n/a	–	–	–	n/a	–
C_3H_8–n-C_4H_{10}–i-C_4H_{10}													
Kayukawa *et al.* (2005a), M1	–	–	–	–	20.0000	60.0000	20.0000	–	–	–	–	–	–
Kayukawa *et al.* (2005a), M2	–	–	–	–	34.0000	33.0000	33.0000	–	–	–	–	–	–
Kayukawa *et al.* (2005a), M3	–	–	–	–	60.0000	20.0000	20.0000	–	–	–	–	–	–
Kayukawa *et al.* (2005a), M1^{s}	–	–	–	–	20.0000	60.0000	20.0000	–	–	–	–	–	–
Kayukawa *et al.* (2005a), M2^{s}	–	–	–	–	34.0000	33.0000	33.0000	–	–	–	–	–	–
Kayukawa *et al.* (2005a), M3^{s}	–	–	–	–	60.0000	20.0000	20.0000	–	–	–	–	–	–
C_3H_8–n-C_5H_{12}–n-C_8H_{18}													
Barrufet & Rahman (1997)	–	–	–	–	54.0400	–	–	20.3200	–	–	–	25.6400	–
n-C_5H_{12}–n-C_6H_{14}–n-C_7H_{16}													
Pecar & Dolecek (2003), M1	–	–	–	–	–	–	–	12.3000	–	37.4000	50.3000	–	–
Pecar & Dolecek (2003), M2	–	–	–	–	–	–	–	12.5000	–	25.4000	62.1000	–	–
Pecar & Dolecek (2003), M3	–	–	–	–	–	–	–	12.5000	–	62.2000	25.3000	–	–
Pecar & Dolecek (2003), M4	–	–	–	–	–	–	–	12.5000	–	75.1000	12.4000	–	–

Table A2.5 (continued)

Authors	Composition (mole per cent)												
	CH_4	N_2	CO_2	C_2H_6	C_3H_8	n-C_4H_{10}	i-C_4H_{10}	n-C_5H_{12}	i-C_5H_{12}	n-C_6H_{14}	n-C_7H_{16}	n-C_8H_{18}	H_2
***pρT* data (continued)**													
n-C_5H_{12}–n-C_6H_{14}–n-C_7H_{16} (continued)													
Pecar & Dolecek (2003), M5	–	–	–	–	–	–	–	12.6000	–	49.9000	37.5000	–	–
Pecar & Dolecek (2003), M6	–	–	–	–	–	–	–	13.6000	–	12.5000	73.9000	–	–
Pecar & Dolecek (2003), M7	–	–	–	–	–	–	–	24.5000	–	39.3000	36.2000	–	–
Pecar & Dolecek (2003), M8	–	–	–	–	–	–	–	24.6000	–	12.7000	62.7000	–	–
Pecar & Dolecek (2003), M9	–	–	–	–	–	–	–	24.9000	–	62.4000	12.7000	–	–
Pecar & Dolecek (2003), M10	–	–	–	–	–	–	–	25.0000	–	25.4000	49.6000	–	–
Pecar & Dolecek (2003), M11	–	–	–	–	–	–	–	25.2000	–	50.1000	24.7000	–	–
Pecar & Dolecek (2003), M12	–	–	–	–	–	–	–	37.4000	–	26.7000	35.9000	–	–
Pecar & Dolecek (2003), M13	–	–	–	–	–	–	–	37.4000	–	37.7000	24.9000	–	–
Pecar & Dolecek (2003), M14	–	–	–	–	–	–	–	37.5000	–	50.0000	12.5000	–	–
Pecar & Dolecek (2003), M15	–	–	–	–	–	–	–	37.6000	–	12.3000	50.1000	–	–
Pecar & Dolecek (2003), M16	–	–	–	–	–	–	–	49.7000	–	37.8000	12.5000	–	–
Pecar & Dolecek (2003), M17	–	–	–	–	–	–	–	49.8000	–	25.1000	25.1000	–	–
Pecar & Dolecek (2003), M18	–	–	–	–	–	–	–	50.0000	–	12.7000	37.3000	–	–
Pecar & Dolecek (2003), M19	–	–	–	–	–	–	–	62.1000	–	25.7000	12.2000	–	–
Pecar & Dolecek (2003), M20	–	–	–	–	–	–	–	62.5000	–	12.7000	24.8000	–	–
Pecar & Dolecek (2003), M21	–	–	–	–	–	–	–	74.7000	–	12.5000	12.8000	–	–

[s] Saturated liquid densities.

[v] Various compositions.

Table A2.6 Summary of the available data for the 98 considered binary mixtures ordered first by the type of thermodynamic property, and then by the type of binary combination

Binary mixture	Number of data points		Covered ranges		
	total[a]	used[b]	Temperature T/K	Pressure p/MPa	Composition[c,d] x
***pρT* data**					
Methane + X					
CH_4–N_2	3619	1465	82.0 – 673	0.04 – 507	0.02 – 0.90
CH_4–CO_2	2392	1107	220 – 673	0.03 – 99.9	0.06 – 0.98
CH_4–C_2H_6	3759	2001	91.0 – 394	0.00 – 35.9	0.04 – 0.81
CH_4–C_3H_8	2901	1889	91.0 – 511	0.03 – 68.9	0.01 – 0.90
CH_4–n-C_4H_{10}	1681	879	108 – 573	0.1 – 68.9	0.01 – 1.00
CH_4–i-C_4H_{10}	593	582	95.0 – 511	0.04 – 34.5	0.04 – 0.84
CH_4–n-C_5H_{12}	1106	699	293 – 511	0.1 – 34.5	0.00 – 1.00
CH_4–i-C_5H_{12}	332	256	257 – 478	1.4 – 10.3	0.21 – 0.85
CH_4–n-C_6H_{14}	971	244	183 – 423	0.5 – 41.4	0.01 – 0.99
CH_4–n-C_7H_{16}	1038	292	278 – 511	0.3 – 69.8	0.00 – 0.99
CH_4–n-C_8H_{18}	89	89	223 – 423	1.0 – 7.1	0.00 – 0.97
CH_4–H_2	1696	1427	130 – 600	0.2 – 107	0.05 – 0.91
CH_4–CO	456	447	116 – 353	0.4 – 160	0.03 – 0.80
CH_4–H_2O	384	253	398 – 699	0.1 – 63.2	0.08 – 0.96
CH_4–Ar	36	36	91.0 – 143	0.1 – 122	0.15 – 0.84
Nitrogen + X					
N_2–CO_2	2856	823	209 – 673	0.1 – 274	0.10 – 0.98
N_2–C_2H_6	812	564	105 – 478	0.2 – 62.1	0.00 – 0.96
N_2–C_3H_8	363	294	100 – 422	0.3 – 42.1	0.00 – 0.98
N_2–n-C_4H_{10}	942	925	270 – 478	0.2 – 68.9	0.02 – 0.91
N_2–i-C_4H_{10}	64	46	255 – 311	0.2 – 20.8	0.03 – 0.99
N_2–n-C_5H_{12}	84	78	277 – 378	0.3 – 20.8	0.01 – 1.00
N_2–i-C_5H_{12}	94	88	278 – 377	0.2 – 20.8	0.01 – 1.00
N_2–n-C_8H_{18}	144	143	293 – 373	25.0 – 100	0.79
N_2–H_2	1488	1479	270 – 573	0.1 – 307	0.15 – 0.87
N_2–O_2	79	–	66.9 – 333	0.1 – 15.7	0.20 – 0.89
N_2–CO	343	343	273 – 353	0.3 – 30.1	0.03
N_2–H_2O	275	212	429 – 707	2.1 – 286	0.05 – 0.95
N_2–He	2669	1259	77.2 – 423	0.1 – 1027	0.06 – 0.99
N_2–Ar	767	652	73.8 – 423	0.01 – 800	0.16 – 0.84
Carbon dioxide + X					
CO_2–C_2H_6	2522	1266	220 – 478	0.03 – 68.9	0.01 – 0.90
CO_2–C_3H_8	1421	862	278 – 511	0.1 – 70.6	0.07 – 0.97
CO_2–n-C_4H_{10}	125	–	311 – 360	1.1 – 10.6	0.03 – 0.20
CO_2–i-C_4H_{10}	126	–	311 – 360	1.0 – 10.5	0.03 – 0.20
CO_2–n-C_5H_{12}	804	366	278 – 423	0.2 – 65.0	0.01 – 0.99
CO_2–i-C_5H_{12}	106	91	278 – 378	0.2 – 9.4	0.00 – 0.99
CO_2–n-C_7H_{16}	141	101	299 – 459	0.1 – 55.5	0.01 – 0.98
CO_2–H_2	413	316	273 – 473	0.2 – 50.7	0.01 – 0.75
CO_2–CO	75	–	323 – 423	0.1 – 6.5	0.43
CO_2–H_2O	448	446	323 – 699	0.1 – 34.6	0.02 – 0.79
CO_2–He	1401	1278	253 – 800	0.2 – 58.8	0.06 – 0.96
CO_2–Ar	572	496	288 – 373	0.3 – 101	0.06 – 0.87

Table A2.6 (continued)

Binary mixture	Number of data points total[a]	Number of data points used[b]	Covered ranges Temperature T/K	Covered ranges Pressure p/MPa	Covered ranges Composition[c,d] x
***pρT* data (continued)**					
Ethane + X					
C_2H_6–C_3H_8	697	360	108 – 322	0.00 – 13.8	0.00 – 0.89
C_2H_6–n-C_4H_{10}	269	223	269 – 414	0.5 – 13.8	0.05 – 0.83
C_2H_6–n-C_5H_{12}	1508	1422	278 – 511	0.1 – 68.9	0.01 – 0.90
C_2H_6–n-C_7H_{16}	212	170	275 – 521	0.3 – 8.6	0.02 – 0.73
C_2H_6–n-C_8H_{18}	64	51	273 – 373	0.4 – 5.3	0.02 – 0.95
C_2H_6–H_2	552	382	275 – 422	0.2 – 26.2	0.10 – 0.80
Propane + X					
C_3H_8–n-C_4H_{10}	899	545	239 – 411	0.1 – 13.8	0.15 – 0.90
C_3H_8–i-C_4H_{10}	788	495	200 – 400	0.1 – 35.4	0.15 – 0.86
C_3H_8–n-C_5H_{12}	283	267	321 – 461	0.1 – 4.6	0.12 – 0.86
C_3H_8–i-C_5H_{12}	640	628	273 – 573	0.1 – 8.1	0.10 – 0.90
C_3H_8–n-C_6H_{14}	235	203	325 – 497	0.1 – 5.0	0.08 – 0.86
C_3H_8–n-C_8H_{18}	155	136	313 – 550	0.7 – 5.9	0.04 – 0.79
C_3H_8–H_2O	55	47	529 – 663	20.0 – 330	0.29 – 0.98
C_3H_8–H_2	73	–	298 – 348	0.3 – 5.1	0.73 – 0.84
n-Butane + X					
n-C_4H_{10}–i-C_4H_{10}	352	16	240 – 380	0.03 – 7.1	0.21 – 0.80
n-C_4H_{10}–n-C_5H_{12}	73	65	358 – 464	1.0 – 3.7	0.13 – 0.86
n-C_4H_{10}–n-C_6H_{14}	157	152	375 – 502	0.6 – 3.9	0.10 – 0.90
n-C_4H_{10}–n-C_7H_{16}	255	250	329 – 530	0.3 – 4.1	0.06 – 0.84
n-C_4H_{10}–n-C_8H_{18}	97	72	339 – 555	0.7 – 4.3	0.05 – 0.82
n-C_4H_{10}–H_2O	219	149	311 – 707	0.7 – 310	0.10 – 0.98
n-C_4H_{10}–Ar	70	66	340 – 380	1.4 – 18.5	0.02 – 0.82
Isobutane + X					
i-C_4H_{10}–H_2O	66	–	547 – 695	13.5 – 306	0.50 – 0.98
n-Pentane + X					
n-C_5H_{12}–n-C_6H_{14}	319	–	273 – 348	0.1 – 40.0	0.10 – 0.90
n-C_5H_{12}–n-C_7H_{16}	326	–	273 – 348	0.1 – 40.0	0.10 – 0.90
n-C_5H_{12}–n-C_8H_{18}	9	–	298	0.1	0.10 – 0.89
n-C_5H_{12}–H_2O	55	55	647	4.3 – 40.9	0.31 – 0.97
n-Hexane + X					
n-C_6H_{14}–n-C_7H_{16}	452	35	273 – 363	0.1 – 71.7	0.09 – 0.91
n-C_6H_{14}–n-C_8H_{18}	61	–	283 – 313	0.1	0.07 – 0.94
n-C_6H_{14}–H_2	423	193	278 – 511	1.4 – 68.9	0.19 – 0.79
n-C_6H_{14}–H_2O	940	88	327 – 699	0.1 – 247	0.01 – 0.96
n-Heptane + X					
n-C_7H_{16}–n-C_8H_{18}	27	–	293 – 298	0.1	0.10 – 0.90
n-Octane + X					
n-C_8H_{18}–H_2O	28	28	623	3.1 – 15.3	0.15 – 0.77
Hydrogen + X					
H_2–CO	54	54	298	0.1 – 17.2	0.34 – 0.67

Table A2.6 (continued)

Binary mixture	Number of data points		Covered ranges		
	total[a]	used[b]	Temperature T/K	Pressure p/MPa	Composition[c,d] x
***pρT* data (continued)**					
Oxygen + X					
O_2–H_2O	154	154	472 – 673	19.5 – 324	0.06 – 0.94
O_2–Ar	36	–	70.4 – 88.8	0.1	0.10 – 0.87
Water + X					
H_2O–Ar	152	152	477 – 663	10.4 – 337	0.05 – 0.80
Helium + X					
He–Ar	500	–	143 – 323	0.2 – 72.3	0.20 – 0.78
Total	**51442**	**30252**	**66.9 – 800**	**0.00 – 1027**	**0.00 – 1.00**
Isochoric heat capacity					
Methane + X					
CH_4–C_2H_6	785	625	101 – 335	67.1^{ρ} – 588^{ρ}	0.10 – 0.84
Carbon dioxide + X					
CO_2–C_2H_6	259	–	218 – 341	67.6^{ρ} – 902^{ρ}	0.26 – 0.75
Ethane + X					
C_2H_6–n-C_5H_{12}	57	–	309	231^{ρ} – 491^{ρ}	0.01 – 0.32
Propane + X					
C_3H_8–i-C_4H_{10}	135	–	203 – 345	484^{ρ} – 649^{ρ}	0.30 – 0.70
Total	**1236**	**625**	**101 – 345**	**67.1^{ρ} – 902^{ρ}**	**0.01 – 0.84**
Speed of sound					
Methane + X					
CH_4–N_2	693	456	170 – 400	0.1 – 750	0.05 – 0.54
CH_4–CO_2	324	324	200 – 450	0.1 – 17.3	0.05 – 0.30
CH_4–C_2H_6	810	411	200 – 375	0.00 – 20.1	0.05 – 0.65
CH_4–C_3H_8	225	222	213 – 375	0.05 – 17.0	0.10 – 0.15
CH_4–n-C_4H_{10}	43	–	311	2.1 – 17.2	0.11 – 0.84
CH_4–n-C_8H_{18}	144	71	293 – 373	25.0 – 100	0.02
Nitrogen + X					
N_2–CO_2	65	65	250 – 350	0.5 – 10.3	0.50
N_2–C_2H_6	112	112	250 – 400	0.05 – 30.2	0.30 – 0.70
N_2–n-C_8H_{18}	144	144	293 – 373	25.0 – 100	0.79
N_2–He	112	–	157 – 298	200 – 1000	0.50
Carbon dioxide + X					
CO_2–C_2H_6	69	–	220 – 450	0.1 – 1.3	0.40
n-Hexane + X					
n-C_6H_{14}–n-C_7H_{16}	28	–	298	0.1	0.01 – 0.96
Helium + X					
He–Ar	50	–	298	198 – 1971	0.10 – 0.50

Table A2.6 (continued)

Binary mixture	Number of data points total[a]	Number of data points used[b]	Covered ranges Temperature T/K	Covered ranges Pressure p/MPa	Covered ranges Composition[c,d] x
Speed of sound (continued)					
Total	**2819**	**1805**	**157 – 450**	**0.00 – 1971**	**0.01 – 0.96**
Isobaric heat capacity					
Methane + X					
CH_4–N_2	111	–	110 – 275	3.0 – 10.0	0.47 – 0.70
CH_4–CO_2	249	–	313 – 424	0.2 – 15.5	0.58 – 0.86
CH_4–C_2H_6	98	72	110 – 350	0.6 – 30.0	0.15 – 0.29
CH_4–C_3H_8	280	215	100 – 422	1.7 – 13.8	0.09 – 0.77
Nitrogen + X					
N_2–CO_2	203	203	313 – 363	0.2 – 16.5	0.68 – 0.93
N_2–C_2H_6	36	–	110 – 270	3.0 – 5.1	0.41
Carbon dioxide + X					
CO_2–C_2H_6	56	–	303 – 393	0.00 – 52.9	0.50
Ethane + X					
C_2H_6–C_3H_8	16	–	120 – 270	5.1	0.39
Propane + X					
C_3H_8–i-C_4H_{10}	23	–	293 – 353	0.1 – 1.2	0.50
Total	**1072**	**490**	**100 – 424**	**0.00 – 52.9**	**0.09 – 0.93**
Enthalpy differences					
Methane + X					
CH_4–N_2	247	–	107 – 367	0.1 – 10.0	0.10 – 0.75
CH_4–C_2H_6	896	22	110 – 525	0.2 – 16.5	0.06 – 0.75
CH_4–C_3H_8	238	99	110 – 366	0.00 – 14.0	0.05 – 0.32
Nitrogen + X					
N_2–C_2H_6	188	77	110 – 343	0.2 – 14.2	0.41 – 0.75
Carbon dioxide + X					
CO_2–C_2H_6	79	–	230 – 350	15.2 – 18.4	0.10 – 0.90
Ethane + X					
C_2H_6–C_3H_8	156	–	110 – 343	0.1 – 14.2	0.20 – 0.39
Total	**1804**	**198**	**107 – 525**	**0.00 – 18.4**	**0.05 – 0.90**
Excess molar enthalpy					
Carbon dioxide + X					
CO_2–n-C_4H_{10}	20	20	221 – 242	0.8 – 4.4	0.17 – 0.85
Ethane + X					
C_2H_6–C_3H_8	157	–	323 – 373	5.0 – 15.0	0.01 – 0.98
Total	**177**	**20**	**221 – 373**	**0.8 – 15.0**	**0.01 – 0.98**

Table A2.6 (continued)

Binary mixture	Number of data points		Covered ranges		
	total[a]	used[b]	Temperature T/K	Pressure p/MPa	Composition[c,d] x
Second acoustic virial coefficient					
Methane + X					
CH_4–C_2H_6	9	–	200 – 375		0.20
CH_4–C_3H_8	12	–	225 – 375		0.15
Total	**21**	**–**	**200 – 375**		**0.15 – 0.20**
Saturated liquid density[e]					
Methane + X					
CH_4–N_2	197	21	95.0 – 183	0.1 – 4.9	0.00 – 1.00
CH_4–C_2H_6	45	20	105 – 250	0.03 – 6.3	0.10 – 0.95
CH_4–C_3H_8	20	20	105 – 130	0.03 – 0.3	0.14 – 0.70
CH_4–n-C_4H_{10}	31	31	105 – 140	0.1 – 0.6	0.07 – 0.41
CH_4–i-C_4H_{10}	17	17	110 – 140	0.1 – 0.6	0.08 – 0.51
Nitrogen + X					
N_2–CO_2	23	–	209 – 268	10.8 – 21.4	0.40 – 0.50
N_2–C_2H_6	11	4	105 – 138	0.4 – 2.8	0.73 – 0.96
N_2–C_3H_8	6	6	100 – 115	0.4 – 0.9	0.93 – 0.98
N_2–n-C_4H_{10}	30	–	339 – 380	1.2 – 22.1	0.50 – 0.98
Carbon dioxide + X					
CO_2–C_3H_8	51	–	278 – 311	0.7 – 6.7	0.06 – 0.98
CO_2–i-C_4H_{10}	29	–	311 – 394	0.7 – 7.2	0.12 – 0.97
Total	**460**	**119**	**95.0 – 394**	**0.03 – 22.1**	**0.00 – 1.00**
VLE data					
Methane + X					
CH_4–N_2	1237	439	78.4 – 190	0.02 – 5.1	0.00 – 1.00
CH_4–CO_2	616	156	143 – 301	0.9 – 8.5	0.00 – 0.99
CH_4–C_2H_6	901	183	111 – 302	0.01 – 6.9	0.00 – 0.99
CH_4–C_3H_8	558	266	91.7 – 363	0.00 – 10.2	0.00 – 1.00
CH_4–n-C_4H_{10}	603	117	144 – 411	0.1 – 13.3	0.02 – 1.00
CH_4–i-C_4H_{10}	171	110	198 – 378	0.5 – 11.8	0.02 – 1.00
CH_4–n-C_5H_{12}	812	40	173 – 461	0.1 – 17.1	0.03 – 1.00
CH_4–i-C_5H_{12}	29	13	344 – 450	2.8 – 6.9	0.70 – 1.00
CH_4–n-C_6H_{14}	472	52	182 – 444	0.1 – 19.8	0.00 – 0.99
CH_4–n-C_7H_{16}	218	44	200 – 511	0.01 – 24.9	0.10 – 0.99
CH_4–n-C_8H_{18}	35	28	298 – 423	1.0 – 7.1	0.71 – 0.97
CH_4–H_2	110	90	90.3 – 174	1.0 – 27.6	0.00 – 0.35
CH_4–O_2	3	–	93.2 – 107	0.1 – 0.4	0.9989 – 0.9990
CH_4–CO	55	54	91.4 – 178	0.03 – 4.7	0.03 – 0.97
CH_4–He	520	489	93.2 – 194	0.1 – 26.2	0.00 – 0.34
CH_4–Ar	163	51	105 – 178	0.2 – 5.1	0.02 – 0.96
Nitrogen + X					
N_2–CO_2	380	115	209 – 303	1.0 – 21.4	0.40 – 1.00
N_2–C_2H_6	901	79	92.8 – 302	0.02 – 13.5	0.00 – 1.00
N_2–C_3H_8	349	117	78.0 – 353	0.03 – 21.9	0.47 – 1.00

Table A2.6 (continued)

Binary mixture	Number of data points			Covered ranges	
	total[a]	used[b]	Temperature T/K	Pressure p/MPa	Composition[c,d] x
VLE data (continued)					
Nitrogen + X (continued)					
N_2–n-C_4H_{10}	292	108	153 – 422	0.2 – 29.1	0.39 – 1.00
N_2–i-C_4H_{10}	98	31	120 – 394	0.2 – 20.8	0.54 – 1.00
N_2–n-C_5H_{12}	42	37	277 – 378	0.3 – 20.8	0.60 – 1.00
N_2–i-C_5H_{12}	47	46	278 – 377	0.2 – 20.8	0.56 – 1.00
N_2–n-C_6H_{14}	52	25	311 – 444	1.7 – 34.5	0.40 – 0.98
N_2–n-C_7H_{16}	114	41	305 – 497	1.2 – 69.1	0.28 – 0.99
N_2–n-C_8H_{18}	26	–	293 – 373	3.2 – 35.0	0.65 – 1.00
N_2–H_2	45	19	77.4 – 113	0.5 – 15.2	0.01 – 0.39
N_2–O_2	526	475	63.0 – 136	0.00 – 3.0	0.01 – 1.00
N_2–CO	117	106	70.0 – 123	0.02 – 2.7	0.07 – 1.00
N_2–He	585	–	64.9 – 126	1.2 – 83.1	0.00 – 0.58
N_2–Ar	487	399	72.2 – 134	0.1 – 2.8	0.00 – 0.98
Carbon dioxide + X					
CO_2–C_2H_6	492	216	207 – 298	0.3 – 6.6	0.01 – 0.99
CO_2–C_3H_8	619	89	211 – 361	0.1 – 6.9	0.02 – 0.99
CO_2–n-C_4H_{10}	438	223	228 – 418	0.03 – 8.2	0.06 – 1.00
CO_2–i-C_4H_{10}	94	73	311 – 394	0.6 – 7.4	0.10 – 0.99
CO_2–n-C_5H_{12}	214	72	253 – 459	0.2 – 9.9	0.02 – 0.99
CO_2–i-C_5H_{12}	53	36	278 – 378	0.2 – 9.4	0.03 – 0.99
CO_2–n-C_6H_{14}	20	20	298 – 313	0.4 – 7.7	0.08 – 0.95
CO_2–n-C_7H_{16}	64	44	311 – 477	0.2 – 13.3	0.05 – 0.98
CO_2–n-C_8H_{18}	20	16	313 – 348	1.5 – 11.4	0.11 – 0.86
CO_2–H_2	138	68	220 – 298	1.1 – 20.3	0.00 – 0.16
CO_2–O_2	144	–	223 – 283	1.0 – 13.2	0.00 – 0.78
CO_2–H_2O	201	–	383 – 623	10.0 – 350	0.57 – 1.00
CO_2–He	30	–	253 – 293	3.0 – 14.1	0.00 – 0.05
CO_2–Ar	31	10	233 – 288	2.6 – 13.2	0.03 – 0.35
Ethane + X					
C_2H_6–C_3H_8	494	286	128 – 369	0.00 – 5.2	0.00 – 1.00
C_2H_6–n-C_4H_{10}	379	114	235 – 419	0.2 – 5.8	0.05 – 0.98
C_2H_6–i-C_4H_{10}	99	34	203 – 394	0.00 – 5.4	0.04 – 0.98
C_2H_6–n-C_5H_{12}	67	59	278 – 444	0.3 – 6.8	0.02 – 1.00
C_2H_6–n-C_6H_{14}	46	43	298 – 450	0.2 – 7.9	0.08 – 0.99
C_2H_6–n-C_7H_{16}	533	–	235 – 540	0.3 – 8.8	0.02 – 1.00
C_2H_6–n-C_8H_{18}	82	47	273 – 373	0.4 – 6.8	0.02 – 0.95
C_2H_6–H_2	117	61	139 – 283	0.7 – 53.3	0.00 – 0.40
C_2H_6–CO	22	21	173 – 273	0.9 – 11.7	0.01 – 0.83
Propane + X					
C_3H_8–n-C_4H_{10}	459	60	237 – 420	0.03 – 11.0	0.05 – 0.99
C_3H_8–i-C_4H_{10}	288	148	237 – 394	0.04 – 4.2	0.00 – 1.00
C_3H_8–n-C_5H_{12}	258	–	321 – 468	0.4 – 4.5	0.04 – 1.00
C_3H_8–i-C_5H_{12}	89	78	273 – 453	0.1 – 4.6	0.02 – 0.97
C_3H_8–n-C_6H_{14}	401	–	288 – 497	0.1 – 5.0	0.02 – 0.96
C_3H_8–n-C_7H_{16}	197	40	333 – 533	2.1 – 5.2	0.02 – 0.98

Table A2.6 (continued)

Binary mixture	Number of data points		Covered ranges		
	total[a]	used[b]	Temperature T/K	Pressure p/MPa	Composition[c,d] x
VLE data (continued)					
Propane + X (continued)					
C_3H_8–H_2	215	140	172 – 361	1.4 – 55.2	0.01 – 0.67
C_3H_8–CO	37	37	148 – 323	1.4 – 15.2	0.02 – 0.43
n-Butane + X					
n-C_4H_{10}–i-C_4H_{10}	228	197	273 – 374	0.1 – 2.0	0.02 – 0.98
n-C_4H_{10}–n-C_5H_{12}	195	–	298 – 464	0.1 – 3.7	0.10 – 0.98
n-C_4H_{10}–n-C_6H_{14}	365	–	358 – 502	0.6 – 3.9	0.10 – 0.90
n-C_4H_{10}–n-C_7H_{16}	477	–	329 – 540	0.3 – 4.1	0.02 – 0.99
n-C_4H_{10}–H_2	64	62	328 – 394	2.8 – 16.9	0.02 – 0.27
n-C_4H_{10}–H_2O[y]	51	–	600 – 700	19.3 – 276	0.65 – 0.98
n-C_4H_{10}–Ar	35	21	340 – 380	1.4 – 18.5	0.02 – 0.56
Isobutane + X					
i-C_4H_{10}–H_2	21	–	311 – 394	3.4 – 20.7	0.02 – 0.25
i-C_4H_{10}–H_2O[y]	77	–	547 – 695	13.5 – 306	0.50 – 0.98
n-Pentane + X					
n-C_5H_{12}–i-C_5H_{12}	13	–	328 – 385	0.2 – 0.8	0.02 – 0.94
n-C_5H_{12}–n-C_6H_{14}	8	–	298	0.03 – 0.1	0.10 – 0.89
n-C_5H_{12}–n-C_7H_{16}	26	–	404 – 526	1.0 – 3.1	0.10 – 0.90
n-C_5H_{12}–n-C_8H_{18}	61	–	292 – 434	0.1 – 1.5	0.05 – 0.95
n-Hexane + X					
n-C_6H_{14}–n-C_7H_{16}	29	14	303 – 367	0.01 – 0.1	0.03 – 0.97
n-C_6H_{14}–H_2	134	98	278 – 478	0.03 – 68.9	0.01 – 0.69
n-Heptane + X					
n-C_7H_{16}–n-C_8H_{18}	43	20	313 – 394	0.00 – 0.1	0.04 – 0.97
n-C_7H_{16}–H_2	29	27	424 – 499	2.5 – 78.5	0.02 – 0.81
Hydrogen + X					
H_2–CO	81	80	68.2 – 122	1.7 – 24.1	0.35 – 0.97
H_2–He	264	–	15.5 – 32.5	0.2 – 10.4	0.00 – 0.36
Oxygen + X					
O_2–He	37	–	77.4 – 143	1.7 – 13.8	0.00 – 0.09
O_2–Ar	616	51	83.8 – 139	0.1 – 2.6	0.00 – 1.00
Carbon monoxide + X					
CO–He	98	–	77.4 – 128	0.7 – 13.8	0.00 – 0.17
CO–Ar	16	15	123 – 137	1.5 – 3.8	0.06 – 0.92
Helium + X					
He–Ar	288	–	91.4 – 160	1.4 – 422	0.40 – 1.00
Total	**20161**	**6350**	**15.5 – 700**	**0.00 – 422**	**0.00 – 1.00**
Total	**79192**	**39859**	**15.5 – 800**	**0.00 – 1971**	**0.00 – 1.00**

[a] Number of all available data points.

[b] Number of data points used for the development of the GERG-2004 equation of state.

Table A2.6 (continued)

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[c] Mole fractions of component X. Values of 0.00 and 1.00 result from a mixture composition close to a pure component.

[d] Mole fractions of component X in the saturated liquid phase for VLE data, unless otherwise stated.

[e] Listed separately due to a different data format. Saturated liquid (and vapour) densities may also be tabulated as ordinary $p\rho T$ or VLE data.

[y] VLE data set contains pTy data only. The specified composition range indicates mole fractions of component X in the saturated vapour phase.

[ρ] Density in kg·m^{-3} instead of pressure.

Table A2.7 Summary of the available VLE data for binary mixtures

Binary mixture	Number of data points total[a]	used[b]	Covered ranges Temperature T/K	Pressure p/MPa	Composition of liquid phase[c], x	Composition of vapour phase[c], y	Distribution of VLE data points $pTxy$[d]	pTx[e]	pTy[f]
Methane + X									
CH_4–N_2	1237	439	78.4 – 190	0.02 – 5.1	0.00 – 1.00	0.01 – 1.00	718	269	250
CH_4–CO_2	616	156	143 – 301	0.9 – 8.5	0.00 – 0.99	0.00 – 0.99	370	65	181
CH_4–C_2H_6	901	183	111 – 302	0.01 – 6.9	0.00 – 0.99	0.00 – 0.97	368	296	237
CH_4–C_3H_8	558	266	91.7 – 363	0.00 – 10.2	0.00 – 1.00	0.00 – 0.97	463	67	28
CH_4–n-C_4H_{10}	603	117	144 – 411	0.1 – 13.3	0.02 – 1.00	0.00 – 0.89	427	5	171
CH_4–i-C_4H_{10}	171	110	198 – 378	0.5 – 11.8	0.02 – 1.00	0.00 – 0.97	136	1	34
CH_4–n-C_5H_{12}	812	40	173 – 461	0.1 – 17.1	0.03 – 1.00	0.00 – 0.99	669	23	120
CH_4–i-C_5H_{12}	29	13	344 – 450	2.8 – 6.9	0.70 – 1.00	0.13 – 0.97	29	–	–
CH_4–n-C_6H_{14}	472	52	182 – 444	0.1 – 19.8	0.00 – 0.99	0.00 – 0.56	205	137	130
CH_4–n-C_7H_{16}	218	44	200 – 511	0.01 – 24.9	0.10 – 0.99	0.00 – 0.79	165	–	53
CH_4–n-C_8H_{18}	35	28	298 – 423	1.0 – 7.1	0.71 – 0.97	0.00 – 0.12	33	2	–
CH_4–H_2	110	90	90.3 – 174	1.0 – 27.6	0.00 – 0.35	0.13 – 0.99	110	–	–
CH_4–O_2	3	–	93.2 – 107	0.1 – 0.4	0.9989 – 0.9990	0.9996 – 0.9997	3	–	–
CH_4–CO	55	54	91.4 – 178	0.03 – 4.7	0.03 – 0.97	0.06 – 0.99	55	–	–
CH_4–He	520	489	93.2 – 194	0.1 – 26.2	0.00 – 0.34	0.03 – 1.00	489	21	10
CH_4–Ar	163	51	105 – 178	0.2 – 5.1	0.02 – 0.96	0.05 – 0.99	92	63	8
Nitrogen + X									
N_2–CO_2	380	115	209 – 303	1.0 – 21.4	0.40 – 1.00	0.14 – 1.00	252	46	82
N_2–C_2H_6	901	79	92.8 – 302	0.02 – 13.5	0.00 – 1.00	0.00 – 0.95	247	199	455
N_2–C_3H_8	349	117	78.0 – 353	0.03 – 21.9	0.47 – 1.00	0.00 – 0.86	167	52	130
N_2–n-C_4H_{10}	292	108	153 – 422	0.2 – 29.1	0.39 – 1.00	0.00 – 0.94	220	5	67
N_2–i-C_4H_{10}	98	31	120 – 394	0.2 – 20.8	0.54 – 1.00	0.00 – 0.90	98	–	–
N_2–n-C_5H_{12}	42	37	277 – 378	0.3 – 20.8	0.60 – 1.00	0.01 – 0.82	42	–	–
N_2–i-C_5H_{12}	47	46	278 – 377	0.2 – 20.8	0.56 – 1.00	0.01 – 0.84	47	–	–
N_2–n-C_6H_{14}	52	25	311 – 444	1.7 – 34.5	0.40 – 0.98	0.01 – 0.43	52	–	–
N_2–n-C_7H_{16}	114	41	305 – 497	1.2 – 69.1	0.28 – 0.99	0.00 – 0.83	92	22	–
N_2–n-C_8H_{18}	26	–	293 – 373	3.2 – 35.0	0.65 – 1.00	0.17 – 0.23	5	21	–

Table A2.7 (continued)

Binary mixture	Number of data points		Covered ranges				Distribution of VLE data points		
	total[a]	used[b]	Temperature T/K	Pressure p/MPa	Composition of liquid phase[c], x	Composition of vapour phase[c], y	$pTxy$[d]	pTx[e]	pTy[f]
Nitrogen + X (continued)									
N_2–H_2	45	19	77.4 – 113	0.5 – 15.2	0.01 – 0.39	0.19 – 0.93	45	–	–
N_2–O_2	526	475	63.0 – 136	0.00 – 3.0	0.01 – 1.00	0.00 – 0.99	503	23	–
N_2–CO	117	106	70.0 – 123	0.02 – 2.7	0.07 – 1.00	0.05 – 0.88	117	–	–
N_2–He	585	–	64.9 – 126	1.2 – 83.1	0.00 – 0.58	0.02 – 1.00	585	–	–
N_2–Ar	487	399	72.2 – 134	0.1 – 2.8	0.00 – 0.98	0.00 – 0.95	463	17	7
Carbon dioxide + X									
CO_2–C_2H_6	492	216	207 – 298	0.3 – 6.6	0.01 – 0.99	0.02 – 0.97	439	50	3
CO_2–C_3H_8	619	89	211 – 361	0.1 – 6.9	0.02 – 0.99	0.01 – 0.97	284	172	163
CO_2–n-C_4H_{10}	438	223	228 – 418	0.03 – 8.2	0.06 – 1.00	0.01 – 0.98	403	13	22
CO_2–i-C_4H_{10}	94	73	311 – 394	0.6 – 7.4	0.10 – 0.99	0.08 – 0.95	94	–	–
CO_2–n-C_5H_{12}	214	72	253 – 459	0.2 – 9.9	0.02 – 0.99	0.00 – 0.93	214	–	–
CO_2–i-C_5H_{12}	53	36	278 – 378	0.2 – 9.4	0.03 – 0.99	0.00 – 0.79	53	–	–
CO_2–n-C_6H_{14}	20	20	298 – 313	0.4 – 7.7	0.08 – 0.95	0.01 – 0.07	20	–	–
CO_2–n-C_7H_{16}	64	44	311 – 477	0.2 – 13.3	0.05 – 0.98	0.01 – 0.89	64	–	–
CO_2–n-C_8H_{18}	20	16	313 – 348	1.5 – 11.4	0.11 – 0.86	0.00 – 0.04	20	–	–
CO_2–H_2	138	68	220 – 298	1.1 – 20.3	0.00 – 0.16	0.04 – 0.93	110	16	12
CO_2–O_2	144	–	223 – 283	1.0 – 13.2	0.00 – 0.78	0.05 – 0.82	143	–	1
CO_2–H_2O	201	–	383 – 623	10.0 – 350	0.57 – 1.00	0.04 – 0.95	201	–	–
CO_2–He	30	–	253 – 293	3.0 – 14.1	0.00 – 0.05	0.04 – 0.82	30	–	–
CO_2–Ar	31	10	233 – 288	2.6 – 13.2	0.03 – 0.35	0.06 – 0.75	15	4	12
Ethane + X									
C_2H_6–C_3H_8	494	286	128 – 369	0.00 – 5.2	0.00 – 1.00	0.00 – 1.00	434	30	30
C_2H_6–n-C_4H_{10}	379	114	235 – 419	0.2 – 5.8	0.05 – 0.98	0.01 – 0.90	129	123	127
C_2H_6–i-C_4H_{10}	99	34	203 – 394	0.00 – 5.4	0.04 – 0.98	0.02 – 0.96	36	33	30
C_2H_6–n-C_5H_{12}	67	59	278 – 444	0.3 – 6.8	0.02 – 1.00	0.00 – 0.96	67	–	–
C_2H_6–n-C_6H_{14}	46	43	298 – 450	0.2 – 7.9	0.08 – 0.99	0.01 – 0.91	46	–	–

Table A2.7 (continued)

Binary mixture	Number of data points		Covered ranges				Distribution of VLE data points		
	total[a]	used[b]	Temperature T/K	Pressure p/MPa	Composition of liquid phase[c], x	Composition of vapour phase[c], y	$pTxy$[d]	pTx[e]	pTy[f]
Ethane + X (continued)									
C_2H_6–n-C_7H_{16}	533	–	235 – 540	0.3 – 8.8	0.02 – 1.00	0.00 – 1.00	123	198	212
C_2H_6–n-C_8H_{18}	82	47	273 – 373	0.4 – 6.8	0.02 – 0.95	0.00 – 0.10	64	18	–
C_2H_6–H_2	117	61	139 – 283	0.7 – 53.3	0.00 – 0.40	0.08 – 1.00	117	–	–
C_2H_6–CO	22	21	173 – 273	0.9 – 11.7	0.01 – 0.83	0.31 – 0.98	22	–	–
Propane + X									
C_3H_8–n-C_4H_{10}	459	60	237 – 420	0.03 – 11.0	0.05 – 0.99	0.01 – 0.98	136	169	154
C_3H_8–i-C_4H_{10}	288	148	237 – 394	0.04 – 4.2	0.00 – 1.00	0.00 – 1.00	246	21	21
C_3H_8–n-C_5H_{12}	258	–	321 – 468	0.4 – 4.5	0.04 – 1.00	0.01 – 0.99	69	93	96
C_3H_8–i-C_5H_{12}	89	78	273 – 453	0.1 – 4.6	0.02 – 0.97	0.02 – 0.94	89	–	–
C_3H_8–n-C_6H_{14}	401	–	288 – 497	0.1 – 5.0	0.02 – 0.96	0.00 – 0.91	36	173	192
C_3H_8–n-C_7H_{16}	197	40	333 – 533	2.1 – 5.2	0.02 – 0.98	0.00 – 0.92	40	81	76
C_3H_8–H_2	215	140	172 – 361	1.4 – 55.2	0.01 – 0.67	0.13 – 1.00	143	34	38
C_3H_8–CO	37	37	148 – 323	1.4 – 15.2	0.02 – 0.43	0.38 – 1.00	37	–	–
n-Butane + X									
n-C_4H_{10}–i-C_4H_{10}	228	197	273 – 374	0.1 – 2.0	0.02 – 0.98	0.02 – 0.98	198	30	–
n-C_4H_{10}–n-C_5H_{12}	195	–	298 – 464	0.1 – 3.7	0.10 – 0.98	0.10 – 0.90	12	103	80
n-C_4H_{10}–n-C_6H_{14}	365	–	358 – 502	0.6 – 3.9	0.10 – 0.90	0.03 – 0.90	55	170	140
n-C_4H_{10}–n-C_7H_{16}	477	–	329 – 540	0.3 – 4.1	0.02 – 0.99	0.01 – 0.98	41	209	227
n-C_4H_{10}–H_2	64	62	328 – 394	2.8 – 16.9	0.02 – 0.27	0.21 – 0.93	64	–	–
n-C_4H_{10}–H_2O^y	51	–	600 – 700	19.3 – 276		0.65 – 0.98	–	–	51
n-C_4H_{10}–Ar	35	21	340 – 380	1.4 – 18.5	0.02 – 0.56	0.20 – 0.82	35	–	–
Isobutane + X									
i-C_4H_{10}–H_2	21	–	311 – 394	3.4 – 20.7	0.02 – 0.25	0.37 – 0.96	21	–	–
i-C_4H_{10}–H_2O^y	77	–	547 – 695	13.5 – 306		0.50 – 0.98	–	–	77

Table A2.7 (continued)

Binary mixture	Number of data points total[a]	Number of data points used[b]	Covered ranges: Temperature T/K	Pressure p/MPa	Composition of liquid phase[c], x	Composition of vapour phase[c], y	Distribution of VLE data points $pTxy$[d]	pTx[e]	pTy[f]
n-Pentane + X									
n-C_5H_{12}–i-C_5H_{12}	13	–	328 – 385	0.2 – 0.8	0.02 – 0.94	0.07 – 0.98	13	–	–
n-C_5H_{12}–n-C_6H_{14}[x]	8	–	298	0.03 – 0.1	0.10 – 0.89		–	8	–
n-C_5H_{12}–n-C_7H_{16}	26	–	404 – 526	1.0 – 3.1	0.10 – 0.90	0.04 – 0.83	26	–	–
n-C_5H_{12}–n-C_8H_{18}	61	–	292 – 434	0.1 – 1.5	0.05 – 0.95	0.00 – 0.78	61	–	–
n-Hexane + X									
n-C_6H_{14}–n-C_7H_{16}	29	14	303 – 367	0.01 – 0.1	0.03 – 0.97	0.01 – 0.94	29	–	–
n-C_6H_{14}–H_2	134	98	278 – 478	0.03 – 68.9	0.01 – 0.69	0.31 – 1.00	100	34	–
n-Heptane + X									
n-C_7H_{16}–n-C_8H_{18}	43	20	313 – 394	0.00 – 0.1	0.04 – 0.97	0.02 – 0.93	20	23	–
n-C_7H_{16}–H_2	29	27	424 – 499	2.5 – 78.5	0.02 – 0.81	0.36 – 0.97	29	–	–
Hydrogen + X									
H_2–CO	81	80	68.2 – 122	1.7 – 24.1	0.35 – 0.97	0.01 – 0.78	81	–	–
H_2–He	264	–	15.5 – 32.5	0.2 – 10.4	0.00 – 0.36	0.03 – 0.98	210	32	22
Oxygen + X									
O_2–He[x]	37	–	77.4 – 143	1.7 – 13.8	0.00 – 0.09		–	37	–
O_2–Ar	616	51	83.8 – 139	0.1 – 2.6	0.00 – 1.00	0.00 – 0.98	561	55	–
Carbon monoxide + X									
CO–He	98	–	77.4 – 128	0.7 – 13.8	0.00 – 0.17	0.24 – 0.99	–	56	42
CO–Ar	16	15	123 – 137	1.5 – 3.8	0.06 – 0.92	0.05 – 0.90	16	–	–
Helium + X									
He–Ar	288	–	91.4 – 160	1.4 – 422	0.40 – 1.00	0.01 – 0.74	228	50	10
Total	**20161**	**6350**	**15.5 – 700**	**0.00 – 422**	**0.00 – 1.00**	**0.00 – 1.00**	**12991**	**3369**	**3801**

[a] Number of all available data points.

Table A2.7 (continued)

[b] Number of data points used for the development of the GERG-2004 equation of state.

[c] Mole fractions of component X. Values of 0.00 and 1.00 result from a mixture composition close to a pure component.

[d] Number of *pTxy* data points.

[e] Number of *pTx* data points.

[f] Number of *pTy* data points.

[x] VLE data set contains *pTx* data only.

[y] VLE data set contains *pTy* data only.

Table A2.8 Summary of the supplementary data for ternary and quaternary mixtures

Ternary/quaternary mixture	N_P[a]	Covered ranges		Distribution of VLE data points		
		Temperature T/K	Pressure p/MPa	$pTxy$[b]	pTx[c]	pTy[d]
***pρT* data**						
Methane + X + Y						
CH_4–N_2–CO_2	271	323 – 573	19.9 – 99.9			
CH_4–N_2–C_2H_6	14	91.0 – 298	0.05 – 17.1			
CH_4–N_2–C_3H_8	2	91.0 – 108	0.1 – 0.2			
CH_4–N_2–n-C_6H_{14}	204	270 – 353	0.5 – 17.8			
CH_4–N_2–H_2	537	144 – 473	0.4 – 70.9			
CH_4–CO_2–C_2H_6	147	283 – 333	0.1 – 8.6			
CH_4–C_2H_6–C_3H_8	10	91.0 – 115	0.03 – 0.1			
CH_4–C_3H_8–n-C_6H_{14}	62	281 – 313	1.9 – 10.2			
Nitrogen + X + Y						
N_2–CO_2–H_2	90	273 – 473	5.1 – 50.7			
Carbon dioxide + X + Y + Z						
CO_2–C_3H_8–n-C_5H_{12}–n-C_8H_{18}	30	311 – 394	3.1 – 6.4			
Propane + X + Y						
C_3H_8–n-C_4H_{10}–i-C_4H_{10}	319	240 – 380	0.1 – 7.1			
C_3H_8–n-C_5H_{12}–n-C_8H_{18}	4	297 – 394	2.0 – 2.7			
n-Pentane + X + Y						
n-C_5H_{12}–n-C_6H_{14}–n-C_7H_{16}	315	298 – 348	0.1 – 40.0			
Total	**2005**	**91.0 – 573**	**0.03 – 99.9**			
VLE data						
Methane + X + Y						
CH_4–N_2–CO_2	53	293	6.0 – 8.3	53	–	–
CH_4–N_2–Ar	37	112 – 123	0.2 – 2.4	31	3	3
CH_4–CO_2–C_2H_6	105	230 – 250	1.2 – 6.6	99	–	6
CH_4–CO_2–C_3H_8	63	230 – 270	0.8 – 8.0	59	1	3
Nitrogen + X + Y						
N_2–CO_2–C_3H_8	47	240 – 330	2.0 – 13.0	35	3	9
N_2–CO_2–n-C_4H_{10}	121	250 – 411	1.5 – 27.6	119	–	2
N_2–O_2–Ar	1657	77.8 – 136	0.1 – 2.6	1656	–	1
Carbon dioxide + X + Y + Z						
CO_2–C_3H_8–n-C_5H_{12}–n-C_8H_{18}	15	311 – 394	3.1 – 6.4	15	–	–
Ethane + X + Y						
C_2H_6–C_3H_8–n-C_4H_{10}	59	305 – 306	0.7 – 4.9	59	–	–
C_2H_6–n-C_4H_{10}–n-C_7H_{16}	127	339 – 450	3.1 – 8.3	108	10	9
Total	**2284**	**77.8 – 450**	**0.1 – 27.6**	**2234**	**17**	**33**
Total	**4289**	**77.8 – 573**	**0.03 – 99.9**			

[a] Number of data points.

[b] Number of *pTxy* data points.

[c] Number of *pTx* data points.

[d] Number of *pTy* data points.

A3 Parameters and Coefficients of the New Equation of State (GERG-2004)

Table A3.1 Coefficients and parameters of $\alpha^{\mathrm{o}}_{\mathrm{o}i}$, Eq. (7.5), for the considered 18 components[a]

k	$n^{\mathrm{o}}_{\mathrm{o}i,k}$	$\vartheta^{\mathrm{o}}_{\mathrm{o}i,k}$	k	$n^{\mathrm{o}}_{\mathrm{o}i,k}$	$\vartheta^{\mathrm{o}}_{\mathrm{o}i,k}$
Methane					
1	19.597538587	–	5	0.004600000	0.936220902
2	−83.959667892	–	6	8.744320000	5.577233895
3	3.000880000	–	7	−4.469210000	5.722644361
4	0.763150000	4.306474465			
Nitrogen					
1	11.083437707	–	5	−0.146600000	−5.393067706
2	−22.202102428	–	6	0.900660000	13.788988208
3	2.500310000	–	7	–	–
4	0.137320000	5.251822620			
Carbon dioxide					
1	11.925182741	–	5	−1.060440000	−2.844425476
2	−16.118762264	–	6	2.033660000	1.589964364
3	2.500020000	–	7	0.013930000	1.121596090
4	2.044520000	3.022758166			
Ethane					
1	24.675465518	–	5	1.237220000	0.731306621
2	−77.425313760	–	6	13.197400000	3.378007481
3	3.002630000	–	7	−6.019890000	3.508721939
4	4.339390000	1.831882406			
Propane					
1	31.602934734	–	5	3.197000000	0.543210978
2	−84.463284382	–	6	19.192100000	2.583146083
3	3.029390000	–	7	−8.372670000	2.777773271
4	6.605690000	1.297521801			
n-Butane					
1	20.884168790	–	5	6.894060000	0.431957660
2	−91.638478026	–	6	24.461800000	4.502440459
3	3.339440000	–	7	14.782400000	2.124516319
4	9.448930000	1.101487798			

Table A3.1 (continued)

k	$n^{\mathrm{o}}_{\mathrm{o}i,k}$	$\vartheta^{\mathrm{o}}_{\mathrm{o}i,k}$	k	$n^{\mathrm{o}}_{\mathrm{o}i,k}$	$\vartheta^{\mathrm{o}}_{\mathrm{o}i,k}$
			Isobutane		
1	20.413751434	–	5	5.251560000	0.485556021
2	−94.467620036	–	6	25.142300000	4.671261865
3	3.067140000	–	7	16.138800000	2.191583480
4	8.975750000	1.074673199			
			n-Pentane		
1	14.536635738	–	5	21.836000000	1.789520971
2	−89.919548319	–	6	33.403200000	3.777411113
3	3.000000000	–	7	–	–
4	8.950430000	0.380391739			
			Isopentane		
1	15.449937973	–	5	20.110100000	1.977271641
2	−101.298172792	–	6	33.168800000	4.169371131
3	3.000000000	–	7	–	–
4	11.761800000	0.635392636			
			n-Hexane		
1	14.345993081	–	5	26.814200000	1.691951873
2	−96.165722367	–	6	38.616400000	3.596924107
3	3.000000000	–	7	–	–
4	11.697700000	0.359036667			
			n-Heptane		
1	15.063809621	–	5	30.470700000	1.548136560
2	−97.345252349	–	6	43.556100000	3.259326458
3	3.000000000	–	7	–	–
4	13.726600000	0.314348398			
			n-Octane		
1	15.864709639	–	5	33.802900000	1.431644769
2	−97.370667555	–	6	48.173100000	2.973845992
3	3.000000000	–	7	–	–
4	15.686500000	0.279143540			
			Hydrogen		
1	13.796474934	–	5	0.454440000	9.847634830
2	−175.864487294	–	6	1.560390000	49.765290750
3	1.479060000	–	7	−1.375600000	50.367279301
4	0.958060000	6.891654113			

Table A3.1 (continued)

k	$n^{\mathrm{o}}_{\mathrm{o}i,k}$	$\vartheta^{\mathrm{o}}_{\mathrm{o}i,k}$	k	$n^{\mathrm{o}}_{\mathrm{o}i,k}$	$\vartheta^{\mathrm{o}}_{\mathrm{o}i,k}$
Oxygen					
1	10.001874708	–	5	1.013340000	7.223325463
2	−14.996095135	–	6	–	–
3	2.501460000	–	7	–	–
4	1.075580000	14.461722565			
Carbon monoxide					
1	10.814500335	–	5	0.004930000	5.305158133
2	−19.843695435	–	6	–	–
3	2.500550000	–	7	–	–
4	1.028650000	11.675075301			
Water					
1	8.203553050	–	5	0.987630000	1.763895929
2	−11.996306443	–	6	3.069040000	3.874803739
3	3.003920000	–	7	–	–
4	0.010590000	0.415386589			
Helium					
1	13.628441975	–	5	–	–
2	−143.470759602	–	6	–	–
3	1.500000000	–	7	–	–
4	–	–			
Argon					
1	8.316662546	–	5	–	–
2	−4.946502600	–	6	–	–
3	1.500000000	–	7	–	–
4	–	–			

[a] The values of the coefficients and parameters are also valid for Eq. (4.15).

Table A3.2 Coefficients and exponents of $\alpha^{\mathrm{r}}_{\mathrm{o}i}$, Eq. (7.7), for propane, n-butane, isobutane, n-pentane, isopentane, n-hexane, n-heptane, n-octane, oxygen, carbon monoxide, and argon[a,b]

k	$n_{\mathrm{o}i,k}$	$n_{\mathrm{o}i,k}$	$n_{\mathrm{o}i,k}$
	Propane	**n-Butane**	**Isobutane**
1	$0.10403973107358\times10^{1}$	$0.10626277411455\times10^{1}$	$0.10429331589100\times10^{1}$
2	$-0.28318404081403\times10^{1}$	$-0.28620951828350\times10^{1}$	$-0.28184272548892\times10^{1}$
3	0.84393809606294	0.88738233403777	0.86176232397850
4	$-0.76559591850023\times10^{-1}$	-0.12570581155345	-0.10613619452487
5	$0.94697373057280\times10^{-1}$	0.10286308708106	$0.98615749302134\times10^{-1}$
6	$0.24796475497006\times10^{-3}$	$0.25358040602654\times10^{-3}$	$0.23948208682322\times10^{-3}$
7	0.27743760422870	0.32325200233982	0.30330004856950
8	$-0.43846000648377\times10^{-1}$	$-0.37950761057432\times10^{-1}$	$-0.41598156135099\times10^{-1}$
9	-0.26991064784350	-0.32534802014452	-0.29991937470058
10	$-0.69313413089860\times10^{-1}$	$-0.79050969051011\times10^{-1}$	$-0.80369342764109\times10^{-1}$
11	$-0.29632145981653\times10^{-1}$	$-0.20636720547775\times10^{-1}$	$-0.29761373251151\times10^{-1}$
12	$0.14040126751380\times10^{-1}$	$0.57053809334750\times10^{-2}$	$0.13059630303140\times10^{-1}$
	n-Pentane	**Isopentane**	**n-Hexane**
1	$0.10968643098001\times10^{1}$	$0.11017531966644\times10^{1}$	$0.10553238013661\times10^{1}$
2	$-0.29988888298061\times10^{1}$	$-0.30082368531980\times10^{1}$	$-0.26120615890629\times10^{1}$
3	0.99516886799212	0.99411904271336	0.76613882967260
4	-0.16170708558539	-0.14008636562629	-0.29770320622459
5	0.11334460072775	0.11193995351286	0.11879907733358
6	$0.26760595150748\times10^{-3}$	$0.29548042541230\times10^{-3}$	$0.27922861062617\times10^{-3}$
7	0.40979881986931	0.36370108598133	0.46347589844105
8	$-0.40876423083075\times10^{-1}$	$-0.48236083488293\times10^{-1}$	$0.11433196980297\times10^{-1}$
9	-0.38169482469447	-0.35100280270615	-0.48256968738131
10	-0.10931956843993	-0.10185043812047	$-0.93750558924659\times10^{-1}$
11	$-0.32073223327990\times10^{-1}$	$-0.35242601785454\times10^{-1}$	$-0.67273247155994\times10^{-2}$
12	$0.16877016216975\times10^{-1}$	$0.19756797599888\times10^{-1}$	$-0.51141583585428\times10^{-2}$
	n-Heptane	**n-Octane**	**Oxygen**
1	$0.10543747645262\times10^{1}$	$0.10722544875633\times10^{1}$	0.88878286369701
2	$-0.26500681506144\times10^{1}$	$-0.24632951172003\times10^{1}$	$-0.24879433312148\times10^{1}$
3	0.81730047827543	0.65386674054928	0.59750190775886
4	-0.30451391253428	-0.36324974085628	$0.96501817061881\times10^{-2}$
5	0.12253868710800	0.12713269626764	$0.71970428712770\times10^{-1}$
6	$0.27266472743928\times10^{-3}$	$0.30713572777930\times10^{-3}$	$0.22337443000195\times10^{-3}$
7	0.49865825681670	0.52656856987540	0.18558686391474
8	$-0.71432815084176\times10^{-3}$	$0.19362862857653\times10^{-1}$	$-0.38129368035760\times10^{-1}$
9	-0.54236895525450	-0.58939426849155	-0.15352245383006
10	-0.13801821610756	-0.14069963991934	$-0.26726814910919\times10^{-1}$
11	$-0.61595287380011\times10^{-2}$	$-0.78966330500036\times10^{-2}$	$-0.25675298677127\times10^{-1}$
12	$0.48602510393022\times10^{-3}$	$0.33036597968109\times10^{-2}$	$0.95714302123668\times10^{-2}$

Table A3.2 (continued)

k	$n_{\text{o}i,k}$	$n_{\text{o}i,k}$
	Carbon monoxide	**Argon**
1	0.92310041400851	0.85095714803969
2	$-0.24885845205800\times10^{1}$	$-0.24003222943480\times10^{1}$
3	0.58095213783396	0.54127841476466
4	$0.28859164394654\times10^{-1}$	$0.16919770692538\times10^{-1}$
5	$0.70256257276544\times10^{-1}$	$0.68825965019035\times10^{-1}$
6	$0.21687043269488\times10^{-3}$	$0.21428032815338\times10^{-3}$
7	0.13758331015182	0.17429895321992
8	$-0.51501116343466\times10^{-1}$	$-0.33654495604194\times10^{-1}$
9	-0.14865357483379	-0.13526799857691
10	$-0.38857100886810\times10^{-1}$	$-0.16387350791552\times10^{-1}$
11	$-0.29100433948943\times10^{-1}$	$-0.24987666851475\times10^{-1}$
12	$0.14155684466279\times10^{-1}$	$0.88769204815709\times10^{-2}$

k	$c_{\text{o}i,k}$	$d_{\text{o}i,k}$	$t_{\text{o}i,k}$
1	–	1	0.250
2	–	1	1.125
3	–	1	1.500
4	–	2	1.375
5	–	3	0.250
6	–	7	0.875
7	1	2	0.625
8	1	5	1.750
9	2	1	3.625
10	2	4	3.625
11	3	3	14.500
12	3	4	12.000

[a] The values of the coefficients and exponents are also valid for Eq. (4.27).

[b] $K_{\text{Pol},i} = 6$, $K_{\text{Exp},i} = 6$.

Table A3.3 Coefficients and exponents of $\alpha^{\mathrm{r}}_{\mathrm{o}i}$, Eq. (7.7), for methane, nitrogen, and ethane[a,b]

k	$n_{\mathrm{o}i,k}$	$n_{\mathrm{o}i,k}$	$n_{\mathrm{o}i,k}$
	Methane	**Nitrogen**	**Ethane**
1	0.57335704239162	0.59889711801201	0.63596780450714
2	$-0.16760687523730\times10^{1}$	$-0.16941557480731\times10^{1}$	$-0.17377981785459\times10^{1}$
3	0.23405291834916	0.24579736191718	0.28914060926272
4	−0.21947376343441	−0.23722456755175	−0.33714276845694
5	$0.16369201404128\times10^{-1}$	$0.17954918715141\times10^{-1}$	$0.22405964699561\times10^{-1}$
6	$0.15004406389280\times10^{-1}$	$0.14592875720215\times10^{-1}$	$0.15715424886913\times10^{-1}$
7	$0.98990489492918\times10^{-1}$	0.10008065936206	0.11450634253745
8	0.58382770929055	0.73157115385532	$0.10612049379745\times10^{1}$
9	−0.74786867560390	−0.88372272336366	$-0.12855224439423\times10^{1}$
10	0.30033302857974	0.31887660246708	0.39414630777652
11	0.20985543806568	0.20766491728799	0.31390924682041
12	$-0.18590151133061\times10^{-1}$	$-0.19379315454158\times10^{-1}$	$-0.21592277117247\times10^{-1}$
13	−0.15782558339049	−0.16936641554983	−0.21723666564905
14	0.12716735220791	0.13546846041701	−0.28999574439489
15	$-0.32019743894346\times10^{-1}$	$-0.33066712095307\times10^{-1}$	0.42321173025732
16	$-0.68049729364536\times10^{-1}$	$-0.60690817018557\times10^{-1}$	$0.46434100259260\times10^{-1}$
17	$0.24291412853736\times10^{-1}$	$0.12797548292871\times10^{-1}$	−0.13138398329741
18	$0.51440451639444\times10^{-2}$	$0.58743664107299\times10^{-2}$	$0.11492850364368\times10^{-1}$
19	$-0.19084949733532\times10^{-1}$	$-0.18451951971969\times10^{-1}$	$-0.33387688429909\times10^{-1}$
20	$0.55229677241291\times10^{-2}$	$0.47226622042472\times10^{-2}$	$0.15183171583644\times10^{-1}$
21	$-0.44197392976085\times10^{-2}$	$-0.52024079680599\times10^{-2}$	$-0.47610805647657\times10^{-2}$
22	$0.40061416708429\times10^{-1}$	$0.43563505956635\times10^{-1}$	$0.46917166277885\times10^{-1}$
23	$-0.33752085907575\times10^{-1}$	$-0.36251690750939\times10^{-1}$	$-0.39401755804649\times10^{-1}$
24	$-0.25127658213357\times10^{-2}$	$-0.28974026866543\times10^{-2}$	$-0.32569956247611\times10^{-2}$

k	$c_{\mathrm{o}i,k}$	$d_{\mathrm{o}i,k}$	$t_{\mathrm{o}i,k}$	k	$c_{\mathrm{o}i,k}$	$d_{\mathrm{o}i,k}$	$t_{\mathrm{o}i,k}$
1	–	1	0.125	13	2	2	4.500
2	–	1	1.125	14	2	3	4.750
3	–	2	0.375	15	2	3	5.000
4	–	2	1.125	16	2	4	4.000
5	–	4	0.625	17	2	4	4.500
6	–	4	1.500	18	3	2	7.500
7	1	1	0.625	19	3	3	14.000
8	1	1	2.625	20	3	4	11.500
9	1	1	2.750	21	6	5	26.000
10	1	2	2.125	22	6	6	28.000
11	1	3	2.000	23	6	6	30.000
12	1	6	1.750	24	6	7	16.000

[a] The values of the coefficients and exponents are also valid for Eq. (4.27).

[b] $K_{\mathrm{Pol},i} = 6$, $K_{\mathrm{Exp},i} = 18$.

Table A3.4 Coefficients and exponents of $\alpha^{\mathrm{r}}_{\mathrm{o}i}$, Eq. (7.7), for carbon dioxide, hydrogen, water, and helium[a]

k	$c_{\mathrm{o}i,k}$	$d_{\mathrm{o}i,k}$	$t_{\mathrm{o}i,k}$	$n_{\mathrm{o}i,k}$
			Carbon dioxide[b]	
1	–	1	0.000	0.52646564804653
2	–	1	1.250	$-0.14995725042592\times10^{1}$
3	–	2	1.625	0.27329786733782
4	–	3	0.375	0.12949500022786
5	1	3	0.375	0.15404088341841
6	1	3	1.375	−0.58186950946814
7	1	4	1.125	−0.18022494838296
8	1	5	1.375	$-0.95389904072812\times10^{-1}$
9	1	6	0.125	$-0.80486819317679\times10^{-2}$
10	1	6	1.625	$-0.35547751273090\times10^{-1}$
11	2	1	3.750	−0.28079014882405
12	2	4	3.500	$-0.82435890081677\times10^{-1}$
13	3	1	7.500	$0.10832427979006\times10^{-1}$
14	3	1	8.000	$-0.67073993161097\times10^{-2}$
15	3	3	6.000	$-0.46827907600524\times10^{-2}$
16	3	3	16.000	$-0.28359911832177\times10^{-1}$
17	3	4	11.000	$0.19500174744098\times10^{-1}$
18	5	5	24.000	−0.21609137507166
19	5	5	26.000	0.43772794926972
20	5	5	28.000	−0.22130790113593
21	6	5	24.000	$0.15190189957331\times10^{-1}$
22	6	5	26.000	$-0.15380948953300\times10^{-1}$
			Hydrogen[c]	
1	–	1	0.500	$0.53579928451252\times10^{1}$
2	–	1	0.625	$-0.62050252530595\times10^{1}$
3	–	2	0.375	0.13830241327086
4	–	2	0.625	$-0.71397954896129\times10^{-1}$
5	–	4	1.125	$0.15474053959733\times10^{-1}$
6	1	1	2.625	−0.14976806405771
7	1	5	0.000	$-0.26368723988451\times10^{-1}$
8	1	5	0.250	$0.56681303156066\times10^{-1}$
9	1	5	1.375	$-0.60063958030436\times10^{-1}$
10	2	1	4.000	−0.45043942027132
11	2	1	4.250	0.42478840244500
12	3	2	5.000	$-0.21997640827139\times10^{-1}$
13	3	5	8.000	$-0.10499521374530\times10^{-1}$
14	5	1	8.000	$-0.28955902866816\times10^{-2}$

Table A3.4 (continued)

k	$c_{\mathrm{o}i,k}$	$d_{\mathrm{o}i,k}$	$t_{\mathrm{o}i,k}$	$n_{\mathrm{o}i,k}$
			Water[d]	
1	–	1	0.500	0.82728408749586
2	–	1	1.250	$-0.18602220416584\times10^{1}$
3	–	1	1.875	$-0.11199009613744\times10^{1}$
4	–	2	0.125	0.15635753976056
5	–	2	1.500	0.87375844859025
6	–	3	1.000	-0.36674403715731
7	–	4	0.750	$0.53987893432436\times10^{-1}$
8	1	1	1.500	$0.10957690214499\times10^{1}$
9	1	5	0.625	$0.53213037828563\times10^{-1}$
10	1	5	2.625	$0.13050533930825\times10^{-1}$
11	2	1	5.000	-0.41079520434476
12	2	2	4.000	0.14637443344120
13	2	4	4.500	$-0.55726838623719\times10^{-1}$
14	3	4	3.000	$-0.11201774143800\times10^{-1}$
15	5	1	4.000	$-0.66062758068099\times10^{-2}$
16	5	1	6.000	$0.46918522004538\times10^{-2}$
			Helium[e]	
1	–	1	0.000	-0.45579024006737
2	–	1	0.125	$0.12516390754925\times10^{1}$
3	–	1	0.750	$-0.15438231650621\times10^{1}$
4	–	4	1.000	$0.20467489707221\times10^{-1}$
5	1	1	0.750	-0.34476212380781
6	1	3	2.625	$-0.20858459512787\times10^{-1}$
7	1	5	0.125	$0.16227414711778\times10^{-1}$
8	1	5	1.250	$-0.57471818200892\times10^{-1}$
9	1	5	2.000	$0.19462416430715\times10^{-1}$
10	2	2	1.000	$-0.33295680123020\times10^{-1}$
11	3	1	4.500	$-0.10863577372367\times10^{-1}$
12	3	2	5.000	$-0.22173365245954\times10^{-1}$

[a] The values of the coefficients and exponents are also valid for Eq. (4.27).

[b] $K_{\mathrm{Pol},i} = 4$, $K_{\mathrm{Exp},i} = 18$.

[c] $K_{\mathrm{Pol},i} = 5$, $K_{\mathrm{Exp},i} = 9$.

[d] $K_{\mathrm{Pol},i} = 7$, $K_{\mathrm{Exp},i} = 9$.

[e] $K_{\mathrm{Pol},i} = 4$, $K_{\mathrm{Exp},i} = 8$.

Table A3.5 Critical parameters and molar masses of the considered 18 components

Component *i*	Formula	$\rho_{c,i}/(\text{mol}\cdot\text{dm}^{-3})$	$T_{c,i}/\text{K}$	$M_i/(\text{g}\cdot\text{mol}^{-1})$[a]
Methane	CH_4	10.139342719	190.564000000	16.042460
Nitrogen	N_2	11.183900000	126.192000000	28.013400
Carbon dioxide	CO_2	10.624978698	304.128200000	44.009500
Ethane	C_2H_6	6.870854540	305.322000000	30.069040
Propane	C_3H_8	5.000043088	369.825000000	44.095620
n-Butane	n-C_4H_{10}	3.920016792	425.125000000	58.122200
Isobutane	i-C_4H_{10}	3.860142940	407.817000000	58.122200
n-Pentane	n-C_5H_{12}	3.215577588	469.700000000	72.148780
Isopentane	i-C_5H_{12}	3.271018581	460.350000000	72.148780
n-Hexane	n-C_6H_{14}	2.705877875	507.820000000	86.175360
n-Heptane	n-C_7H_{16}	2.315324434	540.130000000	100.201940
n-Octane	n-C_8H_{18}	2.056404127	569.320000000	114.228520
Hydrogen	H_2	14.940000000	33.190000000	2.015880
Oxygen	O_2	13.630000000	154.595000000	31.998800
Carbon monoxide	CO	10.850000000	132.800000000	28.010100
Water	H_2O	17.873716090	647.096000000	18.015280
Helium	He	17.399000000	5.195300000	4.002602
Argon	Ar	13.407429659	150.687000000	39.948000

[a] According to Wieser (2006).

Table A3.6 Non-zero F_{ij} parameters of α^{r}, Eq. (7.3), for the binary mixtures taken into account by binary specific and generalised departure functions[a]

Mixture *i*–*j*	F_{ij}
Methane–Nitrogen	$0.100000000000\times10^{1}$
Methane–Carbon dioxide	$0.100000000000\times10^{1}$
Methane–Ethane	$0.100000000000\times10^{1}$
Methane–Propane	$0.100000000000\times10^{1}$
Methane–n-Butane	$0.100000000000\times10^{1}$
Methane–Isobutane	0.771035405688
Methane–Hydrogen	$0.100000000000\times10^{1}$
Nitrogen–Carbon dioxide	$0.100000000000\times10^{1}$
Nitrogen–Ethane	$0.100000000000\times10^{1}$
Ethane–Propane	0.130424765150
Ethane–n-Butane	0.281570073085
Ethane–Isobutane	0.260632376098
Propane–n-Butane	$0.312572600489\times10^{-1}$
Propane–Isobutane	$-0.551609771024\times10^{-1}$
n-Butane–Isobutane	$-0.551240293009\times10^{-1}$

[a] The values of F_{ij} equal zero for all other binary combinations.

Table A3.7 Coefficients and exponents of α_{ij}^{r}, Eq. (7.8), for the binary mixtures taken into account by binary specific and generalised departure functions

k	$d_{ij,k}$	$t_{ij,k}$	$n_{ij,k}$	$\eta_{ij,k}$	$\varepsilon_{ij,k}$	$\beta_{ij,k}$	$\gamma_{ij,k}$
Methane–Nitrogen[a]							
1	1	0.000	$-0.98038985517335\times10^{-2}$	–	–	–	–
2	4	1.850	$0.42487270143005\times10^{-3}$	–	–	–	–
3	1	7.850	$-0.34800214576142\times10^{-1}$	1.000	0.500	1.000	0.500
4	2	5.400	-0.13333813013896	1.000	0.500	1.000	0.500
5	2	0.000	$-0.11993694974627\times10^{-1}$	0.250	0.500	2.500	0.500
6	2	0.750	$0.69243379775168\times10^{-1}$	0.000	0.500	3.000	0.500
7	2	2.800	-0.31022508148249	0.000	0.500	3.000	0.500
8	2	4.450	0.24495491753226	0.000	0.500	3.000	0.500
9	3	4.250	0.22369816716981	0.000	0.500	3.000	0.500
Methane–Carbon dioxide[b]							
1	1	2.600	-0.10859387354942	–	–	–	–
2	2	1.950	$0.80228576727389\times10^{-1}$	–	–	–	–
3	3	0.000	$-0.93303985115717\times10^{-2}$	–	–	–	–
4	1	3.950	$0.40989274005848\times10^{-1}$	1.000	0.500	1.000	0.500
5	2	7.950	-0.24338019772494	0.500	0.500	2.000	0.500
6	3	8.000	0.23855347281124	0.000	0.500	3.000	0.500
Methane–Ethane[c]							
1	3	0.650	$-0.80926050298746\times10^{-3}$	–	–	–	–
2	4	1.550	$-0.75381925080059\times10^{-3}$	–	–	–	–
3	1	3.100	$-0.41618768891219\times10^{-1}$	1.000	0.500	1.000	0.500
4	2	5.900	-0.23452173681569	1.000	0.500	1.000	0.500
5	2	7.050	0.14003840584586	1.000	0.500	1.000	0.500
6	2	3.350	$0.63281744807738\times10^{-1}$	0.875	0.500	1.250	0.500
7	2	1.200	$-0.34660425848809\times10^{-1}$	0.750	0.500	1.500	0.500
8	2	5.800	-0.23918747334251	0.500	0.500	2.000	0.500
9	2	2.700	$0.19855255066891\times10^{-2}$	0.000	0.500	3.000	0.500
10	3	0.450	$0.61777746171555\times10^{1}$	0.000	0.500	3.000	0.500
11	3	0.550	$-0.69575358271105\times10^{1}$	0.000	0.500	3.000	0.500
12	3	1.950	$0.10630185306388\times10^{1}$	0.000	0.500	3.000	0.500
Methane–Propane[d]							
1	3	1.850	$0.13746429958576\times10^{-1}$	–	–	–	–
2	3	3.950	$-0.74425012129552\times10^{-2}$	–	–	–	–
3	4	0.000	$-0.45516600213685\times10^{-2}$	–	–	–	–
4	4	1.850	$-0.54546603350237\times10^{-2}$	–	–	–	–
5	4	3.850	$0.23682016824471\times10^{-2}$	–	–	–	–
6	1	5.250	0.18007763721438	0.250	0.500	0.750	0.500
7	1	3.850	-0.44773942932486	0.250	0.500	1.000	0.500
8	1	0.200	$0.19327374888200\times10^{-1}$	0.000	0.500	2.000	0.500
9	2	6.500	-0.30632197804624	0.000	0.500	3.000	0.500

Table A3.7 (continued)

k	$d_{ij,k}$	$t_{ij,k}$	$n_{ij,k}$	$\eta_{ij,k}$	$\varepsilon_{ij,k}$	$\beta_{ij,k}$	$\gamma_{ij,k}$
Nitrogen–Carbon dioxide[e]							
1	2	1.850	0.28661625028399	–	–	–	–
2	3	1.400	−0.10919833861247	–	–	–	–
3	1	3.200	$-0.11374032082270\times10^{1}$	0.250	0.500	0.750	0.500
4	1	2.500	0.76580544237358	0.250	0.500	1.000	0.500
5	1	8.000	$0.42638000926819\times10^{-2}$	0.000	0.500	2.000	0.500
6	2	3.750	0.17673538204534	0.000	0.500	3.000	0.500
Nitrogen–Ethane[f]							
1	2	0.000	−0.47376518126608	–	–	–	–
2	2	0.050	0.48961193461001	–	–	–	–
3	3	0.000	$-0.57011062090535\times10^{-2}$	–	–	–	–
4	1	3.650	−0.19966820041320	1.000	0.500	1.000	0.500
5	2	4.900	−0.69411103101723	1.000	0.500	1.000	0.500
6	2	4.450	0.69226192739021	0.875	0.500	1.250	0.500
Methane–Hydrogen[g]							
1	1	2.000	−0.25157134971934	–	–	–	–
2	3	−1.000	$-0.62203841111983\times10^{-2}$	–	–	–	–
3	3	1.750	$0.88850315184396\times10^{-1}$	–	–	–	–
4	4	1.400	$-0.35592212573239\times10^{-1}$	–	–	–	–
Methane–n-Butane, Methane–Isobutane, Ethane–Propane, Ethane–n-Butane, Ethane–Isobutane, Propane–n-Butane, Propane–Isobutane, and n-Butane–Isobutane[h]							
1	1	1.000	$0.25574776844118\times10^{1}$	–	–	–	–
2	1	1.550	$-0.79846357136353\times10^{1}$	–	–	–	–
3	1	1.700	$0.47859131465806\times10^{1}$	–	–	–	–
4	2	0.250	−0.73265392369587	–	–	–	–
5	2	1.350	$0.13805471345312\times10^{1}$	–	–	–	–
6	3	0.000	0.28349603476365	–	–	–	–
7	3	1.250	−0.49087385940425	–	–	–	–
8	4	0.000	−0.10291888921447	–	–	–	–
9	4	0.700	0.11836314681968	–	–	–	–
10	4	5.400	$0.55527385721943\times10^{-4}$	–	–	–	–

[a] $K_{\mathrm{Pol},ij} = 2$, $K_{\mathrm{Exp},ij} = 7$.
[b] $K_{\mathrm{Pol},ij} = 3$, $K_{\mathrm{Exp},ij} = 3$.
[c] $K_{\mathrm{Pol},ij} = 2$, $K_{\mathrm{Exp},ij} = 10$.
[d] $K_{\mathrm{Pol},ij} = 5$, $K_{\mathrm{Exp},ij} = 4$.
[e] $K_{\mathrm{Pol},ij} = 2$, $K_{\mathrm{Exp},ij} = 4$.
[f] $K_{\mathrm{Pol},ij} = 3$, $K_{\mathrm{Exp},ij} = 3$.
[g] $K_{\mathrm{Pol},ij} = 4$, $K_{\mathrm{Exp},ij} = 0$.
[h] $K_{\mathrm{Pol},ij} = 10$, $K_{\mathrm{Exp},ij} = 0$.

Table A3.8 Binary parameters of the reducing functions for density and temperature, Eqs. (7.9) and (7.10)

Mixture *i*–*j*	$\beta_{v,ij}$	$\gamma_{v,ij}$	$\beta_{T,ij}$	$\gamma_{T,ij}$
CH_4–N_2	0.998721377	1.013950311	0.998098830	0.979273013
CH_4–CO_2	0.999518072	1.002806594	1.022624490	0.975665369
CH_4–C_2H_6	0.997547866	1.006617867	0.996336508	1.049707697
CH_4–C_3H_8	1.004827070	1.038470657	0.989680305	1.098655531
CH_4–n-C_4H_{10}	0.979105972	1.045375122	0.994174910	1.171607691
CH_4–i-C_4H_{10}	1.011240388	1.054319053	0.980315756	1.161117729
CH_4–n-C_5H_{12}	0.948330120	1.124508039	0.992127525	1.249173968
CH_4–i-C_5H_{12}	1.000000000	1.343685343	1.000000000	1.188899743
CH_4–n-C_6H_{14}	0.958015294	1.052643846	0.981844797	1.330570181
CH_4–n-C_7H_{16}	0.962050831	1.156655935	0.977431529	1.379850328
CH_4–n-C_8H_{18}	0.994740603	1.116549372	0.957473785	1.449245409
CH_4–H_2	1.000000000	1.018702573	1.000000000	1.352643115
CH_4–O_2	1.000000000	1.000000000	1.000000000	0.950000000
CH_4–CO	0.997340772	1.006102927	0.987411732	0.987473033
CH_4–H_2O	1.012783169	1.585018334	1.063333913	0.775810513
CH_4–He	1.000000000	0.881405683	1.000000000	3.159776855
CH_4–Ar	1.034630259	1.014678542	0.990954281	0.989843388
N_2–CO_2	0.977794634	1.047578256	1.005894529	1.107654104
N_2–C_2H_6	0.978880168	1.042352891	1.007671428	1.098650964
N_2–C_3H_8	0.974424681	1.081025408	1.002677329	1.201264026
N_2–n-C_4H_{10}	0.996082610	1.146949309	0.994515234	1.304886838
N_2–i-C_4H_{10}	0.986415830	1.100576129	0.992868130	1.284462634
N_2–n-C_5H_{12}	1.000000000	1.078877166	1.000000000	1.419029041
N_2–i-C_5H_{12}	1.000000000	1.154135439	1.000000000	1.381770770
N_2–n-C_6H_{14}	1.000000000	1.195952177	1.000000000	1.472607971
N_2–n-C_7H_{16}	1.000000000	1.404554090	1.000000000	1.520975334
N_2–n-C_8H_{18}	1.000000000	1.186067025	1.000000000	1.733280051
N_2–H_2	0.972532065	0.970115357	0.946134337	1.175696583
N_2–O_2	0.999521770	0.997082328	0.997190589	0.995157044
N_2–CO	1.000000000	1.008690943	1.000000000	0.993425388
N_2–H_2O	1.000000000	1.094749685	1.000000000	0.968808467
N_2–He	0.969501055	0.932629867	0.692868765	1.471831580
N_2–Ar	1.004166412	1.002212182	0.999069843	0.990034831
CO_2–C_2H_6	1.002525718	1.032876701	1.013871147	0.900949530
CO_2–C_3H_8	0.996898004	1.047596298	1.033620538	0.908772477
CO_2–n-C_4H_{10}	1.174760923	1.222437324	1.018171004	0.911498231
CO_2–i-C_4H_{10}	1.076551882	1.081909003	1.023339824	0.929982936
CO_2–n-C_5H_{12}	1.024311498	1.068406078	1.027000795	0.979217302
CO_2–i-C_5H_{12}	1.060793104	1.116793198	1.019180957	0.961218039
CO_2–n-C_6H_{14}	1.000000000	0.851343711	1.000000000	1.038675574
CO_2–n-C_7H_{16}	1.205469976	1.164585914	1.011806317	1.046169823
CO_2–n-C_8H_{18}	1.026169373	1.104043935	1.029690780	1.074455386

Table A3.8 (continued)

Mixture *i–j*	$\beta_{v,ij}$	$\gamma_{v,ij}$	$\beta_{T,ij}$	$\gamma_{T,ij}$
CO_2–H_2	0.904142159	1.152792550	0.942320195	1.782924792
CO_2–O_2	1.000000000	1.000000000	1.000000000	1.000000000
CO_2–CO	1.000000000	1.000000000	1.000000000	1.000000000
CO_2–H_2O	0.949055959	1.542328793	0.997372205	0.775453996
CO_2–He	0.846647561	0.864141549	0.768377630	3.207456948
CO_2–Ar	1.008392428	1.029205465	0.996512863	1.050971635
C_2H_6–C_3H_8	0.997607277	1.003034720	0.996199694	1.014730190
C_2H_6–n-C_4H_{10}	0.999157205	1.006179146	0.999130554	1.034832749
C_2H_6–i-C_4H_{10}	1.000000000	1.006616886	1.000000000	1.033283811
C_2H_6–n-C_5H_{12}	0.993851009	1.026085655	0.998688946	1.066665676
C_2H_6–i-C_5H_{12}[a]	1.000000000	1.045439246	1.000000000	1.021150247
C_2H_6–n-C_6H_{14}	1.000000000	1.169701102	1.000000000	1.092177796
C_2H_6–n-C_7H_{16}	1.000000000	1.057666085	1.000000000	1.134532014
C_2H_6–n-C_8H_{18}	1.007469726	1.071917985	0.984068272	1.168636194
C_2H_6–H_2	0.925367171	1.106072040	0.932969831	1.902008495
C_2H_6–O_2	1.000000000	1.000000000	1.000000000	1.000000000
C_2H_6–CO	1.000000000	1.201417898	1.000000000	1.069224728
C_2H_6–H_2O	1.000000000	1.000000000	1.000000000	1.000000000
C_2H_6–He	1.000000000	1.000000000	1.000000000	1.000000000
C_2H_6–Ar	1.000000000	1.000000000	1.000000000	1.000000000
C_3H_8–n-C_4H_{10}	0.999795868	1.003264179	1.000310289	1.007392782
C_3H_8–i-C_4H_{10}	0.999243146	1.001156119	0.998012298	1.005250774
C_3H_8–n-C_5H_{12}	1.044919431	1.019921513	0.996484021	1.008344412
C_3H_8–i-C_5H_{12}	1.040459289	0.999432118	0.994364425	1.003269500
C_3H_8–n-C_6H_{14}	1.000000000	1.057872566	1.000000000	1.025657518
C_3H_8–n-C_7H_{16}	1.000000000	1.079648053	1.000000000	1.050044169
C_3H_8–n-C_8H_{18}	1.000000000	1.102764612	1.000000000	1.063694129
C_3H_8–H_2	1.000000000	1.074006110	1.000000000	2.308215191
C_3H_8–O_2	1.000000000	1.000000000	1.000000000	1.000000000
C_3H_8–CO	1.000000000	1.108143673	1.000000000	1.197564208
C_3H_8–H_2O	1.000000000	1.011759763	1.000000000	0.600340961
C_3H_8–He	1.000000000	1.000000000	1.000000000	1.000000000
C_3H_8–Ar	1.000000000	1.000000000	1.000000000	1.000000000
n-C_4H_{10}–i-C_4H_{10}	1.000880464	1.000414440	1.000077547	1.001432824
n-C_4H_{10}–n-C_5H_{12}	1.000000000	1.018159650	1.000000000	1.002143640
n-C_4H_{10}–i-C_5H_{12}[a]	1.000000000	1.002728262	1.000000000	1.000792201
n-C_4H_{10}–n-C_6H_{14}	1.000000000	1.034995284	1.000000000	1.009157060
n-C_4H_{10}–n-C_7H_{16}	1.000000000	1.019174227	1.000000000	1.021283378
n-C_4H_{10}–n-C_8H_{18}	1.000000000	1.046905515	1.000000000	1.033180106
n-C_4H_{10}–H_2	1.000000000	1.232939523	1.000000000	2.509259945
n-C_4H_{10}–O_2	1.000000000	1.000000000	1.000000000	1.000000000
n-C_4H_{10}–CO[a]	1.000000000	1.084740904	1.000000000	1.174055065
n-C_4H_{10}–H_2O	1.000000000	1.223638763	1.000000000	0.615512682

Table A3.8 (continued)

Mixture *i–j*	$\beta_{v,ij}$	$\gamma_{v,ij}$	$\beta_{T,ij}$	$\gamma_{T,ij}$
n-C_4H_{10}–He	1.000000000	1.000000000	1.000000000	1.000000000
n-C_4H_{10}–Ar	1.000000000	1.214638734	1.000000000	1.245039498
i-C_4H_{10}–n-C_5H_{12}[a]	1.000000000	1.002779804	1.000000000	1.002495889
i-C_4H_{10}–i-C_5H_{12}[a]	1.000000000	1.002284197	1.000000000	1.001835788
i-C_4H_{10}–n-C_6H_{14}[a]	1.000000000	1.010493989	1.000000000	1.006018054
i-C_4H_{10}–n-C_7H_{16}[a]	1.000000000	1.021668316	1.000000000	1.009885760
i-C_4H_{10}–n-C_8H_{18}[a]	1.000000000	1.032807063	1.000000000	1.013945424
i-C_4H_{10}–H_2[a]	1.000000000	1.147595688	1.000000000	1.895305393
i-C_4H_{10}–O_2	1.000000000	1.000000000	1.000000000	1.000000000
i-C_4H_{10}–CO[a]	1.000000000	1.087272232	1.000000000	1.161523504
i-C_4H_{10}–H_2O	1.000000000	1.000000000	1.000000000	1.000000000
i-C_4H_{10}–He	1.000000000	1.000000000	1.000000000	1.000000000
i-C_4H_{10}–Ar	1.000000000	1.000000000	1.000000000	1.000000000
n-C_5H_{12}–i-C_5H_{12}[a]	1.000000000	1.000024352	1.000000000	1.000050537
n-C_5H_{12}–n-C_6H_{14}[a]	1.000000000	1.002480637	1.000000000	1.000761237
n-C_5H_{12}–n-C_7H_{16}[a]	1.000000000	1.008972412	1.000000000	1.002441051
n-C_5H_{12}–n-C_8H_{18}	1.000000000	1.069223964	1.000000000	1.016422347
n-C_5H_{12}–H_2[a]	1.000000000	1.188334783	1.000000000	2.013859174
n-C_5H_{12}–O_2	1.000000000	1.000000000	1.000000000	1.000000000
n-C_5H_{12}–CO[a]	1.000000000	1.119954454	1.000000000	1.206195595
n-C_5H_{12}–H_2O	1.000000000	0.956677310	1.000000000	0.447666011
n-C_5H_{12}–He	1.000000000	1.000000000	1.000000000	1.000000000
n-C_5H_{12}–Ar	1.000000000	1.000000000	1.000000000	1.000000000
i-C_5H_{12}–n-C_6H_{14}[a]	1.000000000	1.002996055	1.000000000	1.001204174
i-C_5H_{12}–n-C_7H_{16}[a]	1.000000000	1.009928531	1.000000000	1.003194615
i-C_5H_{12}–n-C_8H_{18}[a]	1.000000000	1.017880981	1.000000000	1.005647480
i-C_5H_{12}–H_2[a]	1.000000000	1.184339122	1.000000000	1.996386669
i-C_5H_{12}–O_2	1.000000000	1.000000000	1.000000000	1.000000000
i-C_5H_{12}–CO[a]	1.000000000	1.116693501	1.000000000	1.199475627
i-C_5H_{12}–H_2O	1.000000000	1.000000000	1.000000000	1.000000000
i-C_5H_{12}–He	1.000000000	1.000000000	1.000000000	1.000000000
i-C_5H_{12}–Ar	1.000000000	1.000000000	1.000000000	1.000000000
n-C_6H_{14}–n-C_7H_{16}	1.000000000	1.001508227	1.000000000	0.999762786
n-C_6H_{14}–n-C_8H_{18}[a]	1.000000000	1.006268954	1.000000000	1.001633952
n-C_6H_{14}–H_2	1.000000000	1.243461678	1.000000000	3.021197546
n-C_6H_{14}–O_2	1.000000000	1.000000000	1.000000000	1.000000000
n-C_6H_{14}–CO[a]	1.000000000	1.155145836	1.000000000	1.233435828
n-C_6H_{14}–H_2O	1.000000000	1.170217596	1.000000000	0.569681333
n-C_6H_{14}–He	1.000000000	1.000000000	1.000000000	1.000000000
n-C_6H_{14}–Ar	1.000000000	1.000000000	1.000000000	1.000000000
n-C_7H_{16}–n-C_8H_{18}	1.000000000	1.006767176	1.000000000	0.998793111
n-C_7H_{16}–H_2	1.000000000	1.159131722	1.000000000	3.169143057

Table A3.8 (continued)

Mixture *i–j*	$\beta_{v,ij}$	$\gamma_{v,ij}$	$\beta_{T,ij}$	$\gamma_{T,ij}$
n-C_7H_{16}–O_2	1.000000000	1.000000000	1.000000000	1.000000000
n-C_7H_{16}–CO[a]	1.000000000	1.190354273	1.000000000	1.256295219
n-C_7H_{16}–H_2O	1.000000000	1.000000000	1.000000000	1.000000000
n-C_7H_{16}–He	1.000000000	1.000000000	1.000000000	1.000000000
n-C_7H_{16}–Ar	1.000000000	1.000000000	1.000000000	1.000000000
n-C_8H_{18}–H_2[a]	1.000000000	1.305249405	1.000000000	2.191555216
n-C_8H_{18}–O_2	1.000000000	1.000000000	1.000000000	1.000000000
n-C_8H_{18}–CO[a]	1.000000000	1.219206702	1.000000000	1.276744779
n-C_8H_{18}–H_2O	1.000000000	0.599484191	1.000000000	0.662072469
n-C_8H_{18}–He	1.000000000	1.000000000	1.000000000	1.000000000
n-C_8H_{18}–Ar	1.000000000	1.000000000	1.000000000	1.000000000
H_2–O_2	1.000000000	1.000000000	1.000000000	1.000000000
H_2–CO	1.000000000	1.121416201	1.000000000	1.377504607
H_2–H_2O	1.000000000	1.000000000	1.000000000	1.000000000
H_2–He	1.000000000	1.000000000	1.000000000	1.000000000
H_2–Ar	1.000000000	1.000000000	1.000000000	1.000000000
O_2–CO	1.000000000	1.000000000	1.000000000	1.000000000
O_2–H_2O	1.000000000	1.143174289	1.000000000	0.964767932
O_2–He	1.000000000	1.000000000	1.000000000	1.000000000
O_2–Ar	0.999746847	0.993907223	1.000023103	0.990430423
CO–H_2O	1.000000000	1.000000000	1.000000000	1.000000000
CO–He	1.000000000	1.000000000	1.000000000	1.000000000
CO–Ar	1.000000000	1.159720623	1.000000000	0.954215746
H_2O–He	1.000000000	1.000000000	1.000000000	1.000000000
H_2O–Ar	1.000000000	1.038993495	1.000000000	1.070941866
He–Ar	1.000000000	1.000000000	1.000000000	1.000000000

[a] The values for the binary parameters $\gamma_{v,ij}$ and $\gamma_{T,ij}$ were calculated from Eq. (5.17).

A4 Binary Parameters of the Alternative (Invariant) Equation of State

Table A4.1 Binary parameters of the invariant reducing functions for density and temperature, Eqs. (7.168) and (7.169)

Mixture *i–j*	$\lambda_{v,ij}$	$\phi_{v,ij}$	$\lambda_{T,ij}$	$\phi_{T,ij}$
CH_4–N_2	−0.002594526	1.013949718	−0.003727066	0.979271745
CH_4–CO_2	−0.000966671	1.002806510	0.043644877	0.975490845
CH_4–C_2H_6	−0.004945543	1.006615585	−0.007705262	1.049702643
CH_4–C_3H_8	0.009989309	1.038461234	−0.022792161	1.098613277
CH_4–n-C_4H_{10}	−0.044459239	1.045192077	−0.013689115	1.171593399
CH_4–i-C_4H_{10}	0.023473280	1.054266276	−0.046158169	1.160953717
CH_4–n-C_5H_{12}	−0.121726735	1.123234541	−0.019745389	1.249146078
CH_4–i-C_5H_{12}	0.000000000	1.343685343	0.000000000	1.188899743
CH_4–n-C_6H_{14}	−0.092044189	1.051822957	−0.048749270	1.330410544
CH_4–n-C_7H_{16}	−0.091214759	1.155906408	−0.062979290	1.379593371
CH_4–n-C_8H_{18}	−0.011809823	1.116535007	−0.125840032	1.448267628
CH_4–H_2	0.000000000	1.018702573	0.000000000	1.352643115
CH_4–O_2	0.000000000	1.000000000	0.000000000	0.950000000
CH_4–CO	−0.005357713	1.006100378	−0.025016937	0.987416393
CH_4–H_2O	0.040362480	1.584931196	0.095103361	0.774765793
CH_4–He	0.000000000	0.881405683	0.000000000	3.159776855
CH_4–Ar	0.069281501	1.014255587	−0.017988429	0.989814175
N_2–CO_2	−0.047052295	1.047390254	0.013019637	1.107640428
N_2–C_2H_6	−0.044659292	1.042179006	0.016791623	1.098628030
N_2–C_3H_8	−0.056419804	1.080749284	0.006423740	1.201260956
N_2–n-C_4H_{10}	−0.009016489	1.146941940	−0.014353178	1.304872730
N_2–i-C_4H_{10}	−0.030260917	1.100493547	−0.018386412	1.284439115
N_2–n-C_5H_{12}	0.000000000	1.078877166	0.000000000	1.419029041
N_2–i-C_5H_{12}	0.000000000	1.154135439	0.000000000	1.381770770
N_2–n-C_6H_{14}	0.000000000	1.195952177	0.000000000	1.472607971
N_2–n-C_7H_{16}	0.000000000	1.404554090	0.000000000	1.520975334
N_2–n-C_8H_{18}	0.000000000	1.186067025	0.000000000	1.733280051
N_2–H_2	−0.053847812	0.969841575	−0.129997862	1.174409194
N_2–O_2	−0.000953457	0.997082236	−0.005599457	0.995154228
N_2–CO	0.000000000	1.008690943	0.000000000	0.993425388
N_2–H_2O	0.000000000	1.094749685	0.000000000	0.968808467
N_2–He	−0.057439409	0.932297970	−1.010004338	1.403319851
N_2–Ar	0.008336546	1.002205958	−0.001842632	0.990034524
CO_2–C_2H_6	0.005209770	1.032874073	0.024820275	0.900888422
CO_2–C_3H_8	−0.006516778	1.047592243	0.060069051	0.908417393
CO_2–n-C_4H_{10}	0.365402991	1.209976841	0.032822959	0.911392590
CO_2–i-C_4H_{10}	0.154764261	1.079557865	0.042900937	0.929806023

Table A4.1 (continued)

Mixture *i–j*	$\lambda_{v,ij}$	$\phi_{v,ij}$	$\lambda_{T,ij}$	$\phi_{T,ij}$
CO_2–n-C_5H_{12}	0.050778398	1.068150222	0.052159382	0.978968906
CO_2–i-C_5H_{12}	0.128265988	1.115192821	0.036518354	0.961094032
CO_2–n-C_6H_{14}	0.000000000	0.851343711	0.000000000	1.038675574
CO_2–n-C_7H_{16}	0.385284587	1.146531907	0.024556438	1.046118312
CO_2–n-C_8H_{18}	0.056179059	1.103706144	0.062846951	1.074126696
CO_2–H_2	−0.227828534	1.148623699	−0.211472229	1.780677507
CO_2–O_2	0.000000000	1.000000000	0.000000000	1.000000000
CO_2–CO	0.000000000	1.000000000	0.000000000	1.000000000
CO_2–H_2O	−0.159454088	1.540880838	−0.004080818	0.775452077
CO_2–He	−0.273822949	0.855102255	−1.632463749	3.129231265
CO_2–Ar	0.017215571	1.029179200	−0.007342529	1.050967051
C_2H_6–C_3H_8	−0.004807651	1.003032612	−0.007727206	1.014724932
C_2H_6–n-C_4H_{10}	−0.001698081	1.006178799	−0.001800244	1.034832469
C_2H_6–i-C_4H_{10}	0.000000000	1.006616886	0.000000000	1.033283811
C_2H_6–n-C_5H_{12}	−0.012681586	1.026070161	−0.002798745	1.066665020
C_2H_6–i-C_5H_{12}	0.000000000	1.045439246	0.000000000	1.021150247
C_2H_6–n-C_6H_{14}	0.000000000	1.169701102	0.000000000	1.092177796
C_2H_6–n-C_7H_{16}	0.000000000	1.057666085	0.000000000	1.134532014
C_2H_6–n-C_8H_{18}	0.015901818	1.071893345	−0.037531734	1.168528466
C_2H_6–H_2	−0.167154232	1.103539451	−0.263294196	1.898739787
C_2H_6–O_2	0.000000000	1.000000000	0.000000000	1.000000000
C_2H_6–CO	0.000000000	1.201417898	0.000000000	1.069224728
C_2H_6–H_2O	0.000000000	1.000000000	0.000000000	1.000000000
C_2H_6–He	0.000000000	1.000000000	0.000000000	1.000000000
C_2H_6–Ar	0.000000000	1.000000000	0.000000000	1.000000000
C_3H_8–n-C_4H_{10}	−0.000410213	1.003264139	0.000625069	1.007392747
C_3H_8–i-C_4H_{10}	−0.001516514	1.001155901	−0.004000247	1.005249352
C_3H_8–n-C_5H_{12}	0.088866176	1.019200323	−0.007103086	1.008339941
C_3H_8–i-C_5H_{12}	0.078696960	0.998855703	−0.011339803	1.003258047
C_3H_8–n-C_6H_{14}	0.000000000	1.057872566	0.000000000	1.025657518
C_3H_8–n-C_7H_{16}	0.000000000	1.079648053	0.000000000	1.050044169
C_3H_8–n-C_8H_{18}	0.000000000	1.102764612	0.000000000	1.063694129
C_3H_8–H_2	0.000000000	1.074006110	0.000000000	2.308215191
C_3H_8–O_2	0.000000000	1.000000000	0.000000000	1.000000000
C_3H_8–CO	0.000000000	1.108143673	0.000000000	1.197564208
C_3H_8–H_2O	0.000000000	1.011759763	0.000000000	0.600340961
C_3H_8–He	0.000000000	1.000000000	0.000000000	1.000000000
C_3H_8–Ar	0.000000000	1.000000000	0.000000000	1.000000000
n-C_4H_{10}–i-C_4H_{10}	0.001760806	1.000413785	0.000155310	1.001432822
n-C_4H_{10}–n-C_5H_{12}	0.000000000	1.018159650	0.000000000	1.002143640
n-C_4H_{10}–i-C_5H_{12}	0.000000000	1.002728262	0.000000000	1.000792201
n-C_4H_{10}–n-C_6H_{14}	0.000000000	1.034995284	0.000000000	1.009157060
n-C_4H_{10}–n-C_7H_{16}	0.000000000	1.019174227	0.000000000	1.021283378

Table A4.1 (continued)

Mixture *i–j*	$\lambda_{v,ij}$	$\phi_{v,ij}$	$\lambda_{T,ij}$	$\phi_{T,ij}$
$n\text{-}C_4H_{10}$–$n\text{-}C_8H_{18}$	0.000000000	1.046905515	0.000000000	1.033180106
$n\text{-}C_4H_{10}$–H_2	0.000000000	1.232939523	0.000000000	2.509259945
$n\text{-}C_4H_{10}$–O_2	0.000000000	1.000000000	0.000000000	1.000000000
$n\text{-}C_4H_{10}$–CO	0.000000000	1.084740904	0.000000000	1.174055065
$n\text{-}C_4H_{10}$–H_2O	0.000000000	1.223638763	0.000000000	0.615512682
$n\text{-}C_4H_{10}$–He	0.000000000	1.000000000	0.000000000	1.000000000
$n\text{-}C_4H_{10}$–Ar	0.000000000	1.214638734	0.000000000	1.245039498
$i\text{-}C_4H_{10}$–$n\text{-}C_5H_{12}$	0.000000000	1.002779804	0.000000000	1.002495889
$i\text{-}C_4H_{10}$–$i\text{-}C_5H_{12}$	0.000000000	1.002284197	0.000000000	1.001835788
$i\text{-}C_4H_{10}$–$n\text{-}C_6H_{14}$	0.000000000	1.010493989	0.000000000	1.006018054
$i\text{-}C_4H_{10}$–$n\text{-}C_7H_{16}$	0.000000000	1.021668316	0.000000000	1.009885760
$i\text{-}C_4H_{10}$–$n\text{-}C_8H_{18}$	0.000000000	1.032807063	0.000000000	1.013945424
$i\text{-}C_4H_{10}$–H_2	0.000000000	1.147595688	0.000000000	1.895305393
$i\text{-}C_4H_{10}$–O_2	0.000000000	1.000000000	0.000000000	1.000000000
$i\text{-}C_4H_{10}$–CO	0.000000000	1.087272232	0.000000000	1.161523504
$i\text{-}C_4H_{10}$–H_2O	0.000000000	1.000000000	0.000000000	1.000000000
$i\text{-}C_4H_{10}$–He	0.000000000	1.000000000	0.000000000	1.000000000
$i\text{-}C_4H_{10}$–Ar	0.000000000	1.000000000	0.000000000	1.000000000
$n\text{-}C_5H_{12}$–$i\text{-}C_5H_{12}$	0.000000000	1.000024352	0.000000000	1.000050537
$n\text{-}C_5H_{12}$–$n\text{-}C_6H_{14}$	0.000000000	1.002480637	0.000000000	1.000761237
$n\text{-}C_5H_{12}$–$n\text{-}C_7H_{16}$	0.000000000	1.008972412	0.000000000	1.002441051
$n\text{-}C_5H_{12}$–$n\text{-}C_8H_{18}$	0.000000000	1.069223964	0.000000000	1.016422347
$n\text{-}C_5H_{12}$–H_2	0.000000000	1.188334783	0.000000000	2.013859174
$n\text{-}C_5H_{12}$–O_2	0.000000000	1.000000000	0.000000000	1.000000000
$n\text{-}C_5H_{12}$–CO	0.000000000	1.119954454	0.000000000	1.206195595
$n\text{-}C_5H_{12}$–H_2O	0.000000000	0.956677310	0.000000000	0.447666011
$n\text{-}C_5H_{12}$–He	0.000000000	1.000000000	0.000000000	1.000000000
$n\text{-}C_5H_{12}$–Ar	0.000000000	1.000000000	0.000000000	1.000000000
$i\text{-}C_5H_{12}$–$n\text{-}C_6H_{14}$	0.000000000	1.002996055	0.000000000	1.001204174
$i\text{-}C_5H_{12}$–$n\text{-}C_7H_{16}$	0.000000000	1.009928531	0.000000000	1.003194615
$i\text{-}C_5H_{12}$–$n\text{-}C_8H_{18}$	0.000000000	1.017880981	0.000000000	1.005647480
$i\text{-}C_5H_{12}$–H_2	0.000000000	1.184339122	0.000000000	1.996386669
$i\text{-}C_5H_{12}$–O_2	0.000000000	1.000000000	0.000000000	1.000000000
$i\text{-}C_5H_{12}$–CO	0.000000000	1.116693501	0.000000000	1.199475627
$i\text{-}C_5H_{12}$–H_2O	0.000000000	1.000000000	0.000000000	1.000000000
$i\text{-}C_5H_{12}$–He	0.000000000	1.000000000	0.000000000	1.000000000
$i\text{-}C_5H_{12}$–Ar	0.000000000	1.000000000	0.000000000	1.000000000
$n\text{-}C_6H_{14}$–$n\text{-}C_7H_{16}$	0.000000000	1.001508227	0.000000000	0.999762786
$n\text{-}C_6H_{14}$–$n\text{-}C_8H_{18}$	0.000000000	1.006268954	0.000000000	1.001633952
$n\text{-}C_6H_{14}$–H_2	0.000000000	1.243461678	0.000000000	3.021197546
$n\text{-}C_6H_{14}$–O_2	0.000000000	1.000000000	0.000000000	1.000000000
$n\text{-}C_6H_{14}$–CO	0.000000000	1.155145836	0.000000000	1.233435828

Table A4.1 (continued)

Mixture *i–j*	$\lambda_{v,ij}$	$\phi_{v,ij}$	$\lambda_{T,ij}$	$\phi_{T,ij}$
n-C_6H_{14}–H_2O	0.000000000	1.170217596	0.000000000	0.569681333
n-C_6H_{14}–He	0.000000000	1.000000000	0.000000000	1.000000000
n-C_6H_{14}–Ar	0.000000000	1.000000000	0.000000000	1.000000000
n-C_7H_{16}–n-C_8H_{18}	0.000000000	1.006767176	0.000000000	0.998793111
n-C_7H_{16}–H_2	0.000000000	1.159131722	0.000000000	3.169143057
n-C_7H_{16}–O_2	0.000000000	1.000000000	0.000000000	1.000000000
n-C_7H_{16}–CO	0.000000000	1.190354273	0.000000000	1.256295219
n-C_7H_{16}–H_2O	0.000000000	1.000000000	0.000000000	1.000000000
n-C_7H_{16}–He	0.000000000	1.000000000	0.000000000	1.000000000
n-C_7H_{16}–Ar	0.000000000	1.000000000	0.000000000	1.000000000
n-C_8H_{18}–H_2	0.000000000	1.305249405	0.000000000	2.191555216
n-C_8H_{18}–O_2	0.000000000	1.000000000	0.000000000	1.000000000
n-C_8H_{18}–CO	0.000000000	1.219206702	0.000000000	1.276744779
n-C_8H_{18}–H_2O	0.000000000	0.599484191	0.000000000	0.662072469
n-C_8H_{18}–He	0.000000000	1.000000000	0.000000000	1.000000000
n-C_8H_{18}–Ar	0.000000000	1.000000000	0.000000000	1.000000000
H_2–O_2	0.000000000	1.000000000	0.000000000	1.000000000
H_2–CO	0.000000000	1.121416201	0.000000000	1.377504607
H_2–H_2O	0.000000000	1.000000000	0.000000000	1.000000000
H_2–He	0.000000000	1.000000000	0.000000000	1.000000000
H_2–Ar	0.000000000	1.000000000	0.000000000	1.000000000
O_2–CO	0.000000000	1.000000000	0.000000000	1.000000000
O_2–H_2O	0.000000000	1.143174289	0.000000000	0.964767932
O_2–He	0.000000000	1.000000000	0.000000000	1.000000000
O_2–Ar	−0.000503368	0.993907199	0.000045763	0.990430423
CO–H_2O	0.000000000	1.000000000	0.000000000	1.000000000
CO–He	0.000000000	1.000000000	0.000000000	1.000000000
CO–Ar	0.000000000	1.159720623	0.000000000	0.954215746
H_2O–He	0.000000000	1.000000000	0.000000000	1.000000000
H_2O–Ar	0.000000000	1.038993495	0.000000000	1.070941866
He–Ar	0.000000000	1.000000000	0.000000000	1.000000000

References

The references cited in this work, which are characterised by the name of the author, the co-author (for more than two authors substituted by *et al.*), and the year of publication, are listed below in alphabetical order. They are ordered first by the name of the (first) author, and then, if necessary, by the year of publication.

Aavatsmark, I. (1995): Mathematische Einführung in die Thermodynamik der Gemische. Akademie Verlag, Berlin, 1995.

Ababio, B. D.; McElroy, P. J. (1993): (Pressure, amount-of-substance density, temperature) of $\{(1-x)CO_2 + xH_2\}$ using a direct method. J. Chem. Thermodynamics, 25 (1993), 1495–1501.

Ababio, B. D.; McElroy, P. J.; Williamson, C. J. (2001): Second and third virial coefficients for (methane + nitrogen). J. Chem. Thermodynamics, 33 (2001), 413–421.

Abdulagatov, I. M.; Magomedov, U. B. (1992): Liquid-liquid-gas phase equilibrium in the water–n-hexane binary system. High Temp. – High Pressures, 24 (1992), 465–468.

Abdulagatov, I. M.; Bazaev, A. R.; Ramazanova, A. E. (1992): P, ρ, T, x-properties and virial coefficients of the binary system water–n-hexane. High Temp., 30 (1992), 736–744.

Abdulagatov, I. M.; Bazaev, A. R.; Ramazanova, A. E. (1993a): Volumetric properties and virial coefficients of (water + methane). J. Chem. Thermodynamics, 25 (1993), 249–259.

Abdulagatov, I. M.; Bazaev, A. R.; Ramazanova, A. E. (1993b): P-V-T-x measurements of aqueous mixtures at supercritical conditions. Int. J. Thermophysics, 14 (1993), 231–250.

Abdulagatov, I. M.; Bazaev, A. R.; Bazaev, E. A.; Saidakhmedova, M. B.; Ramazanova, A. E. (1998): Volumetric properties of near-critical and supercritical water + pentane mixtures: molar, excess, partial, and apparent volumes. J. Chem. Eng. Data, 43 (1998), 451–458.

Abraham, W. H.; Bennett, C. O. (1960): The compressibility of carbon dioxide–argon mixtures. AIChE J., 6 (1960), 257–261.

Achtermann, H. J.; Bose, T. K.; Rögener, H.; St-Arnaud, J. M. (1986): Precise determination of the compressibility factor of methane, nitrogen, and their mixtures from refractive index measurements. Int. J. Thermophysics, 7 (1986), 709–720.

Achtermann, H. J.; Magnus, G.; Bose, T. K. (1991): Refractivity virial coefficients of gaseous CH_4, C_2H_4, C_2H_6, CO_2, SF_6, H_2, N_2, He, and Ar. J. Chem. Phys., 94 (1991), 5669–5684.

Achtermann, H. J.; Hong, J.; Wagner, W.; Pruss, A. (1992): Refractive index and density isotherms for methane from 273 to 373 K and at pressures up to 34 MPa. J. Chem. Eng. Data, 37 (1992), 414–418.

Acosta, G. R.; Swift, G. W. (1976): Liquid densities of binary mixtures of ethane, propane and n-butane. Rev. Inst. Mex. Pet., 8 (1976), 2, 60–69.

Acosta, J. C.; Hevla, E.; Leipziger, S. (1984): Dew and bubble point measurements for carbon dioxide–propane mixtures. J. Chem. Eng. Data, 29 (1984), 304–309.

Ahrendts, J.; Baehr, H. D. (1979): Die direkte Verwendung von Meßwerten beliebiger thermodynamischer Zustandsgrößen zur Bestimmung kanonischer Zustandsgleichungen. Forsch. Ing.-Wes., 45 (1979), 1–11.

Ahrendts, J.; Baehr, H. D. (1981): Direct application of experimental values for any thermodynamic variables of state in establishing canonical equations of state. Int. Chem. Eng., 21 (1981), 557–571.

Aicart, E.; Kumaran, M. K.; Halpin, C. J.; Benson, G. C. (1983): Ultrasonic speeds and isentropic compressibilities of n-heptane + each of the hexane isomers at 298.15 K. J. Chem. Thermodynamics, 15 (1983), 919–925.

Akansu, S. O.; Dulger, Z.; Kahraman, N.; Veziroglu, T. N. (2004): Internal combustion engines fueled by natural gas–hydrogen mixtures. Int. J. Hydrogen Energy, 29 (2004), 1527–1539.

Akers, W. W.; Burns, J. F.; Fairchild, W. R. (1954a): Low-temperature phase equilibria. Methane–propane system. Ind. Eng. Chem., 46 (1954), 2531–2534.

Akers, W. W.; Attwell, L. L.; Robinson, J. A. (1954b): Volumetric and phase behavior of nitrogen–hydrocarbon systems. Nitrogen–butane system. Ind. Eng. Chem., 46 (1954), 2539–2540.

Akers, W. W.; Kehn, D. M.; Kilgore, C. H. (1954c): Volumetric and phase behavior of nitrogen–hydrocarbon systems. Nitrogen–n-heptane system. Ind. Eng. Chem., 46 (1954), 2536–2539.

Akers, W. W.; Kelley, R. E.; Lipscomb, T. G. (1954d): Low-temperature phase equilibria. Carbon dioxide–propane system. Ind. Eng. Chem., 46 (1954), 2535–2536.

Akers, W. W.; Eubanks, L. S. (1960): Vapor-liquid equilibria in the system hydrogen–nitrogen–carbon monoxide. Adv. Cryog. Eng., 3 (1960), 275–293.

Al-Sahhaf, T. A.; Kidnay, A. J.; Sloan, E. D. (1983): Liquid + vapor equilibria in the $N_2 + CO_2 + CH_4$ system. Ind. Eng. Chem., Fundam., 22 (1983), 372–380.

Altunin, V. V.; Dubinin, A. B.; Koposhilov, O. D. (1975): An experimental investigation of the compressibility of helium/carbon dioxide mixtures in the 303–373 K temperature range at pressures up to 250×10^5 Pa. Therm. Eng. (Engl. Transl.), 22 (1975), 6, 103–106; Teploenergetika, 22 (1975), 6, 77–79.

Altunin, V. V.; Koposhilov, O. D. (1977): An experimental investigation of the thermal properties of gaseous mixtures of carbon dioxide and argon. Therm. Eng. (Engl. Transl.), 24 (1977), 8, 66–70; Teploenergetika, 24 (1977), 8, 80–83.

Amick, E. H. (Jr.); Johnson, W. B.; Dodge, B. F. (1952): *P*-*V*-*T*-*X* relationships for the system: methane–isopentane. Chem. Eng. Prog., Symp. Ser., 48 (1952), 3, 65–72.

Anisimov, M. A.; Kiselev, S. B.; Khalidov, S. E. (1988): Scaled equation for the isochoric heat capacity of methane–ethane mixtures in the critical region. Int. J. Thermophysics, 9 (1988), 453–464.

Arai, K.; Kobayashi, R. (1980): Measurement of isochoric *P-V-T* behavior of a nominal 95 mol% methane – 5 mol% propane mixture from near-ambient to cryogenic temperatures. Adv. Cryog. Eng., 25 (1980), 640–653.

Arai, Y.; Kaminishi, G.; Saito, S. (1971): The experimental determination of the *P-V-T-X* relations for the carbon dioxide–nitrogen and the carbon dioxide–methane systems. J. Chem. Eng. Japan, 4 (1971), 113–122.

Armstrong, G. T.; Goldstein, J. M.; Roberts, D. E. (1955): Liquid-vapor phase equilibrium in solutions of oxygen and nitrogen at pressures below one atmosphere. J. Res. Natl. Bur. Stand., 55 (1955), 5, 265–277.

Ashton, G. J.; Haselden, G. G. (1980): Measurements of enthalpy and phase equilibrium for simulated natural gas mixtures and correlation of the results by a modified Starling equation. Cryogenics, 20 (1980), 41–47.

Assael, M. J.; Dalaouti, N. K.; Wakeham, W. A. (2001a): Prediction of the viscosity of liquid mixtures. Int. J. Thermophysics, 22 (2001), 1727–1737.

Assael, M. J.; Dalaouti, N. K.; Vesovic, V. (2001b): Viscosity of natural-gas mixtures: measurements and prediction. Int. J. Thermophysics, 22 (2001), 61–71.

Asselineau, L.; Bogdanic, G.; Vidal, J. (1979): A versatile algorithm for calculating vapour-liquid equilibria. Fluid Phase Equilibria, 3 (1979), 273–290.

Aucejo, A.; Burguet, M. C.; Munoz, R.; Marques, J. L. (1995): Densities, viscosities, and refractive indices of some n-alkane binary liquid systems at 298.15 K. J. Chem. Eng. Data, 40 (1995), 141–147.

Avila, S.; Blanco, S. T.; Velasco, I.; Rauzy, E.; Otín, S. (2002a): Thermodynamic properties of synthetic natural gases. 1. Dew-point curves of synthetic natural gases and their mixtures with water and methanol. Measurement and correlation. Ind. Eng. Chem. Res., 41 (2002), 3714–3721.

Avila, S.; Blanco, S. T.; Velasco, I.; Rauzy, E.; Otín, S. (2002b): Thermodynamic properties of synthetic natural gases. 2. Dew point curves of synthetic natural gases and their mixtures with water and methanol. Measurement and correlation. Energy & Fuels, 16 (2002), 928–934.

Avila, S.; Blanco, S. T.; Velasco, I.; Rauzy, E.; Otín, S. (2002c): Thermodynamic properties of synthetic natural gases. Part 4. Dew point curves of synthetic natural gases and their mixtures with water: measurement and correlation. Fluid Phase Equilibria, 202 (2002), 399–412.

Avila, S.; Blanco, S. T.; Velasco, I.; Rauzy, E.; Otín, S. (2003): Thermodynamic properties of synthetic natural gases. Part 3. Dew point curves of synthetic natural gases and their mixtures with water. Measurement and correlation. Energy & Fuels, 17 (2003), 338–343.

Avlonitis, D.; Danesh, A.; Todd, A. C. (1994): Prediction of VL and VLL equilibria of mixtures containing petroleum reservoir fluids and methanol with a cubic EoS. Fluid Phase Equilibria, 94 (1994), 181–216.

Baker, L. E.; Pierce, A. C.; Luks, K. D. (1982): Gibbs energy analysis of phase equilibria. Soc. Pet. Eng. J., 22 (1982), 731–742.

Banks, R.; Haselden, G. G. (1969): The measurement and prediction of enthalpies and phase equilibria in natural gas mixtures. Bull. Inst. Int. Froid, Annexe, 1 (1969), 117–137.

Barreau, A.; Montel, F.; Ingrain, D.; Peters, C. J.; Stenby, E. H. (1993): Integration of calorimetric and velocimetric measurements in thermodynamic modelling of synthetic hydrocarbon mixtures representative of natural gases. GERTH, DG XII - JOULE Programme, Contract JOU2-CT91-0066, Final Technical Report, 1993.

Barreiros, S. F.; Nunes da Ponte, M. (1989): Excess thermodynamic properties of argon + methane: a standard simple liquid system. Fluid Phase Equilibria, 49 (1989), 9–20.

Barrick, P. L.; Heck, C. K.; Spano, J. O. (1966): Liquid-vapor equilibria of the hydrogen–carbon dioxide system. Univ. Colo., Tech. Rep. AFML TR 66-390, 1966.

Barrufet, M. A.; Rahman, S. (1997): Simultaneous determination of phase equilibria compositions and phase molar densities of hydrocarbon + CO_2 systems. J. Chem. Eng. Data, 42 (1997), 120–123.

Barsuk, S. D.; Skripka, V. G.; Benyaminovich, O. A. (1970): Investigation of the liquid-vapor equilibrium in the methane–isobutane system at low temperatures. Gazov. Promst., 15 (1970), 9, 38–41.

Bartlett, E. P. (1927): The compressibility isotherms of hydrogen, nitrogen and mixtures of these gases at 0° and pressures to 1000 atmospheres. A correction. J. Am. Chem. Soc., 49 (1927), 1955–1957.

Bartlett, E. P.; Cupples, H. L.; Tremearne, T. H. (1928): The compressibility isotherms of hydrogen, nitrogen and a 3:1 mixture of these gases at temperatures between 0 and 400° and at pressures to 1000 atmospheres. J. Am. Chem. Soc., 50 (1928), 1275–1288.

Bartlett, E. P.; Hetherington, H. C.; Kvalnes, H. M.; Tremearne, T. H. (1930): The compressibility isotherms of hydrogen, nitrogen and a 3:1 mixture of these gases at temperatures of −70, −50, −25 and 20° and at pressures to 1000 atmospheres. J. Am. Chem. Soc., 52 (1930), 1363–1373.

Beattie, J. A.; Stockmayer, W. H.; Ingersoll, G. H. (1941): The compressibilities of gaseous mixtures of methane and normal butane. The equation of state for gas mixtures. J. Chem. Phys., 9 (1941), 871–874.

Beatty, H. A.; Calingaert, G. (1934): Vapor-liquid equilibrium of hydrocarbon mixtures. Ind. Eng. Chem., 26 (1934), 504–508.

Beckermann, W. (1993): Messung von Schallgeschwindigkeiten an Arbeitsstoffen der Energietechnik. Fortschr.-Ber. VDI, Reihe 19, Nr. 67, VDI-Verlag, Düsseldorf, 1993.

Beer, H. (1969): Compressibility factors for the argon–carbon dioxide system. Can. J. Chem. Eng., 47 (1969), 92–94.

Bender, E. (1970): Equations of state exactly representing the phase behavior of pure substances. Proc. 5th Symp. Thermophys. Prop., ASME, New York, pp. 227–235, 1970.

Bender, E. (1971): Die Berechnung von Phasengleichgewichten mit der thermischen Zustandsgleichung – dargestellt an den reinen Fluiden Argon, Stickstoff, Sauerstoff und an ihren Gemischen. Habilitationsschrift, Ruhr-Universität Bochum, 1971.

Bender, E. (1973): The calculation of phase equilibria from a thermal equation of state applied to the pure fluids argon, nitrogen, oxygen and their mixtures. C. F. Müller, Karlsruhe, 1973.

Benedict, M.; Webb, G. B.; Rubin, L. C. (1940): An empirical equation for thermodynamic properties of light hydrocarbons and their mixtures. I. Methane, ethane, propane and n-butane. J. Chem. Phys., 8 (1940), 334–345.

Benedict, M.; Webb, G. B.; Rubin, L. C. (1942): An empirical equation for thermodynamic properties of light hydrocarbons and their mixtures. II. Mixtures of methane, ethane, propane and n-butane. J. Chem. Phys., 10 (1942), 747–758.

Benham, A. L.; Katz, D. L. (1957): Vapor-liquid equilibria for hydrogen–light hydrocarbon systems at low temperatures. AIChE J., 3 (1957), 33–36.

Bennett, C. O.; Dodge, B. F. (1952): Compressibilities of mixtures of hydrogen and nitrogen above 1000 atmospheres. Ind. Eng. Chem., 44 (1952), 180–185.

Beranek, P.; Wichterle, I. (1981): Vapour-liquid equilibria in the propane–n-butane system at high pressures. Fluid Phase Equilibria, 6 (1981), 279–282.

Berger, E.; Förg, W.; Heiersted, R. S.; Paurola, P. (2003): The Snøhvit project. The MFC® (mixed fluid cascade) process for the first European baseload LNG production plant. Linde Technology, No. 1, pp. 12–23, 2003. See also Förg (2003) and Buller *et al.* (2004).

Berry, V. M.; Sage, B. H. (1970): Phase behavior in binary and multicomponent systems at elevated pressures: n-pentane and methane–n-pentane. Natl. Stand. Ref. Data Ser. (Natl. Bur. Stand.), NSRDS-NBS 32, 1970.

Besserer, G. J.; Robinson, D. B. (1971): A high pressure autocollimating refractometer for determining coexisting liquid and vapor phase densities. Can. J. Chem. Eng., 49 (1971), 651–656.

Besserer, G. J.; Robinson, D. B. (1973a): Equilibrium-phase properties of i-butane–carbon dioxide system. J. Chem. Eng. Data, 18 (1973), 298–301.

Besserer, G. J.; Robinson, D. B. (1973b): Equilibrium-phase properties of n-pentane–carbon dioxide system. J. Chem. Eng. Data, 18 (1973), 416–419.

Besserer, G. J.; Robinson, D. B. (1973c): Equilibrium-phase properties of i-butane–ethane system. J. Chem. Eng. Data, 18 (1973), 301–304.

Besserer, G. J.; Robinson, D. B. (1975): Equilibrium-phase properties of isopentane–carbon dioxide system. J. Chem. Eng. Data, 20 (1975), 93–96.

Bezanehtak, K.; Combes, G. B.; Dehghani, F.; Foster, N. R.; Tomasko, D. L. (2002): Vapor-liquid equilibrium for binary systems of carbon dioxide + methanol, hydrogen + methanol, and hydrogen + carbon dioxide at high pressures. J. Chem. Eng. Data, 47 (2002), 161–168.

Bian, B.; Wang, Y.; Shi, J.; Zhao, E.; Lu, B. C.-Y. (1993): Simultaneous determination of vapor-liquid equilibrium and molar volumes for coexisting phases up to the critical temperature with a static method. Fluid Phase Equilibria, 90 (1993), 177–187.

Bier, K.; Büsser, J.; Ernst, G. (1973): Experimental heat capacities c_p of non-ideal binary gaseous mixtures from C_3H_8, i-C_4H_{10}, CHF_2Cl and C_2F_5Cl. J. Chem. Thermodynamics, 5 (1973), 83–96.

Bishnoi, P. R.; Robinson, D. B. (1971): Experimental heat capacities of carbon dioxide–methane mixtures at elevated pressures. Can. J. Chem. Eng., 49 (1971), 657–662.

Bishnoi, P. R.; Hamaliuk, G. P.; Robinson, D. B. (1972): Experimental heat capacities of nitrogen–carbon dioxide mixtures at elevated pressures. Can. J. Chem. Eng., 50 (1972), 677–679.

Blagoi, Yu. P.; Rudenko, N. C. (1958): Density of liquified gas solutions N_2–O_2, Ar–O_2. Izv. Vyssh. Uchebn. Zaved. Fiz., 1 (1958), 6, 145–151.

Blagoi, Yu. P.; Orobinskii, N. A. (1965): Liquid-vapour phase equilibrium in the propene–nitrogen system. Russ. J. Phys. Chem. (Engl. Transl.), 39 (1965), 1073–1074; Zh. Fiz. Khim., 39 (1965), 2022–2024.

Blake, A. G.; Bretton, R. H.; Dodge, B. F. (1965): Volumetric behavior of methane, nitrogen and some mixtures at pressures up to 5000 atmospheres. AIChE Symp. Ser. #2 (London), Paper 2.11 for meeting in London, pp. 94–104, 1965.

Blanc, C. J.; Setier, J.-C. B. (1988): Vapor-liquid equilibria for the ethane–propane system at low temperature. J. Chem. Eng. Data, 33 (1988), 111–115.

Blancett, A. L.; Hall, K. R.; Canfield, F. B. (1970): Isotherms for the He–Ar system at 50°C, 0°C and −50°C up to 700 atm. Physica, 47 (1970), 75–91.

Blanco, S. T.; Avila, S.; Velasco, I.; Rauzy, E.; Otín, S. (2000): Dew points of ternary methane + ethane + butane and quaternary methane + ethane + butane + water mixtures: measurement and correlation. Fluid Phase Equilibria, 171 (2000), 233–242.

Blanke, W.; Weiß, R. (1986): Die Schallgeschwindigkeit in Erdgas bei Temperaturen zwischen 0°C und 30°C und Drücken bis 6MPa. Brennst.-Wärme-Kraft, 38 (1986), 448–451.

Blanke, W.; Weiss, R. (1995): Virial coefficients of methane–ethane mixtures in the temperature range from 0 to 60°C determined with an automated expansion apparatus. Int. J. Thermophysics, 16 (1995), 643–653.

Blanke, W.; Lee, W. G.; Weiß, R. (1996): Compressibility factors of propane–methane mixtures in the temperature range from 0 to 50 °C determined with an automated expansion apparatus. PTB-Mitteilungen, Forschen + Prüfen, 106 (1996), 331–335.

Bloomer, O. T.; Parent, J. D. (1952): Physical-chemical properties of methane–nitrogen mixtures. Institute of Gas Technology, Research Bulletin No. 17, 1952.

Bloomer, O. T.; Parent, J. D. (1953): Liquid-vapor phase behavior of the methane–nitrogen system. Chem. Eng. Prog., Symp. Ser., 49 (1953), 6, 11–24.

Bloomer, O. T.; Gami, D. C.; Parent, J. D. (1953): Physical-chemical properties of methane–ethane mixtures. Institute of Gas Technology, Research Bulletin No. 22, 1953.

Boomer, E. H.; Johnson, C. A.; Piercey, A. G. A. (1938a): Equilibria in two-phase, gas-liquid hydrocarbon systems. II. Methane and pentane. Can. J. Res., Sect. B, 16 (1938), 319–327.

Boomer, E. H.; Johnson, C. A.; Piercey, A. G. A. (1938b): Equilibria in two-phase, gas-liquid hydrocarbon systems. IV. Methane and heptane. Can. J. Res., Sect. B, 16 (1938), 396–410.

Bourbo, P.; Ischkin, I. (1936): Untersuchungen über das Gleichgewicht von Flüssigkeit und Dampf des Systems Argon–Sauerstoff (Research on the equilibrium of liquid and vapor for the system argon–oxygen). Physica, 3 (1936), 1067–1081.

Boyes, S. J. (1992): The speed of sound in gases with application to equations of state and sonic nozzles. Ph.D. Thesis, University of London, 1992.

Boyle, T. B.; Carroll, J. J. (2002): Study determines best methods for calculating acid-gas density. Oil Gas J., 100 (2002), 2, 45–53.

BP (2006): BP Statistical Review of World Energy June 2006. BP p.l.c., London, 2006.

Brandt, L. W.; Stroud, L. (1958): Phase equilibria in natural gas systems. Apparatus with windowed cell for 800 P.S.I.G. and temperatures to −320 °F. Ind. Eng. Chem., 50 (1958), 849–852.

British Gas (1989): See Jaeschke *et al.* (1989) and Jaeschke and Humphreys (1991).

Brown, T. S.; Kidnay, A. J.; Sloan, E. D. (1988): Vapor-liquid equilibria in the carbon dioxide–ethane system. Fluid Phase Equilibria, 40 (1988), 169–184.

Brown, T. S.; Niesen, V. G.; Sloan, E. D.; Kidnay, A. J. (1989a): Vapor-liquid equilibria for the binary systems of nitrogen, carbon dioxide, and n-butane at temperatures from 220 to 344 K. Fluid Phase Equilibria, 53 (1989), 7–14.

Brown, T. S.; Sloan, E. D.; Kidnay, A. J. (1989b): Vapor-liquid equilibria in the nitrogen + carbon dioxide + ethane system. Fluid Phase Equilibria, 51 (1989), 299–313.

Brown, T. S.; Sloan, E. D.; Kidnay, A. J. (1994): Vapor-liquid equilibria for the ternary system N_2 + CO_2 + n-C_4H_{10} at 250 and 270 K. Int. J. Thermophysics, 15 (1994), 1211–1219.

Brugge, H. B.; Hwang, C.-A.; Marsh, K. N.; Holste, J. C.; Hall, K. R.; Savidge, J. L. (1989a): Experimental density measurements for a methane + nitrogen mixture: effect of composition uncertainties. Proc. 4th International Gas Research Conference, Tokyo, pp. 271–278, 1989, Government Institutes Inc., Rockville (ed. T. L. Cramer), 1990.

Brugge, H. B.; Hwang, C.-A.; Rogers, W. J.; Holste, J. C.; Hall, K. R.; Lemming, W.; Esper, G. J.; Marsh, K. N.; Gammon, B. E. (1989b): Experimental cross virial coefficients for binary mixtures of carbon dioxide with nitrogen, methane and ethane at 300 and 320 K. Physica, A, 156 (1989), 382–416.

Brugge, H. B.; Holste, J. C.; Hall, K. R.; Gammon, B. E.; Marsh, K. N. (1997): Densities of carbon dioxide + nitrogen from 225 K to 450 K at pressures up to 70 MPa. J. Chem. Eng. Data, 42 (1997), 903–907.

Bücker, D.; Wagner, W. (2006a): A reference equation of state for the thermodynamic properties of ethane for temperatures from the melting line to 675 K and pressures up to 900 MPa. J. Phys. Chem. Ref. Data, 35 (2006), 205–266.

Bücker, D.; Wagner, W. (2006b): Reference equations of state for the thermodynamic properties of fluid phase n-butane and isobutane. J. Phys. Chem. Ref. Data, 35 (2006), 929–1019.

Buller, A. T.; Owren, G. A.; Pettersen, J.; Heiersted, R. S.; Fredheim, A. O. (2004): Liquefied natural gas (LNG). Snøhvit process and plant. Statoil ASA, Research & Technology Memoir No. 6, Stavanger, 2004.

Burfield, D. W.; Richardson, H. P.; Guereca, R. A. (1970): Vapor-liquid equilibria and dielectric constants for the helium–carbon dioxide system. AIChE J., 16 (1970), 97–100.

Burn, I.; Din, F. (1962): Liquid-vapour equilibrium of the system argon + oxygen at pressures up to 10 atmospheres. Trans. Faraday Soc., 58 (1962), 1341–1356.

Burriss, W. L.; Hsu, N. T.; Reamer, H. H.; Sage, B. H. (1953): Phase behavior of the hydrogen–propane system. Ind. Eng. Chem., 45 (1953), 210–213.

Buzyna, G.; Macriss, R. A.; Ellington, R. T. (1963): Vapor-liquid equilibrium in the helium–nitrogen system. Chem. Eng. Progr. Symp. Ser., 59 (1963), 44, 101–111.

Calado, J. C. G.; Staveley, L. A. K. (1972): Excess gibbs energy of argon–methane liquid mixtures at 115.77°K. J. Chem. Phys., 56 (1972), 4718–4719.

Calado, J. C. G.; Garcia, G. A.; Staveley, L. A. K. (1974): Thermodynamics of the liquid system methane + propane. J. Chem. Soc., Faraday Trans., I, 70 (1974), 1445–1451.

Calado, J. C. G.; Guedes, H. J. R.; Nunes Da Ponte, M.; Streett, W. B. (1984): Thermodynamic properties of liquid mixtures of carbon monoxide and methane. Fluid Phase Equilibria, 16 (1984), 185–204.

Calingaert, G.; Hitchcock, L. B. (1927): The application of the phase rule to the calculation of liquid and vapor compositions in binary systems. Deviations from Raoult's law for hydrocarbon mixtures. J. Am. Chem. Soc., 49 (1927), 750–765.

Canfield, F. B.; Leland, T. W.; Kobayashi, R. (1965): Compressibility factors for helium–nitrogen mixtures. J. Chem. Eng. Data, 10 (1965), 92–96.

Capla, L.; Buryan, P.; Jedelsky, J.; Rottner, M.; Linek, J. (2002): Isothermal *pVT* measurements on gas hydrocarbon mixtures using a vibrating-tube apparatus. J. Chem. Thermodynamics, 34 (2002), 657–667.

Carroll, J. J. (2002a): Phase equilibria relevant to acid gas injection, part 1 – non-aqueous phase behaviour. J. Can. Pet. Tech., 41 (2002), 6, 25–31.

Carroll, J. J. (2002b): Phase equilibria relevant to acid gas injection: part 2 – aqueous phase behaviour. J. Can. Pet. Tech., 41 (2002), 7, 39–43.

Cebola, M. J.; Saville, G.; Wakeham, W. A. (2000): V.l.e. measurements at high pressures and high temperatures on (methane + n-hexane). J. Chem. Thermodynamics, 32 (2000), 1265–1284.

Chamorro, C. R.; Martín, M. C.; Segovia, J. J.; Trusler, J. P. M.; Villamañán, M. A. (2000): Combined density and speed of sound measurements for two (methane + nitrogen) gas mixtures. Paper presented at the Fourteenth Symposium on Thermophysical Properties, June 25–30, Boulder, CO, 2000. Preliminary results. See also Chamorro *et al.* (2006) and Estela-Uribe *et al.* (2006).

Chamorro, C. R.; Segovia, J. J.; Martín, M. C.; Villamañán, M. A.; Estela-Uribe, J. F.; Trusler, J. P. M. (2006): Measurement of the (pressure, density, temperature) relation of two (methane + nitrogen) gas mixtures at temperatures between 240 and 400 K and pressures up to 20 MPa using an accurate single-sinker densimeter. J. Chem. Thermodynamics, 38 (2006), 916–922.

Chang, H. L.; Hurt, L. J.; Kobayashi, R. (1966): Vapor-liquid equilibria of light hydrocarbons at low temperatures and high pressures: the methane–n-heptane system. AIChE J., 12 (1966), 1212–1216.

Chang, S.-D.; Lu, B. C.-Y. (1967): Vapor-liquid equilibria in the nitrogen–methane–ethane system. Chem. Eng. Prog., Symp. Ser., 63 (1967), 81, 18–27.

Chen, G.; Knapp, H.; Hou, Y. (1997): Vapor-liquid equilibria for the nitrogen–isobutane system. J. Solution Chem., 26 (1997), 779–790.

Chen, J.; Wu, W.; Han, B.; Gao, L.; Mu, T.; Liu, Z.; Jiang, T.; Du, J. (2003): Phase behavior, densities, and isothermal compressibilities of CO_2 + pentane and CO_2 + acetone systems in various phase regions. J. Chem. Eng. Data, 48 (2003), 1544–1548.

Chen, R. J. J.; Chappelear, P. S.; Kobayashi, R. (1974a): Dew-point loci for methane–n-butane binary system. J. Chem. Eng. Data, 19 (1974), 53–58.

Chen, R. J. J.; Chappelear, P. S.; Kobayashi, R. (1974b): Dew-point loci for methane–n-pentane binary system. J. Chem. Eng. Data, 19 (1974), 58–61.

Chen, R. J. J.; Chappelear, P. S.; Kobayashi, R. (1976): Dew-point loci for methane–n-hexane and methane–n-heptane binary systems. J. Chem. Eng. Data, 21 (1976), 213–219.

Chen, S.-S.; Zwolinski, B. J. (1974): Excess thermodynamic functions of binary mixtures of normal and isomeric alkanes (C_5 and C_6). J. Chem. Soc., Faraday Trans., II, 70 (1974), 1133–1142.

Cheng, H.; Pozo de Fernandez, M. E.; Zollweg, J. A.; Streett, W. B. (1989): Vapor-liquid equilibrium in the system carbon dioxide + n-pentane from 252 to 458 K at pressures to 10 MPa. J. Chem. Eng. Data, 34 (1989), 319–323.

Cheung, H.; Wang, D. I.-J. (1964): Solubility of volatile gases in hydrocarbon solvents at cryogenic temperatures. Ind. Eng. Chem., Fundam., 3 (1964), 355–361.

Chevalier, J. L. E.; Petrino, P. J.; Gaston-Bonhomme, Y. H. (1990): Viscosity and density of some aliphatic, cyclic, and aromatic hydrocarbons binary liquid mixtures. J. Chem. Eng. Data, 35 (1990), 206–212.

Christiansen, L. J.; Fredenslund, Aa.; Mollerup, J. (1973): Vapour-liquid equilibrium of the CH_4–Ar, CH_4–CO, and Ar–CO systems at elevated pressures. Cryogenics, 13 (1973), 405–413.

Chu, T.-C.; Chen, R. J. J.; Chappelear, P. S.; Kobayashi, R. (1976): Vapor-liquid equilibrium of methane–n-pentane system at low temperatures and high pressures. J. Chem. Eng. Data, 21 (1976), 41–44.

Chuang, S.-Y.; Chappelear, P. S.; Kobayashi, R. (1976): Viscosity of methane, hydrogen, and four mixtures of methane and hydrogen from −100°C to 0°C at high pressures. J. Chem. Eng. Data, 21 (1976), 403–411.

Chueh, P. L.; Prausnitz, J. M. (1982): Calculated data, published by Knapp *et al.* (1982).

Chun, S. W.; Kay, W. B.; Rainwater, J. C. (1993): Vapor-liquid equilibria of mixtures of propane and isomeric hexanes. J. Chem. Eng. Data, 38 (1993), 494–501.

Cines, M. R.; Roach, J. T.; Hogan, R. J.; Roland, C. H. (1953): Nitrogen–methane vapor-liquid equilibria. Chem. Eng. Prog., Symp. Ser., 49 (1953), 6, 1–10.

Clark, A. M.; Din, F.; Robb, J. (1954): The liquid-vapour equilibrium of the binary system argon/oxygen. Proc. R. Soc. London, Ser. A, 221 (1954), 517–534.

Clark, A. Q.; Stead, K. (1988): (Vapour + liquid) phase equilibria of binary, ternary, and quaternary mixtures of CH_4, C_2H_6, C_3H_8, C_4H_{10}, and CO_2. J. Chem. Thermodynamics, 20 (1988), 413–428.

Claus, P.; Kleinrahm, R.; Wagner, W. (1999): Density measurements on ethane. Private communication to R. Klimeck (preliminary results), Lehrstuhl für Thermodynamik, Ruhr-Universität Bochum, 1999.

Claus, P.; Kleinrahm, R.; Wagner, W. (2001): Density measurements on ethane and propane in the temperature range from 340 K to 520 K at pressures up to 30 MPa. Report to GERG WG 1.34, Lehrstuhl für Thermodynamik, Ruhr-Universität Bochum, 2001.

Claus, P.; Kleinrahm, R.; Wagner, W. (2003): Measurements of the (p, ρ, T) relation of ethylene, ethane, and sulphur hexafluoride in the temperature range from 235 K to 520 K at pressures up to 30 MPa using an accurate single-sinker densimeter. J. Chem. Thermodynamics, 35 (2003), 159–175.

Cockett, A. H. (1957): The binary system nitrogen–oxygen at 1.3158 atm. Proc. R. Soc. London, Ser. A, 239 (1957), 76–92.

Cohen, A. E.; Hipkin, H. G.; Koppany, C. R. (1967): Experimental vapor-liquid equilibrium data for hydrogen–ethane and hydrogen–methane–ethane. Chem. Eng. Prog., Symp. Ser., 63 (1967), 81, 10–17.

Cooper, E. F.; Asfour, A.-F. A. (1991): Densities and kinematic viscosities of some C_6–C_{16} n-alkane binary liquid systems at 293.15 K. J. Chem. Eng. Data, 36 (1991), 285–288.

Costa Gomes, M. F.; Trusler, J. P. M. (1998): The speed of sound in two methane-rich gas mixtures at temperatures between 250 K and 350 K and at pressures up to 20 MPa. J. Chem. Thermodynamics, 30 (1998), 1121–1129.

Crain, R. W. (Jr.); Sonntag, R. (1966): The P-V-T behavior of nitrogen, argon and their mixtures. Adv. Cryog. Eng., 11 (1966), 379–391.

Cummings, L. W. T. (1933): High pressure rectification. Ph.D. Dissertation, Mass. Inst. Technol., Cambridge, Mass., 1933.

Cummings, L. W. T.; Stones, F. W.; Volante, M. A. (1933): High-pressure rectification. II. n-Pentane–n-heptane system. Ind. Eng. Chem., 25 (1933), 728–732.

Daridon, J. L.; Lagourette, B.; Xans, P. (1994): Thermodynamic properties of liquid mixtures containing gas under pressure based on ultrasonic measurements. Fluid Phase Equilibria, 100 (1994), 269–282.

Dastur, S. P. (1964): Experimental vapor-liquid equilibrium study for the ethane–n-pentane–n-heptane system. Prediction of the *K*-values for ternary and quaternary systems. Ph.D. Dissertation, Northwestern Univ., Evanston, Ill., 1964.

Davalos, J.; Anderson, W. R.; Phelps, R. E.; Kidnay, A. J. (1976): Liquid-vapor equilibria at 250.00 K for systems containing methane, ethane, and carbon dioxide. J. Chem. Eng. Data, 21 (1976), 81–84.

Davis, J. A.; Rodewald, N.; Kurata, F. (1963): An apparatus for phase studies between 20° K. and 300° K. Ind. Eng. Chem., 55 (1963), 11, 36–42.

Dawe, R. A.; Snowdon, P. N. (1975): Enthalpies to 100 bar for nitrogen–methane mixtures in range 247.5–366.7 K. J. Chem. Eng. Data, 20 (1975), 247–251.

Day, C.; Stephan, M.; Oellrich, L. R. (1997): A new flow calorimeter for the measurement of the isobaric enthalpy increment and the isenthalpic Joule-Thomson effect. Results for methane and (methane + ethane). J. Chem. Thermodynamics, 29 (1997), 949–971.

de la Cruz de Dios, J.; Bouchot, C.; Galicia Luna, L. A. (2003): New p-ρ-T measurements up to 70 MPa for the system CO_2 + propane between 298 and 343 K at near critical compositions. Fluid Phase Equilibria, 210 (2003), 175–197.

Dean, M. R.; Tooke, J. W. (1946): Vapor-liquid equilibria in three hydrogen–paraffin systems. Ind. Eng. Chem., 38 (1946), 389–393.

Deiters, U. K. (1985): A modification of Newton-Raphson algorithm for phase equilibria calculations using numerical differentiation of the Gibbs energy. Fluid Phase Equilibria, 19 (1985), 287–293.

DeVaney, W. E.; Dalton, B. J.; Meeks, J. C. (Jr.) (1963): Vapor-liquid equilibria of the helium–nitrogen system. J. Chem. Eng. Data, 8 (1963), 473–478.

DeVaney, W. E.; Rhodes, H. L.; Tully, P. C. (1971): Phase equilibria data for helium–methane system. J. Chem. Eng. Data, 16 (1971), 158–161.

DeVaney, W.; Berryman, J. M.; Kao, P.-L.; Eakin, B. (1978): High temperature V-L-E measurements for substitute gas components. Gas Processors Association, Research Report RR-30, Project 735-A, Tulsa, OK, 1978.

Dillard, D. D.; Edmister, W. C.; Erbar, J. H.; Robinson, R. L. (Jr.) (1968): Calorimetric determination of the isothermal effect of pressure on the enthalpy of methane and two methane–propane mixtures. AIChE J., 14 (1968), 923–928.

Din, F. (1960): The liquid-vapour equilibrium of the system nitrogen + oxygen at pressures up to 10 atm. Trans. Faraday Soc., 56 (1960), 668–681.

Dingrani, J. G.; Thodos, G. (1978): Vapor-liquid equilibrium behavior of the ethane–n-butane–n-hexane system. Can. J. Chem. Eng., 56 (1978), 616–623.

Distrigaz (1989): See Jaeschke *et al.* (1989) and Jaeschke and Humphreys (1991).

Djordjevich, L.; Budenholzer, R. A. (1970): Vapor-liquid equilibrium data for ethane–propane system at low temperatures. J. Chem. Eng. Data, 15 (1970), 10–12.

Dodge, B. F.; Dunbar, A. K. (1927): An investigation of the coexisting liquid and vapor phases of solutions of oxygen and nitrogen. J. Am. Chem. Soc., 49 (1927), 591–610.

Donnelly, H. G.; Katz, D. L. (1954): Phase equilibria in the carbon dioxide–methane system. Ind. Eng. Chem., 46 (1954), 511–517.

Duarte-Garza, H. A.; Holste, J. C.; Hall, K. R.; Marsh, K. N.; Gammon, B. E. (1995): Isochoric pVT and phase equilibrium measurements for carbon dioxide + nitrogen. J. Chem. Eng. Data, 40 (1995), 704–711.

Duarte-Garza, H. A.; Magee, J. W. (1999): Isochoric p-ρ-T and heat capacity c_v measurements on $\{xC_3H_8+(1-x)\text{i-}C_4H_{10}, x$ approximate to 0.7, 0.3$\}$ from 200 to 400 K at pressures to 35 MPa. J. Chem. Eng. Data, 44 (1999), 1048–1054.

Duarte-Garza, H. A.; Magee, J. W. (2001): Isochoric p-ρ-T measurements on $\{(x)CO_2 + (1-x)C_2H_6, x \approx 0.25, 0.49, 0.74\}$ from (220 to 400) K at pressures to 35 MPa. J. Chem. Eng. Data, 46 (2001), 1095–1100.

Duncan, A. G.; Staveley, L. A. K. (1966): Thermodynamic functions for the liquid systems argon + carbon monoxide, oxygen + nitrogen, and carbon monoxide + nitrogen. Trans. Faraday Soc., 62 (1966), 548–552.

Duncan, A. G.; Hiza, M. J. (1972): Heat of mixing derived from liquid-vapor equilibrium data: a study of the argon–methane, normal hydrogen–neon, and normal deuterium–neon systems. Ind. Eng. Chem., Fundam., 11 (1972), 38–45.

Duschek, W.; Kleinrahm, R.; Wagner, W. (1989): Measurement of the (pressure, density, temperature) relation of Ekofisk natural gas in the temperature range from 273.15 to 323.15 K at pressures up to 8 MPa. J. Chem. Thermodynamics, 21 (1989), 1069–1078.

Duschek, W.; Kleinrahm, R.; Wagner, W. (1990): Measurement and correlation of the (pressure, density, temperature) relation of carbon dioxide. II. Saturated-liquid and saturated-vapour densities and the vapour pressure along the entire coexistence curve. J. Chem. Thermodynamics, 22 (1990), 841–864.

Eakin, B. E.; Ellington, R. T.; Gami, D. C. (1955): Physical-chemical Properties of ethane–nitrogen mixtures. Institute of Gas Technology, Research Bulletin No. 26, 1955.

Ellington, R. T.; Eakin, B. E.; Parent, J. D.; Gami, D. C.; Bloomer, O. T. (1959): Vapor-liquid phase equilibria in the binary systems of methane, ethane and nitrogen. Thermodynamic and Transport Properties of Gases, Liquids and Solids, McGraw-Hill, New York, pp. 180–194, 1959.

Ellington, R. T. (1986): Private communication to M. Jaeschke. University of Oklahoma, Norman, 1986. See Jaeschke *et al.* (1997).

Elliot, D. G.; Chen, R. J. J.; Chappelear, P. S.; Kobayashi, R. (1974): Vapor-liquid equilibrium of methane–n-butane system at low temperatures and high pressures. J. Chem. Eng. Data, 19 (1974), 71–77.

Elshayal, I. M.; Lu, B. C.-Y. (1975): Measurement of total pressures for ethylene–propane mixtures. Can. J. Chem. Eng., 53 (1975), 83–87.

Ely, J. F.; Haynes, W. M.; Bain, B. C. (1989): Isochoric (p, V_m, T) measurements on CO_2 and on $(0.982\ CO_2 + 0.01\ N_2)$ from 250 to 330 K at pressures to 35 MPa. J. Chem. Thermodynamics, 21 (1989), 879–894.

Ely, J. F. (1990): A predictive, exact shape factor extended corresponding states model for mixtures. Adv. Cryog. Eng., 35 (1990), 1511–1520.

Ernst, G.; Hochberg, U. E. (1989): Flow-calorimetric results for the specific heat capacity c_p of CO_2, of C_2H_6, and of $(0.5CO_2 + 0.5C_2H_6)$ at high pressures. J. Chem. Thermodynamics, 21 (1989), 407–414.

Esper, G. J. (1987): Direkte und indirekte p-v-T-Messungen an Fluiden. Fortschr.-Ber. VDI, Reihe 3, Nr. 148, VDI-Verlag, Düsseldorf, 1987.

Estela-Uribe, J. F. (1999): Equation of state for natural gas systems. Ph.D. Thesis, Department of Chemical Engineering and Chemical Technology, Imperial College, London, 1999. Data for methane–nitrogen published by Estela-Uribe *et al.* (2006).

Estela-Uribe, J. F. ; Trusler, J. P. M. (2003): Extended corresponding states model for fluids and fluid mixtures. I. Shape factor model for pure fluids. Fluid Phase Equilibria, 204 (2003), 15–40.

Estela-Uribe, J. F.; De Mendoza, A.; Trusler, J. P. M. (2004): Extended corresponding states model for fluids and fluid mixtures. II. Application to mixtures and natural gas systems. Fluid Phase Equilibria, 216 (2004), 59–84.

Estela-Uribe, J. F.; Trusler, J. P. M.; Chamorro, C. R.; Segovia, J. J.; Martín, M. C.; Villamañán, M. A. (2006): Speeds of sound in $\{(1-x)CH_4 + xN_2\}$ with $x = (0.10001, 0.19999, \text{and } 0.5422)$ at temperatures between 170 K and 400 K and pressures up to 30 MPa. J. Chem. Thermodynamics, 38 (2006), 929–937.

Estrada-Alexanders, A. F.; Trusler, J. P. M. (1998): Speed of sound in carbon dioxide at temperatures between (220 and 450) K and pressures up to 14 MPa. J. Chem. Thermodynamics, 30 (1998), 1589–1601.

Estrada-Alexanders, A. F.; Trusler, J. P. M. (1999): Speed of sound in $(0.4C_2H_6 + 0.6CO_2)$ at temperatures between $T = 220$ K and $T = 450$ K and pressures up to $p = 1.2$ MPa. J. Chem. Thermodynamics, 31 (1999), 685–695.

Evans, R. B. (III); Watson, G. M. (1956): Compressibility factors of nitrogen–n-butane mixtures in the gas phase. Ind. Eng. Chem., Chem. Eng. Data Ser., 1 (1956), 1, 67–71.

Ewers, J.; Wagner, W. (1982): A method for optimizing the structure of equations of state and its application to an equation of state for oxygen. Proc. 8th Symp. Thermophys. Prop., ASME, New York, Vol. 1, pp. 78–87, 1982.

Ewing, M. B.; Goodwin, A. R. H. (1992): Speeds of sound, perfect-gas heat capacities, and acoustic virial coefficients for methane determined using a spherical resonator at temperatures between 255 K and 300 K and pressures in the range 171 kPa to 7.1 MPa. J. Chem. Thermodynamics, 24 (1992), 1257–1274.

Ewing, M. B.; Goodwin, A. R. H. (1993): Speeds of sound in a natural gas of specified composition at the temperature 255 K and pressures in the range 64 kPa to 6.1 MPa. J. Chem. Thermodynamics, 25 (1993), 1503–1511.

Fastovskii, V. G.; Petrovskii, Yu. V. (1955): Investigation of equilibrium liquid and vapor in systems of argon–oxygen. Russ. J. Phys. Chem., 29 (1955), 1311–1317.

Fastovskii, V. G.; Petrovskii, Yu. V. (1956): Investigation of the equilibrium liquid and vapor in the system argon–nitrogen II. Russ. J. Phys. Chem., 30 (1956), 76–78.

Fastovskii, V. G.; Petrovskii, Yu. V. (1957a): An investigation of the liquid/vapour equilibrium in the nitrogen–methane system (in Russian). Zh. Fiz. Khim., 31 (1957), 2317–2321.

Fastovskii, V. G.; Petrovskii, Yu. V. (1957b): A study of the vapor-liquid equilibrium in the system oxygen–argon–nitrogen (in Russian). Zh. Fiz. Khim., 31 (1957), 836–841.

Fastowsky, W. G.; Gonikberg, M. G. (1940): The solubility of gases in liquids at low temperatures and high pressures. III. The solubility of hydrogen in liquid methane (in German). Acta Physicochimica URSS, 12 (1940), 485–488.

Fawcett, D. (1995): Measurement and prediction of speed of sound, with application to gas flow metering in Australian natural gases. Ph.D. Thesis, Murdoch University, 1995.

Fenghour, A.; Wakeham, W. A.; Ferguson, D.; Scott, A. C.; Watson, J. T. R. (1993): Densities of (water + nitrogen) in the temperature range 533 K to 703 K and at pressures up to 31 MPa. J. Chem. Thermodynamics, 25 (1993), 1151–1159.

Fenghour, A.; Wakeham, W. A.; Watson, J. T. R. (1996a): Densities of (water + methane) in the temperature range 430 K to 699 K and at pressures up to 30 MPa. J. Chem. Thermodynamics, 28 (1996), 447–458.

Fenghour, A.; Wakeham, W. A.; Watson, J. T. R. (1996b): Densities of (water + carbon dioxide) in the temperature range 415 K to 700 K and pressures up to 35 MPa. J. Chem. Thermodynamics, 28 (1996), 433–446.

Fenghour, A.; Trusler, J. P. M.; Wakeham, W. A. (1999): Phase behaviour and density of (methane + n-butane). Fluid Phase Equilibria, 163 (1999), 139–156.

Fenghour, A.; Trusler, J. P. M.; Wakeham, W. A. (2001): Densities and bubble points of binary mixtures of carbon dioxide and n-heptane and ternary mixtures of n-butane, n-heptane and n-hexadecane. Fluid Phase Equilibria, 185 (2001), 349–358.

Figuiere, P.; Hom, J. F.; Laugier, S.; Renon, H.; Richon, D.; Szwarc, H. (1980): Vapor-liquid equilibria up to 40 000 KPa and 400°C: a new static method. AIChE J., 26 (1980), 872–875.

Fontaine, J. M. (1989): Das Phasengleichgewicht Helium–Methan und die Beschreibung mit einer neuen Gemischzustandsgleichung. Dissertation, Fakultät für Maschinenbau und Elektrotechnik, Technische Universität Carolo-Wilhelmina zu Braunschweig, 1989.

Förg, W. (2003): Liquid energy. Natural gas trade routes and liquefaction processes. Linde Technology, No. 1, pp. 4–11, 2003.

Francis, A. W. (1954): Ternary systems of liquid carbon dioxide. J. Phys. Chem., 58 (1954), 1099–1114.

Fredenslund, A.; Sather, G. A. (1970): Gas-liquid equilibrium of the oxygen–carbon dioxide system. J. Chem. Eng. Data, 15 (1970), 17–22.

Fredenslund, A.; Mollerup, J. (1974): Measurement and prediction of equilibrium rations for the C_2H_6+CO_2 system. J. Chem. Soc., Faraday Trans., I, 70 (1974), 1653–1660.

Freeth, T. A. C.; Verschoyle, T. T. H. (1931): Physical constants of the system methane–hydrogen. Proc. R. Soc. London, Ser. A, 130 (1931), 453–463.

Fuks, S.; Bellemans, A. (1967): Excess free energies and volumes of two simple binary liquid mixtures: methane–krypton and nitrogen–methane. Bull. Soc. Chim. Belg., 76 (1967), 290–299.

Funada, I.; Yoshimura, S.; Masuoka, H.; Yorizane, M.; Fu, C.-T.; Lu, B. C.-Y. (1982): Vapor-liquid equilibrium values for nitrogen–argon–oxygen at high oxygen concentrations. Adv. Cryog. Eng., 27 (1982), 893–901.

Funke, M.; Kleinrahm, R.; Wagner, W. (2002a): Measurement and correlation of the (p, ρ, T) relation of ethane. I. The homogeneous gas and liquid regions in the temperature range from 95 K to 340 K at pressures up to 12 MPa. J. Chem. Thermodynamics, 34 (2002), 2001–2015.

Funke, M.; Kleinrahm, R.; Wagner, W. (2002b): Measurement and correlation of the (p, ρ, T) relation of ethane. II. Saturated-liquid and saturated-vapour densities and vapour pressures along the entire coexistence curve. J. Chem. Thermodynamics, 34 (2002), 2017–2039.

Galicia-Luna, L. A.; Richon, D.; Renon, H. (1994): New loading technique for a vibrating tube densimeter and measurements of liquid densities up to 39.5 MPa for binary and ternary mixtures of the carbon dioxide–methanol–propane system. J. Chem. Eng. Data, 39 (1994), 424–431.

Gammon, B. E.; Douslin, D. R. (1976): The velocity of sound and heat capacity in methane from near-critical to subcritical conditions and equation-of-state implications. J. Chem. Phys., 64 (1976), 203–218.

Gao, W.; Robinson, R. L. (Jr.); Gasem, K. A. M. (2001): Solubilities of hydrogen in hexane and of carbon monoxide in cyclohexane at temperatures from 344.3 to 410.9 K and pressures to 15 MPa. J. Chem. Eng. Data, 46 (2001), 609–612.

Gasunie (1989): See Jaeschke *et al.* (1989).

Gasunie (1990): See Jaeschke *et al.* (1997).

Gaz de France (1989): See Jaeschke *et al.* (1989).

Gaz de France (1990): See Jaeschke *et al.* (1997).

Glos, S.; Kleinrahm, R.; Wagner, W. (2000): Density measurements on the binary gas mixture (CH_4 + CO_2) at temperatures 273.15 K and 290 K and pressures up to 9.5 MPa. Data published by Claus *et al.* (2001).

Gmehling, J.; Fischer, K.; Li, J.; Schiller, M. (1993): Status and results of group contribution methods. Pure Appl. Cbem., 65 (1993), 919–926.

Goates, J. R.; Ott, J. B.; Grigg, R. B. (1981): Excess volumes of n-hexane + n-heptane, + n-octane, + n-nonane, and + n-decane at 283.15, 298.15, and 313.15 K. J. Chem. Thermodynamics, 13 (1981), 907–913.

Gonikberg, M. G.; Fastowsky, W. G. (1940): Solubility of gases in liquids at low temperatures and high pressures. II. Solubility of helium in liquid nitrogen at temperatures from 78.0 to 109.0°K and at pressures up to 295 atmospheres (in German). Acta Physicochimica URSS, 12 (1940), 67–72.

Gonzalez, M. H.; Lee, A. L. (1968): Dew and bubble points of simulated natural gases. J. Chem. Eng. Data, 13 (1968), 172–176.

Goodwin, A. R. H.; Moldover, M. R. (1997): Phase border and density determinations in the critical region of (carbon dioxide + ethane) determined from dielectric permittivity measurements. J. Chem. Thermodynamics, 29 (1997), 1481–1494.

Goodwin, R. D. (1974): The thermophysical properties of methane, from 90 to 500 K at pressures to 700 bar. Natl. Bur. Stand., Technical Note 653, 1974.

Graham, E. B.; Weale, K. E. (1962): The solubility of compressed gases in non-polar liquids. Prog. Int. Res. Thermodyn. Transp. Prop., Symp. Thermophys. Prop., 2nd (1962), 153–158.

Grauso, L.; Fredenslund, A.; Mollerup, J. (1977): Vapor-liquid equilibrium for the systems C_2H_6 + N_2, C_2H_4 + N_2, C_3H_8 + N_2, and C_3H_6 + N_2. Fluid Phase Equilibria, 1 (1977), 13–26.

Gregory, D. P.; Djordjevich, L.; Kao, R.; Anderson, G. L.; Eakin, B. E.; Bodle, W. W.; Starling, K. E. (1973): Thermodynamic properties of a lean natural gas at cryogenic conditions. Inst. Gas Technol., Tech. Rep. 11, 1973.

Grini, P. G. (1994): Flow calorimetry and enthalpy increment measurements for natural gas. Ph.D. Thesis, University of Trondheim, 1994.

Grini, P. G.; Brendeng, E.; Maehlum, H. S. (1994): New enthalpy increment flow calorimeter, and measurements on a mixture of 68 % methane and 32 % propane. Paper presented at the Twelfth Symposium on Thermophysical Properties, June 19–24, Boulder, Colorado, 1994. See also Grini (1994).

Grini, P. G.; Brendeng, E.; Maehlum, H. S. (1995): New enthalpy increment flow calorimeter and measurements on a mixture of 68 % methane and 32 % propane. Int. J. Thermophysics, 16 (1995), 167–176.

Grini, P. G.; Owren, G. A.; Maehlum, H. (1998): Isobaric enthalpy increment and isenthalpic Joule-Thomson effect measurements on synthetic gas containing binary, or ternary mixtures of methane, ethane, propane, and nitrogen. J. Chem. Thermodynamics, 30 (1998), 1011–1027.

Guedes, H. J. R.; Zollweg, J. A.; Streett, W. B. (1991): Enthalpy of mixing of liquid (carbon dioxide + ethane) at the temperature 230.8 K and of liquid (carbon dioxide + n-butane) at 221.4 K and 241.4 K. J. Chem. Thermodynamics, 23 (1991), 239–245.

Gugnoni, R. J.; Eldridge, J. W.; Okay, V. C.; Lee, T. J. (1974): Carbon dioxide–ethane phase equilibrium and densities from experimental measurements and the B-W-R equation. AIChE J., 20 (1974), 357–362.

Gunn, R. D.; McKetta, J. J.; Ata, N. (1974): Measurement and prediction of high-pressure phase equilibria with a dilute component in the gas phase: the methane–n-hexane system. AIChE J., 20 (1974), 347–353.

Guo, X. Y.; Kleinrahm, R.; Wagner, W. (1990a): Messung der Gasdichten von verschiedenen Erdgasen im Temperaturbereich von 0 °C bis 50 °C und Drücken bis 120 bar. Abschlussbericht für die Ruhrgas AG. Lehrstuhl für Thermodynamik, Ruhr-Universität Bochum, 1990.

Guo, X. Y.; Kleinrahm, R.; Wagner, W. (1990b): Messung der Gasdichten von verschiedenen Erdgasen im Temperaturbereich von 0 °C bis 50 °C und Drücken bis 120 bar. Anlagen zum Bericht. Lehrstuhl für Thermodynamik, Ruhr-Universität Bochum, 1990.

Guo, X. Y.; Kleinrahm, R.; Wagner, W. (1993): Experimentelle Untersuchung der systematischen Meßfehler von Betriebsdichteaufnehmern für Erdgas-Meßstrecken. Teil 2: Meßergebnisse für Erdgase. Bericht für die Ruhrgas AG. Lehrstuhl für Thermodynamik, Ruhr-Universität Bochum, 1993.

Hacura, A.; Yoon, J. H.; Baglin, F. G. (1988): Density values of carbon dioxide and nitrogen mixtures from 500 to 2500 bar at 323 and 348 K. J. Chem. Eng. Data, 33 (1988), 152–154.

Hakuta, T.; Nagahama, K.; Suda, S. (1969): Binary vapor-liquid equilibria of CO_2–C_2 hydrocarbons. Kagaku-kogaku, 33 (1969), 904–907.

Hall, K. R.; Canfield, F. B. (1970): Isotherms for the He–N_2 system at −190°C, −170°C and −160°C up to 700 atm. Physica, 47 (1970), 219–226.

Hamam, S. E. M.; Lu, B. C.-Y. (1974): Vapor-liquid equilibrium in the ethane–carbon dioxide system. Can. J. Chem. Eng., 52 (1974), 283–286.

Hamam, S. E. M.; Lu, B. C.-Y. (1976): Isothermal vapor-liquid equilibria in binary system propane–carbon dioxide. J. Chem. Eng. Data, 21 (1976), 200–204.

Hanayama, Y. (1979): Velocity of ultrasound wave in mixed gases at high pressure. J. Phys. Soc. Japan, 46 (1979), 328–333.

Händel, G.; Kleinrahm, R.; Wagner, W. (1992): Measurements of the (pressure, density, temperature) relation of methane in the homogeneous gas and liquid regions in the temperature range from 100 K to 260 K and at pressures up to 8 MPa. J. Chem. Thermodynamics, 24 (1992), 685–695.

Haney, R. E. D.; Bliss, H. (1944): Compressibilities of nitrogen–carbon dioxide mixtures. Ind. Eng. Chem., 36 (1944), 985–989.

Harding, S. T.; Floudas, C. A. (2000): Phase stability with cubic equations of state: Global optimization approach. AIChE J., 46 (2000), 1422–1440.

Haynes, W. M. (1982): Measurements of orthobaric-liquid densities of multicomponent mixtures of LNG components (N_2, CH_4, C_2H_6, C_3H_8, $CH_3CH(CH_3)CH_3$, C_4H_{10}, $CH_3CH(CH_3)C_2H_5$, and C_5H_{12}) between 110 and 130 K. J. Chem. Thermodynamics, 14 (1982), 603–612.

Haynes, W. M. (1983): Orthobaric liquid densities and dielectric constants of (methane + 2-methylpropane) and (methane + n-butane) at low temperatures. J. Chem. Thermodynamics, 15 (1983), 903–911.

Haynes, W. M.; McCarty, R. D. (1983): Low-density isochoric (p, V, T) measurements on (nitrogen + methane). J. Chem. Thermodynamics, 15 (1983), 815–819.

Haynes, W. M.; McCarty, R. D.; Hiza, M. J. (1983): Liquefied natural gas densities: summary of research program at the National Bureau of Standards. Natl. Bur. Stand., Monograph 172, 1983.

Haynes, W. M.; McCarty, R. D.; Eaton, B. E.; Holste, J. C. (1985): Isochoric (p, V_{m}, x, T) measurements on (methane + ethane) from 100 to 320 K at pressures to 35 MPa. J. Chem. Thermodynamics, 17 (1985), 209–232.

Heck, C. K.; Hiza, M. J. (1967): Liquid-vapor equilibrium in the system helium–methane. AIChE J., 13 (1967), 593–599.

Heidemann, R. A. (1983): Computation of high pressure phase equilibria. Fluid Phase Equilibria, 14 (1983), 55–78.

Heidemann, R. A. (1996): Excess free energy mixing rules for cubic equations of state. Fluid Phase Equilibria, 116 (1996), 454–464.

Heidemann, R. A.; Khalil, A. M. (1980): The calculation of critical points. AIChE J., 26 (1980), 769–779.

Henderson, N.; Freitas, L.; Platt, G. M. (2004): Prediction of critical points: a new methodology using global optimization. AIChE J., 50 (2004), 1300–1314.

Higashi, Y.; Funakura, M.; Yoshida, Y. (1994): Vapor-liquid equilibrium for propane/iso-butane mixture. Proc. International Conference: CFCs, The Day After, Padova, Italy, pp. 493–500, 1994.

Hipkin, H. (1966): Experimental vapor-liquid equilibrium data for propane–isobutane. AIChE J., 12 (1966), 484–487.

Hirata, M.; Suda, S. (1968): Equilibrium measurements by the vapor-liquid flow method. Vapor-liquid equilibrium measurements for three binary mixtures of n-butane at 0 °C. Bull. Jpn. Pet. Inst., 10 (1968), 20–27.

Hirata, M.; Suda, S.; Hakuta, T.; Nagahama, K. (1969a): Light hydrocarbon vapor-liquid equilibria. Mem. Fac. Technol., Tokyo Metrop. Univ., 19 (1969), 103–122.

Hirata, M.; Suda, S.; Hakuta, T.; Nagahama, K. (1969b): High pressure vapor-liquid equilibria for binary system containing C_4-hydrocarbons. Sekiyu-gakkai-shi, 12 (1969), 10, 773–777.

Hirata, M.; Suda, S.; Miyashita, R.; Hoshino, T. (1970): High pressure vapor-liquid equilibria. Experimental data on the system propane–isobutane at 66.60 °C. Mem. Fac. Technol., Tokyo Metrop. Univ., 20 (1970), 1811–1817.

Hiza, M. J.; Heck, C. K.; Kidnay, A. J. (1967): Liquid-vapor and solid-vapor equilibrium in the system hydrogen–ethane. Adv. Cryog. Eng., 13 (1967), 343–356.

Hiza, M. J.; Haynes, W. M.; Parrish, W. R. (1977): Orthobaric liquid densities and excess volumes for binary mixtures of low molar-mass alkanes and nitrogen between 105 and 140 K. J. Chem. Thermodynamics, 9 (1977), 873–896.

Hiza, M. J.; Haynes, W. M. (1978): Liquid mixture excess volumes and total vapor pressures using a magnetic suspension densimeter with compositions determined by chromatographic analysis: methane plus ethane. Adv. Cryog. Eng., 23 (1978), 594–601.

Hiza, M. J.; Haynes, W. M. (1980): Orthobaric liquid densities and excess volumes for multicomponent mixtures of low molar-mass alkanes and nitrogen between 105 and 125 K. J. Chem. Thermodynamics, 12 (1980), 1–10.

Hiza, M. J. (1981): Liquid-vapor equilibria in binary systems containing ^{4}He or ^{3}He with nH_2 or nD_2. Fluid Phase Equilibria, 6 (1981), 203–227.

Hiza, M. J.; Kidnay, A. J.; Haynes, W. M. (1990): Liquid-vapor equilibria in binary systems containing nitrogen, oxygen, and argon between 63 and 100 K. Preliminary unpublished results, National Institute of Standards and Technology, Boulder, CO, 1990.

Hodges, R. J.; Burch, R. J. (1967): The equilibrium distribution of methane between the liquid and vapour phases of oxygen. Cryogenics, 7 (1967), 112–113.

Holborn, L.; Otto, J. (1925): Über die Isothermen einiger Gase zwischen +400 und −183°. Z. Phys., 33 (1925), 1–11.

Holst, G.; Hamburger, L. (1916): Untersuchungen über das Gleichgewicht von Flüssigkeit und Dampf des Systems Argon–Stickstoff. Z. Phys. Chem. (Leipzig), 91 (1916), 513–547.

Hoover, A. E. (1965): Virial coefficients of methane and ethane. Ph.D. Dissertation, Rice University, Houston, Texas, 1965. Data reported by Jaeschke and Humphreys (1991) in GERG Technical Monograph 4 (1990).

Hou, H.; Holste, J. C.; Hall, K. R.; Marsh, K. N.; Gammon, B. E. (1996): Second and third virial coefficients for methane + ethane and methane + ethane + carbon dioxide at (300 and 320) K. J. Chem. Eng. Data, 41 (1996), 344–353.

Hsu, J. J.-C.; Nagarajan, N.; Robinson, R. L. (Jr.) (1985): Equilibrium phase compositions, phase densities and interfacial tensions for CO_2 + hydrocarbon systems. 1. CO_2 + n-butane. J. Chem. Eng. Data, 30 (1985), 485–491.

Hua, J. Z.; Brennecke, J. F.; Stadtherr, M. A. (1996): Reliable prediction of phase stability using an interval Newton method. Fluid Phase Equilibria, 116 (1996), 52–59.

Hua, J. Z.; Brennecke, J. F.; Stadtherr, M. A. (1998): Enhanced interval analysis for phase stability: cubic equation of state models. Ind. Eng. Chem. Res., 37 (1998), 1519–1527.

Huang, E. T. S.; Swift, G. W.; Kurata, F. (1967): Viscosities and densities of methane–propane mixtures at low temperatures and high pressures. AIChE J., 13 (1967), 846–850.

Hudziak, J. A.; Kahvand, H.; Yassale, M.; Leipziger, S. (1984): Dew point measurements for nitrogen–propane and nitrogen–butane mixtures. J. Chem. Eng. Data, 29 (1984), 296–301.

Huron, M.-J.; Vidal, J. (1979): New mixing rules in simple equations of state for representing vapour-liquid equilibria of strongly non-ideal mixtures. Fluid Phase Equilibria, 3 (1979), 255–271.

Hwang, C.-A.; Iglesias-Silva, G. A.; Holste, J. C.; Hall, K. R.; Gammon, B. E.; Marsh, K. N. (1997a): Densities of carbon dioxide + methane mixtures from 225 K to 350 K at pressures up to 35 MPa. J. Chem. Eng. Data, 42 (1997), 897–899.

Hwang, C.-A.; Simon, P. P.; Hou, H.; Hall, K. R.; Holste, J. C.; Marsh, K. N. (1997b): Burnett and pycnometric (p, V_m, T) measurements for natural gas mixtures. J. Chem. Thermodynamics, 29 (1997), 1455–1472.

Hwang, S.-C.; Lin, H.-M.; Chappelear, P. S.; Kobayashi, R. (1976): Dew point study in the vapor-liquid region of the methane–carbon dioxide system. J. Chem. Eng. Data, 21 (1976), 493–497.

Ingrain, D.; Pinvidic, J. J.; Desenfant, P. (1993): Experimental measuring of sound velocity in a natural gas from north sea, in a liquefied natural gas from Algeria and in a methane–propane (90%–10%) binary mixture. Gaz de France, M. CERSTA - IN/IN n° 93 1080, 1993.

ISO (1997): ISO 12213. Natural gas – Calculation of compression factor. International Organization for Standardization, Geneva, 1997.

Jacobsen, R. T; Penoncello, S. G.; Lemmon, E. W.; Span, R. (2000): Multiparameter equations of state. In: Equations of state for fluids and fluid mixtures (edited by J. V. Sengers, R. F. Kayser, C. J. Peters, and H. J. White, Jr.). Elsevier, Amsterdam, Experimental Thermodynamics, Vol. V, Part II, pp. 849–881, 2000.

Jaeschke, M.; van Caneghem, P.; Fauveau, M.; Humphreys, A. E.; Janssen-van Rosmalen, R.; Pellei, Q. (1989): GERG round-robin test of Z-meters, Burnett apparatus and an interferometric device for pVT measurements. GERG Technical Monograph 3 (1989). Fortschr.-Ber. VDI, Reihe 6, Nr. 238, VDI-Verlag, Düsseldorf, 1989.

Jaeschke, M.; Hinze, M. (1991): Ermittlung des Realgasverhaltens von Methan und Stickstoff und deren Gemische im Temperaturbereich von 270 K bis 353 K und Drücken bis 30 MPa. Fortschr.-Ber. VDI, Reihe 3, Nr. 262, VDI-Verlag, Düsseldorf, 1991.

Jaeschke, M.; Humphreys, A. E. (1991): The GERG databank of high accuracy compressibility factor measurements. GERG Technical Monograph 4 (1990). Fortschr.-Ber. VDI, Reihe 6, Nr. 251, VDI-Verlag, Düsseldorf, 1991.

Jaeschke, M.; Hinze, H. M.; Achtermann, H. J.; Magnus, G. (1991): PVT data from Burnett and refractive index measurements for the nitrogen–hydrogen system from 270 to 353 K and pressures to 30 MPa. Fluid Phase Equilibria, 62 (1991), 115–139.

Jaeschke, M.; Humphreys, A. E. (1992): Standard GERG virial equation for field use. Simplification of the input data requirements for the GERG virial equation – an alternative means of compressibility factor calculation for natural gases and similar mixtures. GERG Technical Monograph 5 (1991). Fortschr.-Ber. VDI, Reihe 6, Nr. 266, VDI-Verlag, Düsseldorf, 1992.

Jaeschke, M.; Schley, P. (1995): Ideal-gas thermodynamic properties for natural-gas applications. Int. J. Thermophysics, 16 (1995), 1381–1392.

Jaeschke, M.; Schley, P. (1996): Berechnung des Realgasfaktors von Erdgasen mit der AGA8-DC92 Zustandsgleichung. II. Vergleich mit Meßwerten. GWF Gas Erdgas, 137 (1996), 420–425.

Jaeschke, M.; Hinze, H.-M.; Humphreys, A. E. (1997): Supplement to the GERG databank of high-accuracy compression factor measurements. GERG TM7 1996. GERG Technical Monograph 7 (1996). Fortschr.-Ber. VDI, Reihe 6, Nr. 355, VDI Verlag, Düsseldorf, 1997. Data partly published by Jaeschke and Humphreys (1991) in GERG Technical Monograph 4 (1990).

Jaeschke, M.; Schley, P. (1998): Compression factor measurements on rich natural gases. Final report to Gas Research Institute, Chicago, Contract No. 5095-260-3557, 1998.

Janisch, J. (2000a): Private communication to R. Klimeck (preliminary results). Institut für Thermodynamik, Technische Universität Braunschweig, January 2000.

Janisch, J. (2000b): Private communication to R. Klimeck (preliminary results). Institut für Thermodynamik, Technische Universität Braunschweig, February 2000.

Janisch, J. (2000c): Vapor-liquid phase equilibria including saturated densities for systems containing nitrogen, methane and ethane from 130 K to 270 K and pressure up to 10 MPa. Final report to GERG WG 1.34, Institut für Thermodynamik, Technische Universität Braunschweig, 2000.

Japas, M. L.; Franck, E. U. (1985a): High pressure phase equilibria and *PVT*-data of the water–nitrogen system to 673 K and 205 MPa. Ber. Bunsenges. Phys. Chem., 89 (1985), 793–800.

Japas, M. L.; Franck, E. U. (1985b): High pressure phase equilibria and *PVT*-data of the water–oxygen system including water–air to 673 K and 250 MPa. Ber. Bunsenges. Phys. Chem., 89 (1985), 1268–1275.

Jarne, C.; Avila, S.; Blanco, S. T.; Rauzy, E.; Otín, S.; Velasco, I. (2004a): Thermodynamic properties of synthetic natural gases. 5. Dew point curves of synthetic natural gases and their mixtures with water and with water and methanol: measurement and correlation. Ind. Eng. Chem. Res., 43 (2004), 209–217.

Jarne, C.; Blanco, S. T.; Gallardo, M. A.; Rauzy, E.; Otín, S.; Velasco, I. (2004b): Dew points of ternary methane (or ethane) + carbon dioxide + water mixtures: measurement and correlation. Energy & Fuels, 18 (2004), 396–404.

Jett, M.; Fleyfel, F.; Kobayashi, R. (1994): The nature of (p, V_m, T) surfaces of mixtures: (quantum + normal) and (normal + hydrogen-bonded), as summarized by their isochoric inflection loci. J. Chem. Thermodynamics, 26 (1994), 561–569.

Jiang, S.; Wang, Y.; Shi, J. (1990): Determination of compressibility factors and virial coefficients for the systems containing N_2, CO_2 and $CHClF_2$ by the modified Burnett method. Fluid Phase Equilibria, 57 (1990), 105–117.

Jin, Z.-L.; Liu, K.-Y.; Sheng, W.-W. (1993): Vapor-liquid equilibrium in binary and ternary mixtures of nitrogen, argon, and methane. J. Chem. Eng. Data, 38 (1993), 353–355.

Joffe, J. (1976): Vapor-liquid equilibria by the pseudocritical method. Ind. Eng. Chem., Fundam., 15 (1976), 298–303.

Joffrion, L. L.; Eubank, P. T. (1988): *P-V-T* data and virial coefficients for gaseous methane–water mixtures with correction for adsortion effects. Fluid Phase Equilibria, 43 (1988), 263–294.

Kahre, L. C. (1973): Liquid density of light hydrocarbon mixtures. J. Chem. Eng. Data, 18 (1973), 267–270.

Kahre, L. C. (1974): Low-temperature *K* data for methane–n-butane. J. Chem. Eng. Data, 19 (1974), 67–71.

Kahre, L. C. (1975): Low-temperature *K* data for methane–n-pentane. J. Chem. Eng. Data, 20 (1975), 363–367.

Kalra, H.; Krishnan, T. R.; Robinson, D. B. (1976): Equilibrium-phase properties of carbon dioxide–n-butane and nitrogen–hydrogen sulfide systems at subambient temperatures. J. Chem. Eng. Data, 21 (1976), 222–225.

Kalra, H.; Robinson, D. B.; Besserer, G. J. (1977): The equilibrium phase properties of the nitrogen–n-pentane system. J. Chem. Eng. Data, 22 (1977), 215–218.

Kalra, H.; Ng, H.-J.; Miranda, R. D.; Robinson, D. B. (1978a): Equilibrium phase properties of the nitrogen–isobutane system. J. Chem. Eng. Data, 23 (1978), 321–324.

Kalra, H.; Kubota, H.; Robinson, D. B.; Ng, H.-J. (1978b): Equilibrium phase properties of the carbon dioxide–n-heptane system. J. Chem. Eng. Data, 23 (1978), 317–321.

Kamilov, I. K.; Malysheva, L. V.; Rasulov, A. R.; Shakbanov, K. A.; Stepanov, G. V. (1996): The experimental investigation of $C_{v,x}$, P, V, T properties and the equation of state of the n-hexane–water system. Fluid Phase Equilibria, 125 (1996), 177–184.

Kaminishi, G.; Toriumi, T. (1966): Vapor-liquid phase equilibrium in the CO_2–H_2, CO_2–N_2 and CO_2–O_2 systems (in Japanese). Kogyo Kagaku Zasshi, 69 (1966), 175–178.

Kaminishi, G.; Arai, Y.; Saito, S.; Maeda, S. (1968): Vapor-liquid equilibria for binary and ternary systems containing carbon dioxide. J. Chem. Eng. Japan, 1 (1968), 109–116.

Kandil, M. E.; Marsh, K. N.; Goodwin, A. R. H. (2005): A re-entrant resonator for the measurement of phase boundaries: dew points for $\{0.4026CH_4 + 0.5974C_3H_8\}$. J. Chem. Thermodynamics, 37 (2005), 684–691.

Kay, W. B. (1938): Liquid-vapor phase equilibrium relations in the ethane–n-heptane system. Ind. Eng. Chem., 30 (1938), 459–465.

Kay, W. B. (1940): Liquid-vapor equilibrium relations in binary systems. The ethane–n-butane system. Ind. Eng. Chem., 32 (1940), 353–357.

Kay, W. B. (1941): Liquid-vapor equilibrium relations in binary systems. n-Butane–n-heptane system. Ind. Eng. Chem., 33 (1941), 590–594.

Kay, W. B. (1948): Liquid-vapor equilibrium relations in binary systems. Ethylene–n-heptane system. Ind. Eng. Chem., 40 (1948), 1459–1464.

Kay, W. B. (1970): Vapor-liquid equilibrium relations of binary systems. The propane–n-alkane systems. n-Butane and n-pentane. J. Chem. Eng. Data, 15 (1970), 46–52.

Kay, W. B. (1971): Vapor-liquid equilibrium relationships of binary systems. Propane–n-alkane systems, n-hexane and n-heptane. J. Chem. Eng. Data, 16 (1971), 137–140.

Kay, W. B.; Genco, J.; Fichtner, D. A. (1974): Vapor-liquid equilibrium relationships of binary systems propane–n-octane and n-butane–n-octane. J. Chem. Eng. Data, 19 (1974), 275–280.

Kay, W. B.; Hoffman, R. L.; Davies, O. (1975): Vapor-liquid equilibrium relationships of binary systems n-butane–n-pentane and n-butane–n-hexane. J. Chem. Eng. Data, 20 (1975), 333–338.

Kayukawa, Y.; Hasumoto, M.; Kano, Y.; Watanabe, K. (2005a): Liquid-phase thermodynamic properties for the binary and ternary systems of propane (1), n-butane (2), and isobutane (3). J. Chem. Eng. Data, 50 (2005), 565–578.

Kayukawa, Y.; Fujii, K.; Higashi, Y. (2005b): Vapor-liquid equilibrium (VLE) properties for the binary systems propane (1) + n-butane (2) and propane (1) + isobutane (3). J. Chem. Eng. Data, 50 (2005), 579–582.

Kessel'man, P. M.; Alekseenko, G. P. (1974): Experimental investigation of the compressibility of mixtures of carbon dioxide and helium. Therm. Eng. (Engl. Transl.), 21 (1974), 6, 102–105; Teploenergetika, 21 (1974), 6, 73–75.

Kiran, E.; Pöhler, H.; Xiong, Y. (1996): Volumetric properties of pentane + carbon dioxide at high pressures. J. Chem. Eng. Data, 41 (1996), 158–165.

Kleinrahm, R.; Duschek, W.; Wagner, W.; Jaeschke, M. (1988): Measurement and correlation of the (pressure, density, temperature) relation of methane in the temperature range from 273.15 K to 323.15 K at pressures up to 8 MPa. J. Chem. Thermodynamics, 20 (1988), 621–631.

Kleinrahm, R.; Guo, X. Y.; Gómez Mellado, B.; Wagner, W. (1996): Prüfung der Messgenauigkeit von Betriebsdichteaufnehmern des Typs Solartron 7812. Teil 1: Prüfung im Labor. Bericht für die Ruhrgas AG. Lehrstuhl für Thermodynamik, Ruhr-Universität Bochum, 1996.

Klimeck, J.; Kleinrahm, R.; Wagner, W. (2001): Measurements of the (p, ρ, T) relation of methane and carbon dioxide in the temperature range 240 K to 520 K at pressures up to 30 MPa using a new accurate single-sinker densimeter. J. Chem. Thermodynamics, 33 (2001), 251–267.

Klimeck, R.; Span, R.; Kleinrahm, R.; Wagner, W. (1996): Fundamental equation for calorific properties. Collecting of data and test of existing equations. Final report to GERG WG 1.3, Lehrstuhl für Thermodynamik, Ruhr-Universität Bochum, 1996.

Klimeck, R.; Span, R.; Wagner, W. (1999): Development of a reference equation for thermal and caloric properties of natural gases. Phase 1: theoretical results. Report to GERG WG 1.34, Lehrstuhl für Thermodynamik, Ruhr-Universität Bochum, 1999.

Klimeck, R. (2000): Entwicklung einer Fundamentalgleichung für Erdgase für das Gas- und Flüssigkeitsgebiet sowie das Phasengleichgewicht. Dissertation, Fakultät für Maschinenbau, Ruhr-Universität Bochum, 2000.

Klink, A. E.; Chen, H. Y.; Amick, E. H. (Jr.) (1975): The vapor-liquid equilibrium of the hydrogen–n-butane system at elevated pressures. AIChE J., 21 (1975), 1142–1148.

Knapp, H.; Döring, R.; Oellrich, L.; Plöcker, U.; Prausnitz, J. M. (1982): Vapor-liquid equilibria for mixtures of low boiling substances. DECHEMA, Chemistry Data Series, Vol. VI, Frankfurt/Main, 1982.

Knott, T. (2001): Cool future for gas. Frontiers, the BP magazine of technology and innovation, No. 2, pp. 10–16, 2001.

Kohn, J. P.; Bradish, W. F. (1964): Multiphase and volumetric equilibria of methane–n-octane system at temperatures between −110° and 150°C. J. Chem. Eng. Data, 9 (1964), 5–8.

Kosov, N. D.; Brovanov, I. S. (1975): The compressibility of binary mixtures of helium, nitrogen and argon with carbon dioxide from 59×10^5 to 590×10^5 Pa. Teploenergetika, 22 (1975), 11, 87–89.

Kremer, H. (1982): Experimentelle Untersuchung und Berechnung von Hochdruck-Flüssigkeits-Dampf- und Flüssigkeits-Flüssigkeits-Dampf-Gleichgewichten für tiefsiedende Gemische. Dissertation, Technische Universität Berlin, 1982.

Krichevskii, I. R.; Khazanova, N. E.; Lesnevskaya, L. S.; Sandalova, L. Yu. (1962): Equilibrium of liquid-gas at high pressures in the system nitrogen–carbon dioxide (in Russian). Khim. Promst. (Moscow), 38 (1962), 3, 169–171.

Krishnan, T. R.; Kalra, H.; Robinson, D. B. (1977): The equilibrium phase properties of the nitrogen–isopentane system. J. Chem. Eng. Data, 22 (1977), 282–285.

Kritschewsky, I. R.; Markov, V. P. (1940): The compressibility of gas mixtures. I. The *P-V-T* data for binary and ternary mixtures of hydrogen, nitrogen and carbon dioxide. Acta Physicochimica URSS, 12 (1940), 59–66.

Kritschewsky, I. R.; Levchenko, G. T. (1941): The compressibility of gas mixtures. II. The *P-V-T* data for binary and ternary mixtures of methane, nitrogen and hydrogen. Acta Physicochimica URSS, 14 (1941), 271–278.

Ku, P. A.; Dodge, B. F. (1967): Compressibility of the binary systems: helium–nitrogen and carbon dioxide–ethylene. J. Chem. Eng. Data, 12 (1967), 158–164.

Kunz, O. (2000): Ein einfacher Multifluid-Ansatz für Gemische aus Erdgaskomponenten. Diplomarbeit, Lehrstuhl für Thermodynamik, Ruhr-Universität Bochum, 2000.

Kunz, O.; Wagner, W. (2006): Software package for the calculation of thermodynamic properties from the GERG-2004 wide-range reference equation of state for natural gases and other mixtures. Lehrstuhl für Thermodynamik, Ruhr-Universität Bochum, 2006.

Labes, P.; Daridon, J. L.; Lagourette, B.; Saint-Guirons, H. (1994): Measurement and prediction of ultrasonic speed under high pressure in natural gases. Int. J. Thermophysics, 15 (1994), 803–819.

Lammers, J. N. J. J.; van Kasteren, P. H. G.; Kroon, G. F.; Zeldenrust, H. (1978): Enthalpy measurements of natural gas components and mixed refrigerants with a flow calorimeter. Gas Process. Assoc., Proc. Annu. Conv., 57 (1978), 18–24.

Lau, W.-W. R. (1986): A continuously weighed pycnometer providing densities for carbon dioxide + ethane mixtures between 240 and 350 K at pressures up to 35 MPa. Ph.D. Thesis, Texas A&M University, College Station, Texas, 1986.

Lau, W.-W. R.; Hwang, C.-A.; Holste, J. C.; Hall, K. R.; Gammon, B. E.; Marsh, K. N. (1997): Densities of carbon dioxide + ethane mixtures from 240 K to 450 K at pressures up to 35 MPa. J. Chem. Eng. Data, 42 (1997), 900–902.

Laverman, R. J.; Selcukoglu, Y. A. (1968): Calorimeter helps design better LNG liquefaction cycles. Am. Gas. J., 195 (1968), 47–52.

Le Noë, O.; Desentfant, P. (1996): Experimental determination of sound velocity in pure methane, in a binary mixture and in a five component mixture. Report to GERG WG 1.3, 1996.

Leach, J. W.; Chappelear, P. S.; Leland; T. W. (1968): Use of molecular shape factors in vapor-liquid equilibrium calculations with the corresponding states principle. AIChE J., 14 (1968), 568–576.

Lee, G. C.; Smith, R.; Zhu, X. X. (2002): Optimal synthesis of mixed-refrigerant systems for low-temperature processes. Ind. Eng. Chem. Res., 41 (2002), 5016–5028.

Lehigh, W. R.; McKetta, J. J. (1966): Vapor-liquid equilibrium in the ethane–n-butane–nitrogen system. J. Chem. Eng. Data, 11 (1966), 180–182.

Leland, T. W. (Jr.); Chappelear, P. S. (1968): The corresponding states principle. A review of current theory and practice. Ind. Eng. Chem., 60 (1968), 7, 15–43.

Lemming, W. (1989): Experimentelle Bestimmung akustischer und thermischer Virialkoeffizienten von Arbeitsstoffen der Energietechnik. Fortschr.-Ber. VDI, Reihe 19, Nr. 32, VDI-Verlag, Düsseldorf, 1989.

Lemmon, E. W. (1991): The prediction of vapor-liquid equilibrium of nitrogen–argon–oxygen mixtures including air. M.Sc. Thesis, University of Idaho, 1991.

Lemmon, E. W. (1996): A generalized model for the prediction of the thermodynamic properties of mixtures including vapor-liquid equilibrium. Ph.D. Dissertation, University of Idaho, 1996.

Lemmon, E. W.; Jacobsen, R. T (1999): A generalized model for the thermodynamic properties of mixtures. Int. J. Thermophysics, 20 (1999), 825–835.

Lemmon, E. W.; Tillner-Roth, R. (1999): A Helmholtz energy equation of state for calculating the thermodynamic properties of fluid mixtures. Fluid Phase Equilibria, 165 (1999), 1–21.

Lemmon, E. W.; Jacobsen, R. T; Penoncello, S. G.; Friend, D. G. (2000): Thermodynamic properties of air and mixtures of nitrogen, argon, and oxygen from 60 to 2000 K at pressures to 2000 MPa. J. Phys. Chem. Ref. Data, 29 (2000), 331–385.

Lemmon, E. W.; Huber, M. L. (2004): Thermodynamic properties of n-dodecane. Energy & Fuels, 18 (2004), 960–967.

Lemmon, E. W.; Jacobsen, R. T (2004): Equations of state for mixtures of R-32, R-125, R-134a, R-143a, and R-152a. J. Phys. Chem. Ref. Data, 33 (2004), 593–620.

Lemmon, E. W.; Jacobsen, R. T (2005): A new functional form and new fitting techniques for equations of state with application to pentafluoroethane HFC-125. J. Phys. Chem. Ref. Data, 34 (2005), 69–108.

Lemmon, E. W.; Span, R. (2006): Short fundamental equations of state for 20 industrial fluids. J. Chem. Eng. Data, 51 (2006), 785–850.

Lemmon, E. W.; McLinden, M. O.; Wagner, W. (2007): A reference equation of state for the thermodynamic properties of propane for temperatures from the melting line to 650 K and pressures up to 1000 MPa. To be submitted to J. Phys. Chem. Ref. Data, 36 (2007).

Leslie, E. H.; Carr, A. R. (1925): Vapor pressure of organic solutions, and application of Dühring's rule to calculation of equilibrium diagrams. Ind. Eng. Chem., 17 (1925), 810–817.

Leu, A.-D.; Robinson, D. B. (1987): Equilibrium phase properties of the n-butane–carbon dioxide and isobutane–carbon dioxide binary systems. J. Chem. Eng. Data, 32 (1987), 444–447.

Levitskaja, E.; Priannikow, K. (1939): Liquid-vapor equilibrium in the binary system hydrogen–ethane (in Russian). Zh. Tekh. Fiz., 9 (1939), 1849–1853.

Levitskaja, E. P. (1941): Study of the liquid-vapor equilibria of the ternary system ethane–methane–hydrogen (in Russian). Zh. Tekh. Fiz., 11 (1941), 197–204.

Lewis, K. L.; Staveley, L. A. K. (1975): Excess enthalpies of the liquid mixtures nitrogen + oxygen, nitrogen + argon, argon + ethane, and methane + carbon tetrafluoride. J. Chem. Thermodynamics, 7 (1975), 855–864.

Lhoták, V.; Wichterle, I. (1981): Vapour-liquid equilibria in the ethane–n-butane system at high pressures. Fluid Phase Equilibria, 6 (1981), 229–235.

Lhoták, V.; Wichterle, I. (1983): Vapour-liquid equilibria in the ethane – propane – n-butane system at high pressures. Fluid Phase Equilibria, 12 (1983), 307–309.

Lim, J. S.; Ho, Q. N.; Park, J.-Y.; Lee, B. G. (2004): Measurement of vapor-liquid equilibria for the binary mixture of propane (R-290) + isobutane (R-600a). J. Chem. Eng. Data, 49 (2004), 192–198.

Lin, Y.-N.; Chen, R. J. J.; Chappelear, P. S.; Kobayashi, R. (1977): Vapor-liquid equilibrium of the methane–n-hexane system at low temperature. J. Chem. Eng. Data, 22 (1977), 402–408.

Linshits, L. R.; Rodkina, I. B.; Tsiklis, D. S. (1975): Measurement of the compressibilities of carbon dioxide–helium mixtures by Burnett's method. Russ. J. Phys. Chem., 49 (1975), 1258–1260.

Liu, Y. P.; Miller, R. C. (1972): Temperature dependence of excess volumes for simple liquid mixtures: $Ar+CH_4$, N_2+CH_4. J. Chem. Thermodynamics, 4 (1972), 85–98.

Llave, F. M.; Chung, T. H. (1988): Vapor-liquid equilibria of nitrogen–hydrocarbon systems at elevated pressures. J. Chem. Eng. Data, 33 (1988), 123–128.

Machado, J. R. S.; Streett, W. B.; Deiters, U. (1988): *PVT* measurements of hydrogen/methane mixtures at high pressures. J. Chem. Eng. Data, 33 (1988), 148–152.

Magee, J. W.; Pollin, A. G.; Martin, R. J.; Kobayashi, R. (1985): Burnett-isochoric *P*-*V*-*T* measurements of a nominal 20 mol% hydrogen–80 mol% methane mixture at elevated temperatures and pressures. Fluid Phase Equilibria, 22 (1985), 155–173.

Magee, J. W.; Ely, J. F. (1988): Isochoric (p, v, T) measurements on CO_2 and $(0.98\ CO_2 + 0.02\ CH_4)$ from 225 to 400 K and pressures to 35 MPa. Int. J. Thermophysics, 9 (1988), 547–557.

Magee, J. W. (1995): Molar heat capacity at constant volume for [xCO$_2$+(1−x)C$_2$H$_6$] from 220 to 340 K at pressures to 35 MPa. J. Chem. Eng. Data, 40 (1995), 438–442.

Magee, J. W.; Haynes, W. M.; Hiza, M. J. (1997): Isochoric (p, ρ, T) measurements for five natural gas mixtures from T = (225 to 350) K at pressures to 35 MPa. J. Chem. Thermodynamics, 29 (1997), 1439–1454.

Maimoni, A. (1961): Liquid-vapor equilibria in the hydrogen–nitrogen and deuterium–nitrogen systems. AIChE J., 7 (1961), 371–375.

Malewski, M. K. F.; Sandler, S. I. (1989): High-pressure vapor-liquid equilibria of the binary mixtures nitrogen + n-butane and argon + n-butane. J. Chem. Eng. Data, 34 (1989), 424–426.

Mallu, B. V.; Natarajan, G.; Viswanath, D. S. (1987): Compression factors and second virial coefficients of CO$_2$, CO, and $\{x\mathrm{CO} + (1 - x)\mathrm{CO_2}\}$. J. Chem. Thermodynamics, 19 (1987), 549–554.

Marathe, P.; Sandler, S. I. (1991): High-pressure vapor-liquid equilibrium of some binary mixtures of cyclopentane, argon, nitrogen, n-butane, and neopentane. J. Chem. Eng. Data, 36 (1991), 192–197.

Marrucho, I. M.; Palavra, A. M. F.; Ely, J. F. (1994): An improved extended-corresponding-states theory for natural gas mixtures. Int. J. Thermophysics, 15 (1994), 1261–1269.

Martinez-Ortiz, J. A.; Manley, D. B. (1978): Vapor pressures for the system isobutane–isobutylene–n-butane. J. Chem. Eng. Data, 23 (1978), 165–167.

Marx, V.; Pruß, A.; Wagner, W. (1992): Neue Zustandsgleichungen für R12, R22, R11 und R113. Beschreibung des thermodynamischen Zustandsverhaltens bei Temperaturen bis 525 K und Drücken bis 200 MPa. Fortschr.-Ber. VDI, Reihe 19, Nr. 57, VDI-Verlag, Düsseldorf, 1992.

Maslennikova, V. Ya.; Egorov, A. N.; Tsiklis, D. S. (1977): The compressibility of homogeneous gaseous solutions at ultrahigh pressures. The helium–nitrogen system. Russ. J. Phys. Chem., 51 (1977), 1712–1713.

Maslennikova, V. Ya.; Egorov, A. N.; Tsiklis, D. S. (1979): Compressibility of homogeneous gas mixtures at high pressures. The nitrogen–argon system. Russ. J. Phys. Chem., 53 (1979), 919–920.

Mather, A. E.; Powers, J. E.; Katz, D. L. (1969): The direct determination of the effect of pressure on enthalpy of a mixture of methane and propane. AIChE J., 15 (1969), 111–116.

Mathias, P. M.; Klotz, H. C.; Prausnitz, J. M. (1991): Equation-of-state mixing rules for multicomponent mixtures: the problem of invariance. Fluid Phase Equilibria, 67 (1991), 31–44.

Matschke, D. E.; Thodos, G. (1962): Vapor-liquid equilibria for the ethane–propane system. J. Chem. Eng. Data, 7 (1962), 232–234.

May, E. F.; Miller, R. C.; Shan, Z. (2001): Densities and dew points of vapor mixtures of methane + propane and methane + propane + hexane using a dual-sinker densimeter. J. Chem. Eng. Data, 46 (2001), 1160–1166.

May, E. F.; Miller, R. C.; Goodwin, A. R. H. (2002): Dielectric constants and molar polarizabilities for vapor mixtures of methane + propane and methane + propane + hexane obtained with a radio frequency reentrant cavity. J. Chem. Eng. Data, 47 (2002), 102–105.

Mayrath, J. E.; Magee, J. W. (1989): Measurements of molar heat capacity at constant volume: $c_{V,\mathrm{m}}\{x\mathrm{CH_4} + (1-x)\mathrm{C_2H_6},\ T = 100 \text{ to } 320\ \mathrm{K},\ p \leq 35\ \mathrm{MPa}\}$. J. Chem. Thermodynamics, 21 (1989), 499–513.

McCarty, R. D. (1970): Provisional thermodynamic functions for helium 4 for temperatures from 2 to 1500 K with pressures to 100 MN/m^2 (1000 atmospheres). Natl. Bur. Stand., Report 9762, 1970.

McCarty, R. D. (1982): Mathematical models for the prediction of liquefied-natural-gas densities. J. Chem. Thermodynamics, 14 (1982), 837–854.

McCarty, R. D. (1989): Correlations for the thermophysical properties of carbon monoxide. National Institute of Standards and Technology, Boulder, Colorado, 1989.

McCarty, R. D.; Arp, V. D. (1990): A new wide range equation of state for helium. Adv. Cryog. Eng., 35 (1990), 1465–1475.

McClure, D. W.; Lewis, K. L.; Miller, R. C.; Staveley, L. A. K. (1976): Excess enthalpies and Gibbs free energies for nitrogen + methane at temperatures below the critical point of nitrogen. J. Chem. Thermodynamics, 8 (1976), 785–792.

McCormick, R. H.; Walsh, W. H.; Hetrick, S. S.; Zudkevitch, D. (1963): Relative volatility data for isopentane: n-pentane mixtures. J. Chem. Eng. Data, 8 (1963), 504–508.

McDonald, C. M.; Floudas, C. A. (1995): Global optimization for the phase stability problem. AIChE J., 41 (1995), 1798–1814.

McDonald, C. M.; Floudas, C. A. (1997): GLOPEQ: A new computational tool for the phase and chemical equilibrium problem. Comput. Chem. Eng., 21 (1997), 1–23.

McElroy, P. J.; Dowd, M. K.; Battino, R. (1990): Compression-factor measurements on ethane and (ethane + carbon dioxide) using a direct method. J. Chem. Thermodynamics, 22 (1990), 505–512.

McElroy, P. J.; Fang, Ji; Williamson, C. J. (2001): Second and third virial coefficients for (methane + ethane + carbon dioxide). J. Chem. Thermodynamics, 33 (2001), 155–163.

McTaggart, H. A.; Edwards, E. (1919): Composition of the vapour and liquid phases of the system methane–nitrogen. Proc. Trans. Roy. Soc. Can., 13 (1919), 57–65.

Mehra, V. S.; Thodos, G. (1965): Vapor-liquid equilibrium in the ethane–n-butane system. J. Chem. Eng. Data, 10 (1965), 307–309.

Mehra, V. S.; Thodos, G. (1966): Vapor-liquid equilibrium constants for the ethane–n-butane–n-heptane system at 150°, 200°, and 250° F. J. Chem. Eng. Data, 11 (1966), 365–372.

Mehra, V. S.; Thodos, G. (1968): Vapor-liquid equilibrium constants for the ethane–n-butane–n-heptane system at 300° and 350°F. J. Chem. Eng. Data, 13 (1968), 155–160.

Meldrum, A. H.; Nielsen, R. F. (1955): A study of three-phase equilibria for carbon dioxide–hydrocarbon mixtures. Prod. Mon., 19 (1955), 10, 22–35.

Michels, A.; Nederbragt, G. W. (1939): Isotherms of methane – aethane mixtures at 0°, 25° and 50°C up to 60 atmospheres. Physica, 6 (1939), 656–662.

Michels, A.; Goudeket, M. (1941): Compressibilities of hydrogen between 0°C and 150°C up to 3000 atmospheres. Physica, 8 (1941), 347–352.

Michels, A.; Wassenaar, T. (1949): Isotherms of a nitrogen–hydrogen mixture between 0°C and 150°C up to 340 atmospheres. Appl. Sci. Res., 1A (1949), 258–262.

Michels, A.; de Graaff, W.; Wassenaar, T.; Levelt, J. M. H.; Louwerse, P. (1959): Compressibility isotherms of hydrogen and deuterium at temperatures between −175°C and +150°C (at densities up to 960 Amagat). Physica, 25 (1959), 25–42.

Michelsen, M. L. (1980): Calculation of phase envelopes and critical points for multicomponent mixtures. Fluid Phase Equilibria, 4 (1980), 1–10.

Michelsen, M. L. (1982a): The isothermal flash problem. Part I. Stability. Fluid Phase Equilibria, 9 (1982), 1–19.

Michelsen, M. L. (1982b): The isothermal flash problem. Part II. Phase-split calculation. Fluid Phase Equilibria, 9 (1982), 21–40.

Michelsen, M. L. (1984): Calculation of critical points and phase boundaries in the critical region. Fluid Phase Equilibria, 16 (1984), 57–76.

Michelsen, M. L. (1985): Saturation point calculations. Fluid Phase Equilibria, 23 (1985), 181–192.

Michelsen, M. L. (1986): Some aspects of multiphase calculations. Fluid Phase Equilibria, 30 (1986), 15–29.

Michelsen, M. L.; Mollerup, J. (1986): Partial derivatives of thermodynamic properties. AIChE J., 32 (1986), 1389–1392.

Michelsen, M. L.; Heidemann, R. A. (1988): Calculation of tri-critical points. Fluid Phase Equilibria, 39 (1988), 53–74.

Michelsen, M. L.; Kistenmacher, H. (1990): On composition-dependent interaction coefficients. Fluid Phase Equilibria, 58 (1990), 229–230.

Michelsen, M. L. (1994): A simple method for calculation of approximate phase boundaries. Fluid Phase Equilibria, 98 (1994), 1–11.

Michelsen, M. L. (1999): State function based flash specifications. Fluid Phase Equilibria, 158–160 (1999), 617–626.

Michelsen, M. L. (2001): Computer code including algorithms for stability analysis, and *pT* flash and phase envelope calculations using cubic equations of state. Private communication, Department of Chemical Engineering, Technical University of Denmark (DTU), Lyngby, 2001.

Michelsen, M. L. (2004): Computer code including an algorithm for volume-based phase-envelope calculations using cubic equations of state. Private communication, Department of Chemical Engineering, Technical University of Denmark (DTU), Lyngby, 2004.

Michelsen, M. L.; Mollerup, J. M. (2004): Thermodynamic models: fundamentals & computational aspects. Tie-Line Publications, Holte, 2004.

Michelsen, M. L. (2005): Private communication, Department of Chemical Engineering, Technical University of Denmark (DTU), Lyngby, 2005.

Mihara, S.; Sagara, H. (1977): The compressibility factors of hydrogen–methane, hydrogen–ethane and hydrogen–propane gaseous mixtures. J. Chem. Eng. Japan, 10 (1977), 395–399.

Mihara, S.; Sagara, H.; Arai, Y.; Saito, S. (1977): The compressibility factors of hydrogen–methane, hydrogen–ethane and hydrogen–propane gaseous mixtures. J. Chem. Eng. Japan, 10 (1977), 395–399.

Miksovsky, J.; Wichterle, I. (1975): Vapour-liquid equilibria in the ethane–propane system at high pressures. Collect. Czech. Chem. Commun., 40 (1975), 365–370.

Miller, J. E.; Stroud, L.; Brandt, L. W. (1960): Compressibility of helium–nitrogen mixtures. J. Chem. Eng. Data, 5 (1960), 6–9.

Miller, R. C.; Kidnay, A. J.; Hiza, M. J. (1973): Liquid-vapor equilibria at 112.00 K for systems containing nitrogen, argon, and methane. AIChE J., 19 (1973), 145–151.

Miller, R. C.; Staveley, L. A. K. (1976): Excess enthalpies for some binary liquid mixtures of low-molecular-weight alkanes. Adv. Cryog. Eng., 21 (1976), 493–500.

Miller, R. C.; Kidnay, A. J.; Hiza, M. J. (1977): Liquid + vapor equilibria in methane + ethene and in methane + ethane from 150.00 to 190.00 K. J. Chem. Thermodynamics, 9 (1977), 167–178.

Miniovich, V. M.; Sorina, G. A. (1971): *P*-*V*-*T*-*N* relations in the system ethane–propane. Trudy GIAP, 12 (1971), 125–132.

Miyamoto, H.; Watanabe, K. (2003): Helmholtz-type equations of state for hydrocarbon refrigerant mixtures of propane/n-butane, propane/isobutane, n-butane/isobutane, and propane/n-butane/isobutane. Int. J. Thermophysics, 24 (2003), 1007–1031.

Mohr, P. J.; Taylor, B. N. (2005): CODATA recommended values of the fundamental physical constants: 2002. Rev. Mod. Phys., 77 (2005), 1–107.

Möller, D.; Gammon, B. E.; Marsh, K. N.; Hall, K. R.; Holste, J. C. (1993): Enthalpy-increment measurements from flow calorimetry of CO_2 and of $\{xCO_2+(1-x)C_2H_6\}$ from pressures of 15 MPa to 18 MPa between the temperatures 230 K and 350 K. J. Chem. Thermodynamics, 25 (1993), 1273–1279.

Mollerup, J. M.; Michelsen, M. L. (1992): Calculation of thermodynamic equilibrium properties. Fluid Phase Equilibria, 74 (1992), 1–15.

Mørch, Ø.; Nasrifar, Kh.; Bolland, O.; Solbraa, E.; Fredheim, A. O.; Gjertsen, L. H. (2006): Measurement and modeling of hydrocarbon dew points for five synthetic natural gas mixtures. Fluid Phase Equilibria, 239 (2006), 138–145.

Mraw, S. C.; Hwang, S.-C.; Kobayashi, R. (1978): Vapor-liquid equilibrium of the CH_4–CO_2 system at low temperatures. J. Chem. Eng. Data, 23 (1978), 135–139.

Mu, T.; Liu, Z.; Han, B.; Li, Z.; Zhang, J.; Zhang, X. (2003): Effect of phase behavior, density, and isothermal compressibility on the constant-volume heat capacity of ethane + n-pentane mixed fluids in different phase regions. J. Chem. Thermodynamics, 35 (2003), 2033–2044.

Mueller, W. H.; Leland, T. W. (Jr.); Kobayashi, R. (1961): Volumetric properties of gas mixtures at low temperatures and high pressures by the Burnett method: the hydrogen–methane system. AIChE J., 7 (1961), 267–272.

Nagahama, K.; Konishi, H.; Hoshino, D.; Hirata, M. (1974): Binary vapor-liquid equilibria of carbon dioxide–light hydrocarbons at low temperatures. J. Chem. Eng. Japan, 7 (1974), 323–328.

Nagarajan, N. R.; Cullick, A. S.; Griewank, A. (1991): New strategy for phase equilibrium and critical point calculations by thermodynamic energy analysis. Part I. Stability analysis and flash. Fluid Phase Equilibria, 62 (1991), 191–210.

Narinskii, G. B. (1957): Investigation of the equilibrium of liquid-vapor in the system oxygen–argon. Kislorod, 10 (1957), 3, 9–16.

Narinskii, G. B. (1966): Liquid-vapour equilibrium in the argon–nitrogen system. I. Experimental data and their verification. Russ. J. Phys. Chem. (Engl. Transl.), 40 (1966), 1093–1096; Zh. Fiz. Khim., 40 (1966), 2022–2029.

Narinskii, G. B. (1969): Liquid-vapour equilibrium in the oxygen–argon–nitrogen system. I. Experimental data. Russ. J. Phys. Chem. (Engl. Transl.), 43 (1969), 219–221; Zh. Fiz. Khim., 43 (1969), 408–412.

Nederbragt, G. W. (1938): Gas-liquid equilibria for the system methane–butane. Ind. Eng. Chem., 30 (1938), 587–588.

Nelson, E. E.; Bonnell, W. S. (1943): Solubility of hydrogen in n-butane. Ind. Eng. Chem., 35 (1943), 204–206.

Neumann, A.; Walch, W. (1968): Dampf/Flüssigkeits-Gleichgewicht CO_2/CH_4 im Bereich tiefer Temperaturen und kleiner CO_2-Molenbrüche. Chem.-Ing.-Tech., 40 (1968), 241–244.

Ng, H.-J.; Mather, A. E. (1976): Isothermal Joule-Thomson coefficients in mixtures of methane and carbon dioxide. J. Chem. Eng. Data, 21 (1976), 291–295.

Ng, H.-J.; Mather, A. E. (1977): Measurement and prediction of the enthalpy of mixtures of methane + ethane + nitrogen + carbon dioxide. J. Chem. Thermodynamics, 9 (1977), 1027–1033.

Ng, H.-J.; Mather, A. E. (1978): Enthalpy of gaseous mixtures of methane + ethane + carbon dioxide under pressure. J. Chem. Eng. Data, 23 (1978), 224–227.

Ng, H.-J.; Robinson, D. B.; Leu, A.-D. (1985): Critical phenomena in a mixture of methane, carbon dioxide and hydrogen sulfide. Fluid Phase Equilibria, 19 (1985), 273–286.

Nichita, D. V.; Gomez, S.; Luna, E. (2002a): Phase stability analysis with cubic equations of state by using a global optimization method. Fluid Phase Equilibria, 194–197 (2002), 411–437.

Nichita, D. V.; Gomez, S.; Luna, E. (2002b): Multiphase equilibria calculation by direct minimization of Gibbs free energy with a global optimization method. Comput. Chem. Eng., 26 (2002), 1703–1724.

Nichita, D. V. (2005): Calculation of critical points using a reduction method. Fluid Phase Equilibria, 228–229 (2005), 223–231.

Nichols, W. B.; Reamer, H. H.; Sage, B. H. (1957): Volumetric and phase behavior in the hydrogen–n-hexane system. AIChE J., 3 (1957), 262–267.

Niesen, V. G.; Rainwater, J. C. (1990): Critical locus, (vapor + liquid) equilibria, and coexisting densities of (carbon dioxide + propane) at temperatures from 311 K to 361 K. J. Chem. Thermodynamics, 22 (1990), 777–795.

Nowak, P.; Kleinrahm, R.; Wagner, W. (1995): Supplementary measurements of the thermal properties of methane. Unpublished work, Lehrstuhl für Thermodynamik, Ruhr-Universität Bochum, 1995.

Nunes da Ponte, M.; Streett, W. B.; Staveley, L. A. K. (1978): An experimental study of the equation of state of liquid mixtures of nitrogen and methane, and the effect of pressure on their excess thermodynamic functions. J. Chem. Thermodynamics, 10 (1978), 151–168.

Nysewander, C. N.; Sage, B. H.; Lacey, W. N. (1940): Phase equilibria in hydrocarbon systems. The propane–n-butane system in the critical region. Ind. Eng. Chem., 32 (1940), 118–123.

Ohgaki, K.; Katayama, T. (1976): Isothermal vapor-liquid equilibrium data for binary systems containing carbon dioxide at high pressures: methanol–carbon dioxide, n-hexane–carbon dioxide, and benzene–carbon dioxide systems. J. Chem. Eng. Data, 21 (1976), 53–55.

Ohgaki, K.; Sano, F.; Katayama, T. (1976): Isothermal vapor-liquid equilibrium data for binary systems containing ethane at high pressures. J. Chem. Eng. Data, 21 (1976), 55–58.

Ohgaki, K.; Katayama, T. (1977): Isothermal vapor-liquid equilibrium data for the ethane–carbon dioxide system at high pressures. Fluid Phase Equilibria, 1 (1977), 27–32.

Olds, R. H.; Sage, B. H.; Lacey, W. N. (1942): Methane–isobutane system. Ind. Eng. Chem., 34 (1942), 1008–1013.

Olds, R. H.; Reamer, H. H.; Sage, B. H.; Lacey, W. N. (1949): Phase equilibria in hydrocarbon systems. The n-butane–carbon dioxide system. Ind. Eng. Chem., 41 (1949), 475–482.

Orbey, H.; Sandler, S. I. (1995): On the combination of equation of state and excess free energy models. Fluid Phase Equilibria, 111 (1995), 53–70.

Ott, J. B.; Brown, P. R.; Moore, J. D.; Lewellen, A. C. (1997): Excess molar enthalpies and excess molar volumes for (propane + ethane) over the temperature range from 273.15 K to 373.15 K and the pressure range from 5 MPa to 15 MPa. J. Chem. Thermodynamics, 29 (1997), 149–178.

Owren, G.; Grini, P. G.; Maehlum, H. S.; Jorstad, O. (1996): Enthalpy measurements on natural gas. Report to GERG WG 1.3, 1996.

Palavra, A. M. (1979): Effect of pressure and temperature on excess properties in the system argon–nitrogen. Master's Thesis, Instituto Superior Tecnico Universidade Tecnica De Lisboa, 1979.

Pan, W. P.; Mady, M. H.; Miller, R. C. (1975): Dielectric constants and Clausius-Mossotti functions for simple liquid mixtures: systems containing nitrogen, argon and light hydrocarbons. AIChE J., 21 (1975), 283–289.

Panagiotopoulos, A. Z.; Reid, R. C. (1986): New mixing rule for cubic equations of state for highly polar, asymmetric systems. American Chemical Society, Symp. Ser., 300 (1986), 571–582.

Parrish, W. R.; Hiza, M. J. (1973): Liquid-vapor equilibria in the nitrogen–methane system between 95 and 120 K. Cryogenic Engineering Conference, August 8–10, Atlanta, Georgia, Paper K-9, 1973. Data also published by Parrish and Hiza (1974).

Parrish, W. R.; Hiza, M. J. (1974): Liquid-vapor equilibria in the nitrogen–methane system between 95 and 120 K. Adv. Cryog. Eng., 19 (1974), 300–308.

Parrish, W. R.; Steward, W. G. (1975): Vapor-liquid equilibria data for helium–carbon monoxide and helium–nitrous oxide systems. J. Chem. Eng. Data, 20 (1975), 412–416.

Parrish, W. R. (1984): Compressed liquid densities of ethane–propane mixtures between 10 and 49°C at pressures up to 9.6 MPa. Fluid Phase Equilibria, 18 (1984), 279–297.

Parrish, W. R. (1986): Compressed liquid densities of propane–normal butane mixtures between 10 and 60°C at pressures up to 9.6 MPa. Fluid Phase Equilibria, 25 (1986), 65–90.

Patel, M. R.; Eubank, P. T. (1988): Experimental densities and derived thermodynamic properties for carbon dioxide–water mixtures. J. Chem. Eng. Data, 33 (1988), 185–193.

Pecar, D.; Dolecek, V. (2003): Isothermal compressibilities and isobaric expansibilities of pentane, hexane, heptane and their binary and ternary mixtures from density measurements. Fluid Phase Equilibria, 211 (2003), 109–127.

Pedersen, K. S.; Michelsen, M. L.; Fredheim, A. O. (1996): Phase equilibrium calculations for unprocessed well streams containing hydrate inhibitors. Fluid Phase Equilibria, 126 (1996), 13–28.

Peng, D.-Y.; Robinson, D. B. (1976): A new two-constant equation of state. Ind. Eng. Chem., Fundam., 15 (1976), 59–64.

Peter, S.; Reinhartz, K. (1960): Das Phasengleichgewicht in den Systemen H_2–n-Heptan, H_2–Methylcyclohexan und H_2–2,2,4-Trimethylpentan bei höheren Drucken und Temperaturen. Z. physik. Chem. Neue Folge, 24 (1960), 103–118.

Plantier, F.; Danesh, A.; Sohrabi, M.; Daridon, J.-L.; Gozalpour, F.; Todd, A. C. (2005): Measurements of the speed of sound for mixtures of methane + butane with a particular focus on the critical state. J. Chem. Eng. Data, 50 (2005), 673–676.

Pool, R. A. H.; Saville, G.; Herrington, T. M.; Shields, B. D. C.; Staveley, L. A. K. (1962): Some excess thermodynamic functions for the liquid systems argon + oxygen, argon + nitrogen, nitrogen + oxygen, nitrogen + carbon monoxide, and argon + carbon monoxide. Trans. Faraday Soc., 58 (1962), 1692–1704.

Poon, D. P. L.; Lu, B. C.-Y. (1974): Phase equilibria for systems containing nitrogen, methane and propane. Adv. Cryog. Eng., 19 (1974), 292–299.

Poston, R. S.; McKetta, J. J. (1966a): Vapor-liquid equilibrium in the methane–n-hexane system. J. Chem. Eng. Data, 11 (1966), 362–363.

Poston, R. S.; McKetta, J. J. (1966b): Vapor-liquid equilibrium in the n-hexane–nitrogen system. J. Chem. Eng. Data, 11 (1966), 364–365.

Powers, J. E.; Furtado, A. W.; Kant, R.; Kwan, A. (1979): Smoothed experimental enthalpy data for four mixtures: three methane–ethane binary mixtures and a ternary mixture with propane. J. Chem. Eng. Data, 24 (1979), 46–67.

Pozo de Fernandez, M. E.; Zollweg, J. A.; Streett, W. B. (1989): Vapor-liquid equilibrium in the binary system carbon dioxide + n-butane. J. Chem. Eng. Data, 34 (1989), 324–328.

Prausnitz, J. M.; Chueh, P. L. (1968): Computer calculations for high-pressure vapor-liquid equilibria. Prentice-Hall, Englewood Cliffs, New Jersey, 1968.

Press, W. H.; Flannery, B. P.; Teukolsky, S. A.; Vetterling, W. T. (1986): Numerical recipes. The art of scientific computing. Cambridge University Press, Cambridge, 1986.

Price, A. R. (1957): Ph.D. Dissertation, Rice Inst., Houston, Tex., 1957. Data published by Matschke and Thodos (1962).

Price, A. R.; Kobayashi, R. (1959): Low temperature vapor-liquid equilibrium in light hydrocarbon mixtures: methane–ethane–propane system. J. Chem. Eng. Data, 4 (1959), 40–52.

Provine, J. A.; Canfield, F. B. (1971): Isotherms for the He–Ar system at −130, −115, and −90°C up to 700 atm. Physica, 52 (1971), 79–91.

Raabe, G.; Janisch, J.; Koehler, J. (2001): Experimental studies of phase equilibria in mixtures relevant for the description of natural gases. Fluid Phase Equilibria, 185 (2001), 199–208.

Raabe, G.; Köhler, J. (2004): Phase equilibria in the system nitrogen–ethane and their prediction using cubic equations of state with different types of mixing rules. Fluid Phase Equilibria, 222–223 (2004), 3–9.

Rachford, H. H. (Jr.); Rice, J. D. (1952): Procedure for use of electronic digital computers in calculating flash vaporization hydrocarbon equilibrium. Trans. Am. Inst. Min. Metal. Eng., 195 (1952), 327–328.

Ramos-Estrada, M.; Iglesias-Silva, G. A.; Hall, K. R. (2006): Experimental measurements and prediction of liquid densities for n-alkane mixtures. J. Chem. Thermodynamics, 38 (2006), 337–347.

Rasulov, S. M.; Rasulov, A. R. (2001): The *P-V-T-x* properties and liquid-liquid and liquid-vapor phase equilibria of n-hexane–water binary system. High Temperature, 39 (2001), 826–834.

Reamer, H. H.; Olds, R. H.; Sage, B. H.; Lacey, W. N. (1944): Phase equilibria in hydrocarbon systems. Methane–carbon dioxide system in the gaseous region. Ind. Eng. Chem., 36 (1944), 88–90.

Reamer, H. H.; Olds, R. H.; Sage, B. H.; Lacey, W. N. (1945): Phase equilibria in hydrocarbon systems. Volumetric behavior of ethane–carbon dioxide system. Ind. Eng. Chem., 37 (1945), 688–691.

Reamer, H. H.; Korpi, K. J.; Sage, B. H.; Lacey, W. N. (1947): Phase equilibria in hydrocarbon systems. Volumetric behavior of methane–n-butane system at higher pressures. Ind. Eng. Chem., 39 (1947), 206–209.

Reamer, H. H.; Sage, B. H.; Lacey, W. N. (1950): Phase equilibria in hydrocarbon systems. Volumetric and phase behavior of the methane–propane system. Ind. Eng. Chem., 42 (1950), 534–539.

Reamer, H. H.; Sage, B. H.; Lacey, W. N. (1951): Phase equilibria in hydrocarbon systems. Volumetric and phase behavior of the propane–carbon dioxide system. Ind. Eng. Chem., 43 (1951), 2515–2520.

Reamer, H. H.; Selleck, F. T.; Sage, B. H.; Lacey, W. N. (1952a): Phase equilibria in hydrocarbon systems. Volumetric behavior of the nitrogen–ethane system. Ind. Eng. Chem., 44 (1952), 198–201.

Reamer, H. H.; Sage, B. H.; Lacey, W. N. (1952b): Phase equilibria in hydrocarbon systems. n-Butane–water system in the two-phase region. Ind. Eng. Chem., 44 (1952), 609–615.

Reamer, H. H.; Sage, B. H.; Lacey, W. N. (1956): Volumetric and phase behavior of the methane–n-heptane system. Chem. Eng. Data Ser., 1 (1956), 1, 29–42.

Reamer, H. H.; Sage, B. H.; Lacey, W. N. (1960): Phase equilibria in hydrocarbon systems. Volumetric and phase behavior of ethane–n-pentane system. J. Chem. Eng. Data, 5 (1960), 44–50.

Rhodes, H. L.; DeVaney, W. E.; Tully, P. C. (1971): Phase equilibria data for helium–methane in the vapor-liquid and fluid-fluid region. J. Chem. Eng. Data, 16 (1971), 19–23.

Ricardo, A. A.; Barreiros, S. F.; Nunes da Ponte, M.; Albuquerque, G. M. N.; Calado, J. C. G. (1992): (p, V_m, T) of ($0.476Ar + 0.524N_2$)(l) and the calculation of thermodynamic properties of liquid air. J. Chem. Thermodynamics, 24 (1992), 1281–1291.

Rigas, T. J.; Mason, D. F.; Thodos, G. (1958): Vapor-liquid equilibria. Microsampling technique applied to a new variable-volume cell. Ind. Eng. Chem., 50 (1958), 1297–1300.

Rivkin, S. L. (1975): Experimental investigation of the compressibility of gases. Nitrogen and nitrogen-and-carbon dioxide mixtures. Thermophys. Prop. Matter Substances, 8 (1975), 190–209.

Roberts, L. R.; McKetta, J. J. (1961): Vapor-liquid equilibrium in the n-butane–nitrogen system. AIChE J., 7 (1961), 173–174.

Roberts, L. R.; Wang, R. H.; Azarnoosh, A.; McKetta, J. J. (1962): Methane–n-butane system in the two-phase region. J. Chem. Eng. Data, 7 (1962), 484–485.

Robinson, D. B.; Kalra, H. (1974): The phase behavior of selected hydrocarbon–non hydrocarbon systems. Gas Process. Assoc., Proc. Annu. Conv., 53 (1974), 14–29.

Robinson, R. L. (Jr.); Jacoby, R. H. (1965): Better Compressibility Factors. Hydrocarbon Process. Pet. Refiner, 44 (1965), 4, 141–145.

Rodewald, N. C.; Davis, J. A.; Kurata, F. (1964): The heterogeneous phase behavior of the helium–nitrogen system. AIChE J., 10 (1964), 937–943.

Rodosevich, J. B.; Miller, R. C. (1973): Experimental liquid mixture densities for testing and improving correlations for liquefied natural gas. AIChE J., 19 (1973), 729–735.

Rodrigues, A. B. J.; McCaffrey, D. S. (Jr.); Kohn, J. P. (1968): Heterogeneous phase and volumetric equilibrium in the ethane–n-octane system. J. Chem. Eng. Data, 13 (1968), 164–168.

Roe, D. R. (1972): Thermodynamic properties of gases and gas mixtures at low temperatures and high pressures. Ph.D. Thesis, Imperial College, London, 1972.

Ruhrgas (1989): See Jaeschke *et al.* (1989) and Jaeschke *et al.* (1997).

Ruhrgas (1990): See Jaeschke and Humphreys (1991) and Jaeschke *et al.* (1997).

Ruhrgas (1993): See Jaeschke *et al.* (1997).

Ruhrgas (1994): See Jaeschke *et al.* (1997).

Ruhrgas (1999): Private communication to R. Klimeck by M. Jaeschke and P. Schley, Ruhrgas AG, Essen, 1999.

Sagara, H.; Arai, Y.; Saito, S. (1972): Vapor-liquid equilibria of binary and ternary systems containing hydrogen and light hydrocarbons. J. Chem. Eng. Japan, 5 (1972), 339–348.

Sage, B. H.; Lacey, W. N.; Schaafsma, J. G. (1934): Phase equilibria in hydrocarbon systems. II. Methane–propane system. Ind. Eng. Chem., 26 (1934), 214–217.

Sage, B. H.; Webster, D. C.; Lacey, W. N. (1936): Phase equilibria in hydrocarbon systems. XVI. Solubility of methane in four light hydrocarbons. Ind. Eng. Chem., 28 (1936), 1045–1047.

Sage, B. H.; Lacey, W. N. (1939): Phase equilibria in hydrocarbon systems. The methane–ethane system in the gaseous region. Ind. Eng. Chem., 31 (1939), 1497–1509.

Sage, B. H.; Lacey, W. N. (1940): Phase equilibria in hydrocarbon systems. Propane–n-pentane system. Ind. Eng. Chem., 32 (1940), 992–996.

Sage, B. H.; Budenholzer, R. A.; Lacey, W. N. (1940a): Phase equilibria in hydrocarbon systems. Methane–n-butane system in the gaseous and liquid regions. Ind. Eng. Chem., 32 (1940), 1262–1277.

Sage, B. H.; Hicks, B. L.; Lacey, W. N. (1940b): Phase equilibria in hydrocarbon systems. The methane–n-butane system in the two-phase region. Ind. Eng. Chem., 32 (1940), 1085–1092.

Sage, B. H.; Reamer, H. H.; Olds, R. H.; Lacey, W. N. (1942): Phase equilibria in hydrocarbon systems. Volumetric and phase behavior of methane–n-pentane system. Ind. Eng. Chem., 34 (1942), 1108–1117.

Sage, B. H.; Olds, R. H.; Lacey, W. N. (1948): Two gaseous mixtures containing hydrogen and nitrogen. Thermodynamic properties. Ind. Eng. Chem., 40 (1948), 1453–1459.

Sanchez, M.; Coll, R. (1978): System propane–water at high pressures and temperatures. I. Region of two phases. An. Quim., 74 (1978), 11, 1329–1335.

Sarashina, E.; Arai, Y.; Saito, S. (1971): The *P-V-T-X* relation for the carbon dioxide–argon system. J. Chem. Eng. Japan, 4 (1971), 379–381.

Sauer, R. N. (1959): Vapor-liquid equilibria in the nitrogen–methane–n-butane system. Ph.D. Thesis, Tex. Univ., Austin, 1959.

Sault, R. A. (1952): Physical-chemical properties of methane–nitrogen mixtures. M.S. Thesis, Illinois Institute of Technology, Chicago, Ill., 1952. See also Bloomer and Parent (1952).

Schamp, H. W. (Jr.); Mason, E. A.; Richardson, A. C. B.; Altman, A. (1958): Compressibility and Intermolecular forces in gases: methane. Phys. Fluids, 1 (1958), 329–337.

Schilling, G. (2003): Private communication, Lehrstuhl für Thermodynamik, Ruhr-Universität Bochum, 2003.

Schindler, D. L.; Swift, G. W.; Kurata, F. (1966): More low temperature V-L design data. Hydrocarbon Process. Pet. Refiner, 45 (1966), 11, 205–210.

Schmidt, R.; Wagner, W. (1985): A new form of the equation of state for pure substances and its application to oxygen. Fluid Phase Equilibria, 19 (1985), 175–200.

Schoch, E. P.; Hoffmann, A. E.; Mayfield, F. D. (1941): Solubility of methane in n-hexane. Ind. Eng. Chem., 33 (1941), 688–691.

Scott, G. A. (1929): The isotherms of hydrogen, carbon monoxide and their mixtures. Proc. R. Soc. London, Ser. A, 125 (1929), 330–344.

Seitz, J. C.; Blencoe, J. G. (1996): Volumetric properties for $\{(1-x)CO_2 + xCH_4\}$, $\{(1-x)CO_2 + xN_2\}$, and $\{(1-x)CH_4 + xN_2\}$ at the pressures (19.94, 29.94, 39.94, 59.93, 79.93, and 99.93) MPa and the temperature 673.15 K. J. Chem. Thermodynamics, 28 (1996), 1207–1213.

Seitz, J. C.; Blencoe, J. G.; Bodnar, R. J. (1996a): Volumetric properties for $\{(1-x)CO_2 + xCH_4\}$, $\{(1-x)CO_2 + xN_2\}$, and $\{(1-x)CH_4 + xN_2\}$ at the pressures (9.94, 19.94, 29.94, 39.94, 59.93, 79.93, and 99.93) MPa and temperatures (323.15, 373.15, 473.15, and 573.15) K. J. Chem. Thermodynamics, 28 (1996), 521–538.

Seitz, J. C.; Blencoe, J. G.; Bodnar, R. J. (1996b): Volumetric properties for $\{x_1CO_2+x_2CH_4+(1-x_1-x_2)N_2\}$ at the pressures (19.94, 39.94, 59.93, and 99.93) MPa and temperatures (323.15, 373.15, 473.15, and 573.15) K. J. Chem. Thermodynamics, 28 (1996), 539–550.

Setzmann, U.; Wagner, W. (1989): A new method for optimizing the structure of thermodynamic correlation equations. Int. J. Thermophysics, 10 (1989), 1103–1126.

Setzmann, U.; Wagner, W. (1991): A new equation of state and tables of thermodynamic properties for methane covering the range from the melting line to 625 K at pressures up to 1000 MPa. J. Phys. Chem. Ref. Data, 20 (1991), 1061–1155.

Shana'a, M. Y.; Canfield, F. B. (1968): Liquid density and excess volume of light hydrocarbon mixtures at −165°C. Trans. Faraday Soc., 64 (1968), 2281–2286.

Shatskaya, L. V.; Zhirnova, N. A. (1976): Liquid-vapour phase equilibria in binary systems at low temperatures. I. Argon–methane system. Russ. J. Phys. Chem., 50 (1976), 298.

Sherman, G. J.; Magee, J. W.; Ely, J. F. (1989): *PVT* relationships in a carbon dioxide-rich mixture with ethane. Int. J. Thermophysics, 10 (1989), 47–59.

Shibata, S. K.; Sandler, S. I. (1989): High-pressure vapor-liquid equilibria involving mixtures of nitrogen, carbon dioxide, and n-butane. J. Chem. Eng. Data, 34 (1989), 291–298.

Shim, J.; Kohn, J. P. (1962): Multiphase and volumetric equilibria of methane–n-hexane binary system at temperatures between −110° and 150°C. J. Chem. Eng. Data, 7 (1962), 3–8.

Simon, R.; Fesmire, C. J.; Dicharry, R. M.; Vorhis, F. H. (1977): Compressibility factors for carbon dioxide–methane mixtures. J. Pet. Technol., 29 (1977), 81–85.

Sinor, J. E.; Kurata, F. (1966): Solubility of helium in liquid argon, oxygen, and carbon monoxide. J. Chem. Eng. Data, 11 (1966), 537–539.

Sinor, J. E.; Schindler, D. L.; Kurata, F. (1966): Vapor-liquid phase behavior of the helium–methane system. AIChE J., 12 (1966), 353–357.

Sivaraman, A.; Gammon, B. E. (1986): Speed of sound measurements in natural gas fluids. Gas Research Institute, Report 86/0043, 1986.

Skripka, V. G.; Barsuk, S. D.; Nikitina, I. E.; Gubkina, G. F.; Benyaminovich, O. A. (1969): Investigation of liquid-vapor equilibrium in the nitrogen–n-butane system. Gazov. Promst., 14 (1969), 4, 41–45.

Skripka, V. G.; Nikitina, I. E.; Zhdanovich, L. A.; Sirotin, A. G.; Benyaminovich, O. A. (1970): Liquid-vapor phase equilibrium at low temperatures in binary systems. Components produced from natural gas. Gazov. Promst., 15 (1970), 12, 35–36.

Smukala, J.; Span, R.; Wagner, W. (2000): New equation of state for ethylene covering the fluid region for temperatures from the melting line to 450 K at pressures up to 300 MPa. J. Phys. Chem. Ref. Data, 29 (2000), 1053–1121.

Smyth, C. P.; Engel, E. W. (1929): Molecular orientation and the partial vapor pressures of binary mixtures. I. Systems composed of normal liquids. J. Am. Chem. Soc., 51 (1929), 2646–2661.

SNAM (1989): See Jaeschke *et al.* (1989).

Sneed, C. M.; Sonntag, R. E.; Van Wylen, G. J. (1968): Helium–hydrogen liquid-vapor equilibrium to 100 atm. J. Chem. Phys., 49 (1968), 2410–2414.

Soave, G. S. (1995): A noncubic equation of state for the treatment of hydrocarbon fluids at reservoir conditions. Ind. Eng. Chem. Res., 34 (1995), 3981–3994.

Solbrig, C. W.; Ellington, R. T. (1963): The *P-V-T* behavior of selected hydrogen–methane and hydrogen–ethane mixtures. Chem. Eng. Prog., Symp. Ser., 59 (1963), 44, 127–136.

Somait, F. A.; Kidnay, A. J. (1978): Liquid-vapor equilibria at 270.00 K for systems containing nitrogen, methane, and carbon dioxide. J. Chem. Eng. Data, 23 (1978), 301–305.

Sonntag, R. E.; Van Wylen, G. J.; Crain, R. W. (Jr.) (1964): Liquid-vapor equilibrium in the system equilibrium hydrogen–helium. J. Chem. Phys., 41 (1964), 2399–2402.

Sood, S. K.; Haselden, G. G. (1972): Measured enthalpy changes for a simulated natural gas mixture and their prediction using a modified BWR equation. AIChE J., 18 (1972), 999–1004.

Span, R.; Wagner, W. (1996): A new equation of state for carbon dioxide covering the fluid region from the triple-point temperature to 1100 K at pressures up to 800 MPa. J. Phys. Chem. Ref. Data, 25 (1996), 1509–1596.

Span, R.; Wagner, W. (1997): On the extrapolation behavior of empirical equations of state. Int. J. Thermophysics, 18 (1997), 1415–1443.

Span, R.; Collmann, H.-J.; Wagner, W. (1998): Simultaneous optimization as a method to establish generalized functional forms for empirical equations of state. Int. J. Thermophysics, 19 (1998), 491–500.

Span, R. (2000a): A simultaneously optimised equation of state for isopentane. Private communication, Lehrstuhl für Thermodynamik, Ruhr-Universität Bochum, 2000.

Span, R. (2000b): Multiparameter equations of state. An accurate source of thermodynamic property data. Springer, Berlin, 2000.

Span, R.; Lemmon, E. W.; Jacobsen, R. T; Wagner, W.; Yokozeki, A. (2000): A reference equation of state for the thermodynamic properties of nitrogen for temperatures from 63.151 to 1000 K and pressures to 2200 MPa. J. Phys. Chem. Ref. Data, 29 (2000), 1361–1433.

Span, R.; Wagner, W.; Lemmon, E. W.; Jacobsen, R. T (2001): Multiparameter equations of state – recent trends and future challenges. Fluid Phase Equilibria, 183–184 (2001), 1–20.

Span, R.; Wagner, W. (2003a): Equations of state for technical applications. I. Simultaneously optimized functional forms for nonpolar and polar fluids. Int. J. Thermophysics, 24 (2003), 1–39.

Span, R.; Wagner, W. (2003b): Equations of state for technical applications. II. Results for nonpolar fluids. Int. J. Thermophysics, 24 (2003), 41–109.

Spano, J. O.; Heck, C. K.; Barrick, P. L. (1968): Liquid-vapor equilibria of the hydrogen–carbon dioxide system. J. Chem. Eng. Data, 13 (1968), 168–171.

Sprow, F. B.; Prausnitz, J. M. (1966): Vapor-liquid equilibria for five cryogenic mixtures. AIChE J., 12 (1966), 780–784.

Srivastan, S.; Darwish, N. A.; Gasem, K. A. M.; Robinson, R. L. (Jr.) (1992): Solubility of methane in hexane, decane, and dodecane at temperatures from 311 to 423 K and pressures to 10.4 MPa. J. Chem. Eng. Data, 37 (1992), 516–520.

Starling, K. E. (1973): Fluid thermodynamic properties for light petroleum systems. Gulf Publishing, Houston, Texas, 1973.

Starling, K. E.; Savidge, J. L. (1992): Compressibility factors of natural gas and other related hydrocarbon gases. American Gas Association, Transmission Measurement Committee Report No. 8, Second Edition, 1992.

Steckel, F. A.; Zinn, N. M. (1939): Investigation of the liquid-vapor phase behavior of the system methane–nitrogen–hydrogen (in Russian). Zurnal Chimiceskoj Promyslennosti, 16 (1939), 24–28.

Stephan, K.; Hildwein, H. (1987): Recommended data of selected compounds and binary mixtures. DECHEMA, Chemistry Data Series, Vol. IV, Parts 1 and 2, Frankfurt, 1987.

Straty, G. C. (1974): Velocity of sound in dense fluid methane. Cryogenics, 14 (1974), 367–370.

Straty, G. C.; Diller, D. E. (1980): (p, V, T) of compressed and liquefied (nitrogen + methane). J. Chem. Thermodynamics, 12 (1980), 937–953.

Streett, W. B.; Sonntag, R. E.; Van Wylen, G. J. (1964): Liquid-vapor equilibrium in the system normal hydrogen–helium. J. Chem. Phys., 40 (1964), 1390–1395.

Streett, W. B. (1967): Gas-liquid and fluid-fluid phase separation in the system helium–nitrogen near the critical temperature of nitrogen. Chem. Eng. Prog., Symp. Ser., 63 (1967), 81, 37–42.

Streett, W. B. (1969): Gas-liquid and fluid-fluid phase separation in the system helium + argon at high pressures. Trans. Faraday Soc., 65 (1969), 696–702.

Streett, W. B.; Hill, J. L. E. (1971): Phase equilibria in fluid mixtures at high pressures: the helium + argon system. Trans. Faraday Soc., 37 (1971), 622–630.

Stryjek, R.; Chappelear, P. S.; Kobayashi, R. (1974a): Low-temperature vapor-liquid equilibria of nitrogen–methane system. J. Chem. Eng. Data, 19 (1974), 334–339.

Stryjek, R.; Chappelear, P. S.; Kobayashi, R. (1974b): Low-temperature vapor-liquid equilibria of nitrogen–ethane system. J. Chem. Eng. Data, 19 (1974), 340–343.

Sun, A. C.; Seider, W. D. (1995): Homotopy-continuation method for stability analysis in the global minimization of the Gibbs free energy. Fluid Phase Equilibria, 103 (1995), 213–249.

Takenouchi, S.; Kennedy, G. C. (1964): The binary system H_2O–CO_2 at high temperatures and pressures. Am. J. Sci., 262 (1964), 1055–1074.

Tegeler, Ch.; Span, R.; Wagner, W. (1999): A new equation of state for argon covering the fluid region for temperatures from the melting line to 700 K at pressures up to 1000 MPa. J. Phys. Chem. Ref. Data, 28 (1999), 779–850.

Thorogood, R. M.; Haselden, G. G. (1963): The determination of equilibrium data for the oxygen–nitrogen system at high oxygen concentrations. Br. Chem. Eng., 8 (1963), 623–625.

Thorpe, P. L. (1968): Liquid-vapour equilibrium of the system nitrogen + argon at pressures up to 10 atm. Trans. Faraday Soc., 64 (1968), 2273–2280.

Tian, Y.; Zhao, X.; Chen, L.; Zhu, H.; Fu, H. (2004): High pressure phase equilibria and critical phenomena of water + iso-butane and water + n-butane systems to 695 K and 306 MPa. J. of Supercritical Fluids, 30 (2004), 145–153.

Tillner-Roth, R. (1993): Die thermodynamischen Eigenschaften von R152a, R134a und ihren Gemischen. Messungen und Fundamentalgleichungen. Forschungsberichte des DKV, Nr. 41, 1993.

Tillner-Roth, R. (1998): Fundamental equations of state. Berichte aus der Thermodynamik, Shaker Verlag, Aachen, 1998.

Tillner-Roth, R.; Friend, D. G. (1998): A Helmholtz free energy formulation of the thermodynamic properties of the mixture {water + ammonia}. J. Phys. Chem. Ref. Data, 27 (1998), 63–96.

Tillner-Roth, R.; Li, J.; Yokozeki, A.; Sato, H.; Watanabe, K. (1998): Thermodynamic properties of pure and blended hydrofluorocarbon (HFC) refrigerants. Japan Society of Refrigerating and Air Conditioning Engineers, Tokyo, 1998. See also Tillner-Roth (1998).

Tochigi, K.; Hasegawa, K.; Asano, N.; Kojima, K. (1998): Vapor-liquid equilibria for the carbon dioxide + pentane and carbon dioxide + toluene systems. J. Chem. Eng. Data, 43 (1998), 954–956.

Tödheide, K.; Franck, E. U. (1963): Das Zweiphasengebiet und die kritische Kurve im System Kohlendioxid–Wasser bis zu Drucken von 3500 bar. Z. physik. Chem. Neue Folge, 37 (1963), 387–401.

Torotscheschnikow, N. (1937): Isotherms and isobars of the nitrogen–carbon monoxide system. Tech. Phys. of the USSR, 4 (1937), 365–369.

Townend, D. T. A.; Bhatt, L. A. (1931): Isotherms of hydrogen, carbon monoxide and their mixtures. Proc. R. Soc. London, Ser. A, 134 (1931), 502–512.

Townsend, P. W. (1956): Pressure-volume-temperature relationships of binary gaseous mixtures. Ph.D. Dissertation, Faculty of Pure Science, Columbia University, New York, 1956.

Trappehl, G. (1987): Experimentelle Untersuchung der Dampf-Flüssigkeits-Phasengleichgewichte und kalorischen Eigenschaften bei tiefen Temperaturen und hohen Drücken an Stoffgemischen bestehend aus N_2, CH_4, C_2H_6, C_3H_8 und CO_2. Dissertation, Technische Universität Berlin, 1987.

Trappeniers, N. J.; Wassenaar, T.; Abels, J. C. (1979): Isotherms and thermodynamic properties of methane at temperatures between 0° and 150°C and at densities up to 570 Amagat. Physica, A, 98 (1979), 289–297.

Trusler, J. P. M.; Zarari, M. (1992): The speed of sound and derived thermodynamic properties of methane at temperatures between 275 K and 375 K and pressures up to 10 MPa. J. Chem. Thermodynamics, 24 (1992), 973–991.

Trusler, J. P. M.; Wakeham, W. A.; Zarari, M. P. (1993): The speed of sound in a gaseous mixture of methane and propane. High Temp. – High Pressures, 25 (1993), 291–296.

Trusler, J. P. M. (1994): The speed of sound in $(0.8CH_4 + 0.2C_2H_6)(g)$ at temperatures between 200 K and 375 K and amount-of-substance densities up to 5 $mol \cdot dm^{-3}$. J. Chem. Thermodynamics, 26 (1994), 751–763.

Trusler, J. P. M.; Zarari, M. P. (1995): Second and third acoustic virial coefficients of methane at temperatures between 125 K and 375 K. J. Chem. Thermodynamics, 27 (1995), 771–778.

Trusler, J. P. M.; Costa Gomes, M. F. (1996): The speed of sound in methane and in two methane-rich gas mixtures. Report to GERG WG 1.3, Department of Chemical Engineering and Chemical Technology, Imperial College, London, 1996.

Trusler, J. P. M.; Wakeham, W. A.; Zarari, M. P. (1996): Second and third interaction virial coefficients of the (methane + propane) system determined from the speed of sound. Int. J. Thermophysics, 17 (1996), 35–42.

Trusler, J. P. M. (2000): Speeds of sound in the gas mixtures: $\{(1-x)CH_4 + xN_2\}$ with $x = 0.1$ or 0.2 and $\{(1-x)C_2H_6 + xN_2\}$ with $x = 0.3$ or 0.7. Report to GERG WG 1.34, Department of Chemical Engineering and Chemical Technology, Imperial College, London, 2000. Data for methane–nitrogen published by Estela-Uribe *et al.* (2006).

Trust, D. B.; Kurata, F. (1971a): Vapor-liquid and liquid-liquid vapor phase behavior of the carbon monoxide–propane and the carbon monoxide–ethane systems. AIChE J., 17 (1971), 415–419.

Trust, D. B.; Kurata, F. (1971b): Vapor-liquid phase behavior of the hydrogen–propane and hydrogen–carbon monoxide–propane systems. AIChE J., 17 (1971), 86–91.

Tsiklis, D. S. (1946): Heterogeneous equilibria in binary systems (in Russian). Zh. Fiz. Khim., 20 (1946), 181–188.

Tsiklis, D. S.; Linshits, L. R.; Rodkina, I. B. (1974a): Study of the volume of gas mixtures by Burnett's method. I. Molar volumes and second virial coefficients of mixtures of carbon dioxide and helium at 100°C. Russ. J. Phys. Chem., 48 (1974), 906–908.

Tsiklis, D. S.; Linshits, L. R.; Rodkina, I. B. (1974b): Study of the volume of gas mixtures by Burnett's method. II. Molar volumes and second virial coefficients of mixtures of carbon dioxide and helium at 150°C. Russ. J. Phys. Chem., 48 (1974), 908–909.

Tsuji, T.; Honda, S.; Hiaki, T.; Hongo, M. (1998): Measurement of the *P-V-T* relationship for carbon dioxide + n-butane and carbon dioxide + i-butane in the vicinity of the critical point. J. of Supercritical Fluids, 13 (1998), 15–21.

Tsuji, T.; Tanaka, S.; Hiaki, T. (2004): *P-V-T-x* relationship for $CO_2 + C_4H_{10}$ and $CO_2 + iC_4H_{10}$ binary gas mixtures and the partial molar volume of C_4H_{10} and iC_4H_{10} at 360.00 K. J. of Supercritical Fluids, 29 (2004), 215–220.

Tully, P. C.; DeVaney, W. E.; Rhodes, H. L. (1971): Phase equilibria of the helium–nitrogen system from 122 to 126°K. Adv. Cryog. Eng., 16 (1971), 88–95.

van Kasteren, P. H. G.; Zeldenrust, H. (1979): A flow calorimeter for condensable gases at low temperatures and high pressures. 2. Compilation of experimental results and comparison with predictions based on a modified Redlich-Kwong equation of state. Ind. Eng. Chem., Fundam., 18 (1979), 339–345.

van Laar, J. J. (1910): Über Dampfspannungen von binären Gemischen. Z. Phys. Chem. (Leipzig), 72 (1910), 723–751.

Vaughan, W. E.; Collins, F. C. (1942): *P-V-T-x* relations of the system propane–isopentane. Ind. Eng. Chem., 34 (1942), 885–890.

Verschoyle, T. T. H. (1926): Isotherms of hydrogen, of nitrogen, and of hydrogen–nitrogen mixtures, at 0° and 20° C., up to a pressure of 200 atmospheres. Proc. R. Soc. London, Ser. A, 111 (1926), 552–576.

Verschoyle, T. T. H. (1931): The ternary system carbon monoxide–nitrogen–hydrogen and the component binary systems between temperatures of −185° and −215° C., and between pressures of 0 and 225 atm. Philos. Trans. R. Soc. London, Ser. A, 230 (1931), 189–220.

VonNiederhausern, D. M.; Giles, N. F. (2001): Vapor-liquid equilibrium measurements on propane, n-butane, isobutane, ethane, n-pentane and n-hexane. Gas Processors Association, Research Report RR-179, GPA Project 012, Tulsa, OK, 2001.

Vrabec, J.; Fischer, J. (1996): Vapor-liquid equilibria of binary mixtures containing methane, ethane, and carbon dioxide from molecular simulation. Int. J. Thermophysics, 17 (1996), 889–908.

Vrabec, J.; Fischer, J. (1997): Vapor-liquid equilibria of the ternary mixture CH_4+C_2H_6+CO_2 from molecular simulation. AIChE J., 43 (1997), 212–217.

Wagner, W. (1970): Eine thermische Zustandsgleichung zur Berechnung der Phasengleichgewichte flüssig-gasförmig für Stickstoff. Dissertation, Technische Universität Carolo-Wilhelmina zu Braunschweig, 1970.

Wagner, W. (1972): A method to establish equations of state exactly representing all saturated state variables applied to nitrogen. Cryogenics, 12 (1972), 214–221.

Wagner, W. (1974): Eine mathematisch statistische Methode zum Aufstellen thermodynamischer Gleichungen – gezeigt am Beispiel der Dampfdruckkurve reiner fluider Stoffe. Fortschr.-Ber. VDI-Z., Reihe 3, Nr. 39, VDI-Verlag, Düsseldorf, 1974.

Wagner, W.; de Reuck, K. M. (1996): Methane. International thermodynamic tables of the fluid state – 13. Blackwell Science, Oxford, 1996.

Wagner, W.; Cooper, J. R.; Dittmann, A.; Kijima, J.; Kretzschmar, H.-J.; Kruse, A.; Mares, R.; Oguchi, K.; Sato, H.; Stöcker, I.; Sifner, O.; Takaishi, Y.; Tanishita, I.; Trübenbach, J.; Willkommen, Th. (2000): The IAPWS Industrial Formulation 1997 for the thermodynamic properties of water and steam. ASME J. Eng. Gas Turbines and Power, 122 (2000), 150–182.

Wagner, W.; Pruß, A. (2002): The IAPWS Formulation 1995 for the thermodynamic properties of ordinary water substance for general and scientific use. J. Phys. Chem. Ref. Data, 31 (2002), 387–535.

Wang, D. I. J. (1960): Vapor-liquid equilibrium studies on the system argon–oxygen. Adv. Cryog. Eng., 3 (1960), 294–304.

Wang, R. H.; McKetta, J. J. (1964): Vapor-liquid equilibrium of the methane–n-butane–carbon dioxide system at low temperatures and elevated pressures. J. Chem. Eng. Data, 9 (1964), 30–35.

Wäterling, U.; Zheng, D.; Knapp, H. (1991): Vapor-liquid equilibria at high temperatures and pressures in binary mixtures containing H_2, CH_4 and CO_2 with high boiling hydrocarbons: experimental equipment and results (Dampf-Flüssigkeitsgleichgewichte bei hohen Temperaturen und Drücken in Zwei-Stoffgemischen aus H_2, CH_4 und CO_2 mit hoch siedenden Kohlenwasserstoffen: Apparatur und experimentelle Ergebnisse). Chem. Eng. Process., 29 (1991), 155–164.

Watson, G. M.; Stevens, A. B.; Evans, R. B. (III); Hodges, D. (Jr.) (1954): Compressibility factors of nitrogen–propane mixtures in the gas phase. Ind. Eng. Chem., 46 (1954), 362–364.

Watson, J. T. R.; Millington, B. (1998): The density of rich natural gas mixtures. A joint industrial project. NEL, Project No. DRG001, Report No. 110/97, 1998.

Weber, L. A. (1989): Simple apparatus for vapor-liquid equilibrium measurements with data for the binary systems of carbon dioxide with n-butane and isobutane. J. Chem. Eng. Data, 34 (1989), 171–175.

Weber, L. A. (1992): Measurements of the virial coefficients and equation of state of the carbon dioxide + ethane system in the supercritical region. Int. J. Thermophysics, 13 (1992), 1011–1032.

Webster, L. A.; Kidnay, A. J. (2001): Vapor-liquid equilibria for the methane–propane–carbon dioxide systems at 230 K and 270 K. J. Chem. Eng. Data, 46 (2001), 759–764.

Weems, G. W.; Miller, N. L. (1969): Compressibility factors for helium and carbon dioxide mixtures at 0°, 10°, 20°, 23° and 35° C and to 900 psia. U.S. Bur. Mines, Rep. Invest., Number 7233, pp. 1–41, 1969.

Weems, G. W.; Howard, A. R. (1970): Compressibility factors for helium and carbon dioxide mixtures at −10° and −20° C and pressures to 1,000 psia. U.S. Bur. Mines, Rep. Invest., Number 7412, pp. 1–44, 1970.

Wei, M. S.-W.; Brown, T. S.; Kidnay, A. J.; Sloan, E. D. (1995): Vapor + liquid equilibria for the ternary system methane + ethane + carbon dioxide at 230 K and its constituent binaries at temperatures from 207 to 270 K. J. Chem. Eng. Data, 40 (1995), 726–731.

Weishaupt, J. (1948): Determination of the equilibria of boiling nitrogen–argon–oxygen mixtures at 1000 Torr (Bestimmung des Gleichgewichtes siedender Stickstoff–Argon–Sauerstoffgemische bei 1000 Torr). Angewandte Chemie, B, 20 (1948), 12, 321–326.

Wendland, M. (1994): Hochdruckmehrphasengleichgewichte in ternären Gemischen aus Kohlendioxid, Wasser und einem organischen Lösungsmittel. Dissertation, Universität Kaiserslautern, 1994.

Weng, W. L.; Lee, M. J. (1992): Vapor-liquid equilibrium of the octane/carbon dioxide, octane/ethane, and octane/ethylene systems. J. Chem. Eng. Data, 37 (1992), 213–215.

Wichterle, I.; Chappelear, P. S.; Kobayashi, R. (1971): Determination of critical exponents from measurements of binary vapor-liquid equilibrium in the neighborhood of the critical line. J. Comput. Phys., 7 (1971), 606–620.

Wichterle, I.; Kobayashi, R. (1972a): Vapor-liquid equilibrium of methane–ethane system at low temperatures and high pressures. J. Chem. Eng. Data, 17 (1972), 9–12.

Wichterle, I.; Kobayashi, R. (1972b): Vapor-liquid equilibrium of methane–propane system at low temperatures and high pressures. J. Chem. Eng. Data, 17 (1972), 4–9.

Wiebe, R.; Gaddy, V. L. (1938): The compressibilities of hydrogen and of four mixtures of hydrogen and nitrogen at 0, 25, 50, 100, 200 and 300° and to 1000 atmospheres. J. Am. Chem. Soc., 60 (1938), 2300–2303.

Wiese, H. C.; Jacobs, J.; Sage, B. H. (1970): Phase equilibria in the hydrocarbon systems. Phase behavior in the methane–propane–n-butane system. J. Chem. Eng. Data, 15 (1970), 82–91.

Wieser, M. E. (2006): Atomic weights of the elements 2005 (IUPAC Technical Report). Pure Appl. Chem., 78 (2006), 2051–2066.

Williams, R. B.; Katz, D. L. (1954): Vapor liquid equilibria in binary systems. Hydrogen with ethylene, ethane, propylene, and propane. Ind. Eng. Chem., 46 (1954), 2512–2520.

Wilson, G. M.; Silverberg, P. M.; Zellner, M. G. (1965): Argon–oxygen–nitrogen three-component system experimental vapor-liquid equilibrium data. Adv. Cryog. Eng., 10 (1965), 192–208.

Wilson, G. M.; Barton, S. T. (1967): Enthalpy data for heat exchanger design; new calorimeter. Nat. Gas Process. Assoc., Proc. Annu. Conv. (Tech. Paper), 46 (1967), 18–20.

Wilson, G. M. (1975): Vapor-liquid equilibria of nitrogen, methane, ethane and propane binary mixtures at LNG temperatues from total pressure measurements. Adv. Cryog. Eng., 20 (1975), 164–171.

Wirbser, H.; Keil, B.; Ernst, G. (1996): Flow-calorimetric results for the specific heat capacity c_p and the Joule-Thomson-coefficient of CH_4, a binary mixture (85 mol per cent CH_4, 15 mol per cent C_2H_6) and a mixture similar to natural gas. Report to GERG WG 1.3, 1996.

Wisniak, J.; Magen, E.; Shachar, M.; Zeroni, I.; Reich, R.; Segura, H. (1997a): Phase equilibria in the systems hexane + heptane and methyl 1,1-dimethylethyl ether + hexane + heptane. J. Chem. Eng. Data, 42 (1997), 458–462.

Wisniak, J.; Embon, G.; Shafir, R.; Segura, H.; Reich, R. (1997b): Isobaric vapor-liquid equilibria in the systems methyl 1,1-dimethylethyl ether + octane and heptane + octane. J. Chem. Eng. Data, 42 (1997), 1191–1194.

Wöll, O. (2003): Private communication, Lehrstuhl für Thermodynamik, Ruhr-Universität Bochum, 2003.

Wöll, O.; El Hawary, T. (2003): Messung der dynamischen Viskosität und der Dichte von vier Erdgasgemischen für Drücke bis 15 MPa und Temperaturen bis 373 K in einer kombinierten Viskositäts-Dichte-Messaparatur. Private communication, Lehrstuhl für Thermodynamik, Ruhr-Universität Bochum, 2003.

Wu, G.; Heilig, M.; Lentz, H.; Franck, E. U. (1990): High pressure phase equilibria of the water–argon system. Ber. Bunsenges. Phys. Chem., 94 (1990), 24–27.

Wu, P. C.; Ehrlich, P. (1973): Volumetric properties of supercritical ethane–n-heptane mixtures: molar volumes and partial molar volumes. AIChE J., 19 (1973), 533–540.

Xu, N.; Yao, J.; Wang, Y.; Shi, J.; Lu, B. C.-Y. (1991): Vapor-liquid equilibria of five binary systems containing R-22. Fluid Phase Equilibria, 69 (1991), 261–270.

Xu, N.; Dong, J.; Wang, Y.; Shi, J. (1992): High pressure vapor liquid equilibria at 293 K for systems containing nitrogen, methane and carbon dioxide. Fluid Phase Equilibria, 81 (1992), 175–186.

Yesavage, V. F.; Katz, D. L.; Powers, J. E. (1969): Experimental determinations of several thermal properties of a mixture containing 77 mole % propane in methane. J. Chem. Eng. Data, 14 (1969), 137–149.

Yiling, T.; Michelberger, Th.; Franck, E. U. (1991): High-pressure phase equilibria and critical curves of (water + n-butane) and (water + n-hexane) at temperatures to 700 K and pressures to 300 MPa. J. Chem. Thermodynamics, 23 (1991), 105–112.

Yorizane, M.; Sadamoto, S.; Yoshimura, S.; Masuoka, H.; Shiki, N.; Kimura, T.; Toyama, A. (1968a): Vapor-liquid equilibria at low temperature. Kagaku-kogaku, 32 (1968), 257–264.

Yorizane, M.; Yoshimura, S.; Masuoka, H.; Toyama, A. (1968b): Low temperature vapour-liquid equilibria of hydrogen-containing binaries. Proc. 1st Int. Cryog. Eng. Conf., pp. 57–62, 1968.

Yorizane, M.; Yoshimura, S.; Masuoka, H. (1970): Vapor-liquid equilibrium at high pressures (N_2–CO_2, H_2–CO_2). Kagaku-kogaku, 34 (1970), 953–957.

Yorizane, M.; Yoshimura, S.; Masuoka, H.; Toyama, A.; Nakako, Y.; Funada, I. (1978): Measurement and estimation of low temperature vapor-liquid equilibrium for the system oxygen–argon at high oxygen concentrations. Chem. Eng. Sci., 33 (1978), 641–649.

Yorizane, M.; Yoshimura, S.; Masuoka, H.; Miyano, Y.; Kakimoto, Y. (1985): New procedure for vapor-liquid equilibria. Nitrogen + carbon dioxide, methane + freon 22, and methane + freon 12. J. Chem. Eng. Data, 30 (1985), 174–176.

Younglove, B. A. (1982): Thermophysical properties of fluids. I. Argon, ethylene, parahydrogen, nitrogen, nitrogen trifluoride, and oxygen. J. Phys. Chem. Ref. Data, Suppl. No. 1, 11 (1982), 1–353.

Younglove, B. A.; Frederick, N. V.; McCarty, R. D. (1993): Speed of sound data and related models for mixtures of natural gas constituents. NIST, Monograph 178, Boulder, Colorado, 1993.

Yucelen, B.; Kidnay, A. J. (1999): Vapor-liquid equilibria in the nitrogen + carbon dioxide + propane system from 240 to 330 K at pressures to 15 MPa. J. Chem. Eng. Data, 44 (1999), 926–931.

Zais, E. J.; Silberberg, I. H. (1970): Vapor-liquid equilibria in the ethane–n-hexane system. J. Chem. Eng. Data, 15 (1970), 253–256.

Zenner, G. H.; Dana, L. I. (1963): Liquid-vapor equilibrium compositions of carbon dioxide–oxygen–nitrogen mixtures. Chem. Eng. Prog., Symp. Ser., 59 (1963), 44, 36–41.

Zhang, W.; Schouten, J. A. (1992a): The sound velocity of a mixture of CH_4 and N_2 from 2 kbar to 8 kbar and from 173 K to 298 K. Physica, A, 189 (1992), 493–502.

Zhang, W.; Schouten, J. A. (1992b): The sound velocity of a mixture of He and N_2 up to 10 kbar and from 157 K to 298 K. Fluid Phase Equilibria, 79 (1992), 211–220.

Zhang, W.; Biswas, S. N.; Schouten, J. A. (1992): Compressibility isotherms of helium–nitrogen mixtures at 298.15 K up to 10 kbar. Physica, A, 182 (1992), 353–364.

Zielkiewicz, J. (1992): (Vapour + liquid) equilibria in (propan-1-ol + heptane + octane) at the temperature 313.15 K. J. Chem. Thermodynamics, 24 (1992), 455–462.