

A NEW HELMHOLTZ ENERGY MODEL FOR HUMID GASES AND CCS MIXTURES

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TABLE OF CONTENTS

Table of Symbols	III
1 Introduction	1
2 The New Mixture Model for Humid Gases and CCS Mixtures	4
2.1 Previous Work on Mixture Models for Humid Gases and CCS Mixtures	9
2.2 Applications, Components and Mixtures Considered in the New Mixture Model	10
2.3 General Structure	15
2.4 Calculation of Thermodynamic Properties from the Mixture Model	19
2.5 Parameters	24
3 Stability Analysis and Flash Calculation	27
3.1 Phase Stability Condition	27
3.2 Stability Calculation	30
3.2.1 The Tangent Plane Condition	31
3.2.2 Stability Calculation Algorithm	32
3.3 The Isothermal Two-Phase Flash	37
3.4 The Isenthalpic and Isentropic Stability Analysis and Two-Phase Flash	39
3.5 Phase Envelope Calculation	42
3.5.1 Phase Envelope Characteristics	43
3.5.2 Saturation Point Calculation	44
3.5.3 Phase Envelope Calculation Algorithm	44
3.6 Derivatives of the Helmholtz Energy Mixture Model Required for Flash Calculations	52
3.6.1 Derivatives of the Fugacity Coefficient	52
3.6.2 Derivatives of Enthalpy and Entropy	59
3.7 Density Solver	64
3.7.1 The Problem of Multiple Density Roots	65
3.7.2 Advanced Root Finding Algorithm	66
3.7.3 Density Search Strategy	69
4 Parameter Fitting	72
4.1 Building the Sum of Squares	73
4.2 The Nonlinear Minimization Algorithm	77
4.3 Fitting Mixture Equations of State Using REFPROP	79

5	Comparison of the New Mixture Model with Experimental Data and other Models	90
5.1	Experimental Data Used for the Development of the New Mixture Model	91
5.2	Representation of Thermodynamic Properties of Binary Mixtures	98
5.2.1	Binary Mixtures with Carbon Dioxide	98
5.2.2	Binary Mixtures with Water	106
5.2.3	Other Binary Mixtures	122
5.2.4	Representation of Virial Coefficients	127
5.3	Representation of Multi-Component Mixtures	130
6	Conclusions and Outlook	135
	References	140
A1	Graphical Representation of Experimental Data	162
A2	Numerical Representation of Experimental Data	191

TABLE OF SYMBOLS

Latin Symbols

A	Total Helmholtz free energy
a	– Molar Helmholtz free energy – Interaction parameter in cubic EOS
B	Second virial coefficient
b	– Volume parameter in cubic EOS – Parameter
C	Third virial coefficient
c	EOS parameter
c_p	Molar isobaric heat capacity
c_v	Molar isochoric heat capacity
d	Total differential
D	Fourth virial coefficient
F	– Departure function parameter – Function
$\bar{F}$	Vector of equations
f	– Fugacity – Function
f_w	Vapor pressure enhancement factor
G	Total Gibbs energy
g	– Molar Gibbs energy – Function
H	Total enthalpy
h	Molar enthalpy
$\mathbf{J}_{\bar{F}}$	Jacobian matrix of the vector of equations $\bar{F}$
K	K -factor
k	Binary adjustable interaction parameter in cubic EOS
L	Determinant of Legendre transforms with the critical point criteria
M	– Molar mass – Determinant of Legendre transforms with the critical point criteria
m	Parameter in the temperature-dependent correction factor in the SRK
N	Number of components in a mixture
n	– Amount of substance, mole number – Iteration step
$\bar{n}$	Vector of mole numbers
p	Pressure
Q	Modified tangent plane distance function

Latin Symbols *continued*

q	Variable thermodynamic property of a constraint
R	Universal gas constant
S	– Total entropy – Sensitivity
s	Molar entropy
T	Temperature
U	Total internal energy
u	– Molar internal energy – Independent variable of the cubic extrapolation function
V	Total volume
v	Molar volume
W	Weight assigned to a data point or constraint in the fitting process
w	– Speed of sound – Dependent variable of the cubic extrapolation function
$\bar{w}$	Molar composition of the new phase (vector of mole fractions)
$\bar{X}$	Vector of unknowns
x	– Mole fraction of one component in a mixture – Mole fraction of one component in the liquid phase
$\bar{x}$	Molar composition (vector of mole fractions)
y	– Mole fraction of one component in the gas phase – Legendre transform of the state function $U(S, V, \bar{n})$
Z	Compressibility factor
z	Arbitrary thermodynamic property
$\bar{z}$	Molar composition of the saturated phase (vector of mole fractions)

Greek Symbols

∂	Partial derivative
φ	Fugacity coefficient
Δ	Finite change of a variable
α	– Reduced Helmholtz free energy, $\alpha = a/RT$ – Temperature-dependent parameter in the SRK
β	– Molar vapor fraction – Binary reducing function parameter – Adjustable parameter in the binary departure function α_{ij}^r
δ	– Reduced density, $\delta = \rho / \rho_r$ – Differential quantity
ε	Adjustable parameter in the binary departure function α_{ij}^r

Greek Symbols *continued*

γ	Adjustable parameter in the binary departure function α_{ij}^r
η	Adjustable parameter in the binary departure function α_{ij}^r
μ	Chemical potential
μ_{JT}	Joule-Thomson coefficient
ψ	Reduced volume, $\psi = v/v_r$
ρ	Molar density
σ	Expanded experimental uncertainty
$\mathcal{G}$	Reduced temperature, $\mathcal{G} = T/T_r$
τ	Inverse reduced temperature, $\tau = T_r/T$
ω	Acentric factor
π	Reduced pressure, $\pi = p/p_r$
ξ	Partial derivative of the Legendre transform y
ζ	Function used in the uncertainty calculation

Subscripts

c, crit	Property at critical conditions
calc	Calculated property
CCB	Cricondenbar (pressure maximum) on the phase envelope
CCT	Cricondentherm (temperature maximum) on the phase envelope
exp	Experimental property
i,j,k,m	Component indices
N	Last component in the mixture
n	Point indicator on the phase envelope, iteration count
o	Pure fluid property
r	Reducing parameter
sat	Property at saturation
tp	Property at the triple point
trial,H	Heavy trial phase in the stability check
trial,L	Light trial phase in the stability check
x	– Saturated property of the incipient phase – Partial derivative with respect to the mole fraction x
z	Saturated property of the original phase
δ	Partial derivative with respect to δ
τ	Partial derivative with respect to τ

Superscripts

'	Property of the saturated liquid
"	Property of the saturated vapor
E	Excess property
k	Order of transformation of the Legendre transform y
o	Ideal-gas property
r	Residual property

Abbreviations

AAD	Absolute average deviation
CCB	Cricondenbar (pressure maximum) in the phase envelope
CCS	Carbon capture and storage
CCT	Cricodentherm (temperature maximum) in the phase envelope
EOS	Equation of state
EOS-CG	The new mixture model for humid gases and CCS mixtures
LKP	Lee-Kesler-Ploecker equation
LLE	Liquid-liquid equilibrium
<i>PIP</i>	Phase identification parameter
PSRK	Predictive Soave-Redlich-Kwong equation
$p\rho T$	Pressure-density-temperature relation
$pTxy$	Data set of liquid and vapor phase compositions at given T and p
SAFT	Statistical associating fluid theory
<i>SOS</i>	Sum of squares
SRK	Soave-Redlich-Kwong equation
<i>TPD</i>	Tangent plane distance
<i>tpd</i>	Reduced tangent plane distance
VLE	Vapor-liquid equilibrium

1 INTRODUCTION

It is common understanding that an increase in atmospheric greenhouse gas concentrations may result in a hazardous global change of climatic conditions. Although details of the effect on regional systems and the impact of the global climate change are still under discussion, there is a common consensus that carbon dioxide emissions pose the most relevant anthropogenic contribution to the increase of atmospheric greenhouse gases. In order to stabilize atmospheric conditions, a reduction of global atmospheric carbon dioxide (CO₂) emissions by at least 60% seems to be mandatory. A corresponding demand was presented by the Intergovernmental Panel on Climate Change (IPCC) [Watson *et al.* (2001)].

About one third of the global anthropogenic CO₂ emissions are generated by burning fossil fuels for power and heat production, with a much higher contribution in industrialized countries. Since fossil-fuelled power plants are the largest “point sources” in this sector, the focus of policy makers is a reduction of CO₂ emissions from power generation. Beside the increase in process efficiency, the separation of CO₂ produced in the combustion of the fossil fuel before it enters the atmosphere is one strategy that both power producers and companies involved in building turbo machineries consider as a valid interim solution until the power production from renewable energy sources can replace fossil-fuelled power generation.

The long-term goal of a drastically increased use of renewable energy sources incorporates serious challenges regarding supply fluctuations and grid stability. Therefore, the development of efficient storage technologies becomes mandatory. Besides pumped-storage hydropower plants, which are geographically constrained, diabatic and adiabatic compressed air energy storage solutions are among the most promising storage technologies.

Though the technical challenges mentioned above (increase of efficiencies, separating CO₂, energy storage) are very different, they have one common feature: Design and simulation of the corresponding processes involve thermodynamic property calculations at states where the ideal-gas thermodynamic property models common in energy technologies are less valid. Technologies such as capture and storage of CO₂ (CCS), the compression and cooling of humid air for compressed air energy storage (CAES) or the use of CO₂-rich mixtures as a gas-turbine working fluid (oxyfuel GTCC) involve handling highly non-ideal fluid mixtures at high pressures and low temperatures, and possibly complex phase equilibria. Using ideal-gas models in these processes leads to erroneous results (e.g. over 150 % deviation in density of CO₂ at pipeline pressure). Corresponding demands for accurate thermophysical property models of mixtures were formulated both by companies

involved in the development of CCS technologies and by international standardization organizations [Span and Hiegemann (2002)].

Many different technology options are under discussion in this context, and each application has its own specific requirements on the description of thermodynamic properties. However, a group of mixture components can be identified that are present in the major part of processes related to the transport and storage of CO₂ separated from gas streams, as well as a variety of advanced power generation and transformation processes. Beside CO₂, the main components of any process with air or a combustion gas as the working fluid are nitrogen (N₂), oxygen (O₂), argon (Ar), and water (H₂O). Additionally, carbon monoxide (CO) plays a certain role as a secondary combustion gas component in a number of CCS related combustion processes.

The most accurate thermodynamic model currently available for the description of fluid mixtures of these components is the GERG-2008 by Kunz and Wagner (2012). Originally, this model was developed for natural gas mixtures and incorporates 21 components, including the six substances mentioned above. It uses accurate, state-of-the-art Helmholtz energy equations of state for the description of the contribution of the pure fluids to the mixture properties and thus allows for a much more accurate prediction of gas and liquid phase properties than the often used cubic equations of state. However, since the substances relevant in CCS and humid gas mixtures were not in the focus of the development of the GERG-2008 model, it shows shortcomings, especially in the description of phase boundaries of CO₂-mixtures and the solubility of gases in water.

The new Helmholtz energy mixture model for humid gases and CCS mixtures (also referred to as *Equation of State for Combustion Gases and Combustion Gas like Mixtures*, EOS-CG) proposed in this work addresses these shortcomings. Using the mathematical approach presented in the GERG-2008 with some minor adjustments, it aims to improve the description for binary and multi-component mixtures of the six components, with a focus on the accurate prediction of the phase boundaries over a wide temperature and pressure range.

In Chapter 2, the state of the art on the description of thermodynamic properties of mixtures is discussed before the new mixture model is introduced. Different from thermal equations of state (e.g. any cubic equation or corresponding states model explicit in the compression factor) the new mixture model explicit in the Helmholtz free energy is a fundamental equation of state, which means that all thermal and caloric properties can be calculated from the model, using combinations of partial derivatives. The relation between the model and all common thermodynamic properties is given in Section 2.4.

Beside an accurate model, a robust algorithm for the calculation of the phase boundaries and the determination of stability is crucial. An improved algorithm for the combined

stability and flash calculation, based on the formulations suggested by Michelsen (1982a), Michelsen (1982b), and Michelsen and Mollerup (2004) is proposed and extended to Helmholtz energy models in Chapter 3. In addition to the flash calculation using different input variables an algorithm for the flexible and fast calculation of phase envelopes is given in Section 3.5. All partial derivatives of the new mixture model necessary for the solution of the phase equilibrium conditions are given in Section 3.6. Finally, a reliable and robust density solver, which is a crucial tool for the calculation of thermodynamic properties at input variables other than temperature and density, is presented in Section 3.7.

Chapter 4 gives the description of the fitting method used to adjust the model parameters to experimental data, including a short discussion of the algorithm and tools employed in this work. Finally, the results are given in Chapter 5, where the new mixture model is evaluated by comparing it to the available experimental data of thermodynamic properties of binary and multi-component mixtures. This evaluation also includes comparisons to other established thermodynamic models, mainly the GERG-2008. Due to the large data volume a part of this comparison is transferred to appendices A1 and A2, which hold an extensive graphical and numerical evaluation for all experimental data collected in the course of this work.

2 THE NEW MIXTURE MODEL FOR HUMID GASES AND CCS MIXTURES

The description of thermodynamic properties of mixtures using equations of state is of great interest for many industrial applications. Consequently it has been in the focus of experimental and theoretical research for many years. The simplest model for the description of mixtures is the mixture of ideal gases. The assumption that molecules of a single gas have no volume and no interacting forces is simply transferred to a mixture. The only influences of the pure components on the mixture are the differences in molar mass and in the ideal-gas heat capacity that describes the temperature dependence of the energetic state of the molecules due to vibrational, rotational and translational excitement. However, even in such a simple approach, the entropy of mixing has to be accounted for, which adds a sole mixture specific term to the model. This formulation is still widely used for the description of combustion gases or ambient air [VDI 4670 (2003)]. The ideal-gas model is only a valid approximation of a real fluid for temperatures far above the critical temperature or densities far below the critical density. For a wider temperature and pressure range, molecular interactions have to be taken into account using an equation of state. Regardless of the equations of state used for the description of the pure components, the next logical step in describing fluid mixtures is the ideal mixture of real gases approach that was formulated as an alternative to the ideal gas model by the ASME Standards Technology (2008) as a standard for gas turbine working gases. Such a model increases the range of validity to lower temperatures and higher pressures, but is only applicable for mixtures and states where the interaction of unlike molecules can be neglected.

The SRK and PSRK Equations of State

Different approaches have been developed over the last several decades to describe real mixtures of real gases and to account for the interaction of different molecule types. These developments were usually based on the experience from the respective types of equations of state for pure fluids. The van-der-Waals type cubic equations of state were extended to mixtures, e.g. the Soave-Redlich-Kwong (SRK) equation of state by Soave (1972), using generalized combining rules for the volume parameter b and empirical mixing rules with an adjustable parameter for the interaction parameter a . The general form of the SRK equation for mixtures reads

$$p = \frac{RT}{v-b} - \frac{a(T)}{v(v+b)}, \quad 2.1$$

with the interaction parameter a

$$a(T) = \sum_{i=1}^{N-1} \sum_{j=i+1}^N x_i x_j \sqrt{a_i(T) a_j(T)} (1 - k_{ij}), \quad 2.2$$

built from quadratic mixing rules using the arithmetic mean of the pure-fluid energy parameters a_i and empirical adjustable binary interaction parameters k_{ij} . Linear combining rules are employed for the description of the volume parameter b

$$b = \sum_{i=1}^N x_i b_i. \quad 2.3$$

The pure-fluid energy parameters are calculated from the critical properties T_c and p_c , the acentric factor ω , and a temperature-dependent term $\alpha(T)$, according to

$$a_i(T) = a_{c,i} \alpha(T). \quad 2.4$$

The pure-fluid critical parameter $a_{c,i}$ and the volume parameter b_i are derived from the fact, that at the critical point the first and second pressure derivatives with respect to the volume are zero for every fluid. They read

$$a_{c,i} = 0.42747 \frac{R^2 T_{c,i}^2}{p_{c,i}} \quad 2.5$$

and

$$b_i = 0.08664 \frac{RT_{c,i}}{p_{c,i}}. \quad 2.6$$

The temperature-dependent correction factor α is given by

$$\alpha_i(T) = \left[1 + m_i (1 - \sqrt{\mathcal{G}_i}) \right]^2, \quad 2.7$$

with the parameter m_i

$$m_i = 0.480 + 1.57\omega_i - 0.176\omega_i^2 \quad 2.8$$

being a quadratic function of the acentric factor ω_i , which is defined from the reduced vapor pressure $\pi_{sat,i} = p_{sat,i}/p_{c,i}$ at a reduced temperature $\mathcal{G}_i = T/T_{c,i} = 0.7$ according to

$$\omega_i = -\log[\pi_{sat,i}(\mathcal{G}_i = 0.7)] - 1. \quad 2.9$$

The Predictive Soave-Redlich-Kwong equation of state by Holderbaum and Gmehling (1991) introduces an extension to the correction factor α developed by Mathias and Copeman (1983) with three adjustable temperature coefficients c_1 , c_2 , and c_3 :

$$\alpha_i(T) = \left[1 + c_{1,i} (1 - \sqrt{\mathcal{G}_i}) + c_{2,i} (1 - \sqrt{\mathcal{G}_i})^2 + c_{3,i} (1 - \sqrt{\mathcal{G}_i})^3 \right]^2. \quad 2.10$$

This extension increases the capability of the model to reproduce the vapor pressure curve, even for polar fluids, since the parameters c_1 , c_2 , and c_3 were adjusted to vapor-liquid equilibrium data. For $c_{1,i} = m_i$ and $c_{2,i} = c_{3,i} = 0$ the PSRK corresponds to the original SRK.

The second modification in the PSRK concerns the mixing rules for the interaction parameter a . From thermodynamic relations between the Helmholtz free energy and the pressure, a mixing rule for a was derived by Huron and Vidal (1979), which included the excess Gibbs energy at standard pressure, g_0^E :

$$a = b \left(\frac{g_0^E}{A_1} + \sum_{i=1}^N x_i \frac{a_i}{b_i} + \frac{RT}{A_1} \sum_{i=1}^N x_i \ln \frac{b}{b_i} \right). \quad 2.11$$

This approach was adopted in the PSRK model, in combination with the UNIFAC method for the description of the excess Gibbs energy. This method is based on the idea of splitting complex molecules into functional groups that contribute to the excess Gibbs energy by their interactions with the other functional groups present in the system. This way, an unknown mixture can be described by this method as long as the contributions of all functional groups within the molecules of all of its component are known (see Holderbaum and Gmehling (1991) for more details).

The LKP Equation of State

For the virial equations of state, several extensions to mixtures were applied, including the development of second and third mixture virial coefficients based on considerations from statistical thermodynamics, e.g. by Hirschfelder *et al.* (1954), and empirical multi-parameter models such as the Lee-Kesler-Plöcker (LKP) equation of state by Plöcker *et al.* (1978), which uses a corresponding-states approach with the modified Benedict-Webb-Rubin equation by Lee and Kesler (1975) as a basis. In this model, the compressibility factor Z is related to the compressibility factors of a *reference fluid* Z^{ref} and a *simple fluid* Z^0 by

$$Z = Z^0 + \frac{\omega}{\omega^{\text{ref}}} (Z^{\text{ref}} - Z^0). \quad 2.12$$

The general functional form for the correlation of the compressibility factor reads

$$Z = \frac{\pi\psi}{g} = 1 + \frac{B}{\psi} + \frac{C}{\psi^2} + \frac{D}{\psi^5} + \frac{c_4}{g^3\psi^2} \left(\beta + \frac{\gamma}{\psi^2} \right) \exp \left(-\frac{\gamma}{\psi^2} \right), \quad 2.13$$

with the temperature-dependence of the virial coefficients described by

$$\begin{aligned} B &= b_1 - b_2/g - b_3/g^2 - b_4/g^3, \\ C &= c_1 - c_2/g - c_3/g^3, \quad \text{and} \\ D &= d_1 + d_2/g. \end{aligned} \quad 2.14$$

For the *simple fluid* (argon or nitrogen) and the *reference fluid* (*n*-octane) fixed sets of parameters b_i , c_i , d_i , β and γ are given, independent from the fluid or mixture to be calculated. The parameters ψ , g , and π are the reduced molar volume, temperature, and pressure respectively, the reducing parameters being the (pseudo-) critical pressure and temperature p_r and T_r of the pure fluid (or mixture) according to

$$g = \frac{T}{T_r}, \quad \psi = \frac{p_r v}{RT_r}, \quad \text{and} \quad \pi = \frac{p}{p_r}. \quad 2.15$$

For mixtures, the mixing rule for the pseudo-critical temperature is

$$T_r = \frac{1}{v_r^\eta} \sum_i \sum_j x_i x_j v_{c,ij}^\eta T_{c,ij}, \quad 2.16$$

with

$$v_r = \sum_i \sum_j x_i x_j v_{c,ij}, \quad T_{c,ij} = (T_{c,i} T_{c,j})^{1/2} k_{ij}, \quad \text{and} \quad v_{c,ij} = \frac{1}{8} (v_{c,i}^{1/3} + v_{c,j}^{1/3})^3, \quad 2.17$$

and the pseudo-critical pressure is calculated from

$$p_r = (0.2905 - 0.085\omega) R \frac{T_r}{v_r}, \quad 2.18$$

with

$$\omega = \sum_i x_i \omega_i. \quad 2.19$$

The empirical exponent η , which is adjustable between zero and unity, the adjustable binary parameter k_{ij} , and the functional form of the mixing rules enable accurate phase equilibrium calculations of symmetric and asymmetric mixtures.

Models like the SRK or LKP enable the description of the whole fluid region of a mixture, including the phase equilibria up to high pressures. For the calculation of thermodynamic properties and phase equilibria at low pressures, excess Gibbs energy models were developed to account for the interaction of unlike molecules in the mixture. In most of the approaches (e.g. the Wilson equation by Wilson (1964), the NRTL model by Renon and Prausnitz (1968), or the UNIQUAC by Abrams and Prausnitz (1975)) the excess volume is assumed to be zero, resulting in the excess Gibbs energy as a function solely of the temperature.

Multi-Parameter Helmholtz Energy Equations of State

A new class of equations of state formulated in the Helmholtz free energy was first introduced by Keenan *et al.* (1969). However, a breakthrough in accuracy was only achieved 16 years later by Schmidt and Wagner (1985) with their equation of state for oxygen. These empirical multi-parameter models are formulated in the reduced Helmholtz free energy and not in the pressure or compression factor. Therefore, a more flexible use of terms was possible to fit the model parameters to experimental data. These flexible mathematical models together with sophisticated structure optimization and fitting algorithms like the one developed by Setzmann and Wagner (1989) and the increasing computing power enabled the development of new reference equations of state for pure fluids, which were fitted to experimental data of multiple thermodynamic properties and which are able to reproduce the most accurate measurements within their experimental uncertainty over the whole fluid region. Especially the poor representation of thermal and caloric properties in the liquid and critical region by cubic equations of state could be overcome by these new Helmholtz models (see Span (2000) for a comprehensive overview on the structure and development of pure-fluid Helmholtz free energy equations of state).

The first extension of Helmholtz free energy equations of state to mixtures was proposed independently by Tillner-Roth (1993) and Lemmon (1996). A revised and generalized description of these mixture models was published by Lemmon and Tillner-Roth (1999) and shall be shortly described here. The model enables the description of multi-component mixtures based on binary mixing rules and was developed for mixtures of hydrocarbons and other components of typical natural gas mixtures. The equation for the Helmholtz free energy given in their work is

$$A = A^{\text{idmix}} + A^E, \quad 2.20$$

with the Helmholtz energy for an “ideal mixture”¹

$$A^{\text{idmix}} = \sum_{i=1}^N x_i \left[A_i^0(\rho, T) + A_i^r(\delta, \tau) + RT \ln x_i \right], \quad 2.21$$

where ρ and T are the mixture density and temperature, δ and τ are the reduced mixture density and temperature, and A_i^0 , A_i^r and x_i are the ideal gas part and residual part of the Helmholtz energy and the mole fraction of component i in a mixture of N components. The term A^E is used for the description of residual mixing effects that cannot be accounted for by the corresponding states approach alone; it reads

$$A^E = RT \sum_{i=1}^{N-1} \sum_{j=i+1}^N x_i x_j F_{ij} \sum_{k=1}^N n_k \delta^{d_k} \tau^{t_k}. \quad 2.22$$

Although it holds the same notation, it is not to be confused with the excess part of the Helmholtz energy. The reduced density and inverse reduced temperature of the mixture are

$$\delta = \rho / \rho_r \quad \text{and} \quad \tau = T_r / T, \quad 2.23$$

with the reducing parameters ρ_r and T_r as functions of the composition and the critical parameters of the pure fluids $\rho_{c,i}$ and $T_{c,i}$

$$\rho_r = \left[\sum_{i=1}^N \frac{x_i}{\rho_{c,i}} + \sum_{i=1}^{N-1} \sum_{j=i+1}^N x_i x_j \xi_{ij} \right]^{-1} \quad \text{and} \quad T_r = \sum_{i=1}^N x_i T_{c,i} + \sum_{i=1}^{N-1} \sum_{j=i+1}^N x_i x_j \beta_{ij} \phi_{ij} \zeta_{ij}. \quad 2.24$$

The parameters ξ_{ij} , β_{ij} , ϕ_{ij} , and ζ_{ij} are adjustable to binary mixture data and define the shape of the reducing parameter functions.

Based on this work, Klimeck (2000) developed a preliminary multi-fluid mixture model for natural gas mixtures that was developed further by Kunz *et al.* (2007) and is known as the GERG-2004 equation of state. It includes pure fluid equations and mixing rules for 18 components and sets new standards for the highly accurate description of multi-component natural gas mixtures. Recently, this model was extended to 21 components [GERG-2008, Kunz and Wagner (2012)] and will be adopted as an ISO standard for natural gases in the

¹ Although stated that way by Lemmon and Jacobsen (1999), the relation given in Eqn. 2.21 is strictly speaking not an ideal mixture, since the Helmholtz energy is not evaluated at the mixture pressure and temperature.

near future (ISO 20765-2/3). The mathematical structure of this model is basically identical with the new mixture model and is described in Section 2.3.

2.1 Previous Work on Mixture Models for Humid Gases and CCS Mixtures

A number of thermodynamic models have been published for the calculation of humid air properties. Goff and Gratch (1945), and later Hyland and Wexler (1983), developed a virial model using second and third binary cross virial coefficients fitted to experimental data, and treated humid air as a mixture of two real gases – dry air and water. Also the model by Rabinovich and Beketov (1995) is a virial equation of state, but the cross virial coefficients are calculated using theoretical considerations on the potential of intermolecular interactions, based on the Lennard-Jones potential. They also extended their model to other humid gases, including carbon dioxide, some noble gases, and methane and ethane. Ji and Yan (2006) used a modified Redlich-Kwong cubic equation of state in combination with correlation equations for the enthalpy and entropy of the ideal gas for the description of humid air up to 20 MPa and 573 K. A detailed description of mixture models for humid air and dew point calculation methods including several Poynting models is given by Herrmann *et al.* (2009). Lately, the group of Harvey at the National Institute for Standards and Technology (NIST) developed *ab initio* models for several water-gas mixtures (see e.g. Tulegenov *et al.* (2007) for the system water + nitrogen) from which second cross virial coefficients (see Section 5.2.4 for more details) are calculated.

A large number of models have been developed for the binary system carbon dioxide + water. Modeling such a system including its phase equilibria is particularly challenging due to the polarity of the components and the large difference in their critical temperatures. Most of these models focus on the mutual solubility and hydrate formation boundaries. Diamond and Akinfiev (2003) give a comprehensive qualitative overview over the whole phase diagram of the carbon dioxide + water system, including hydrate and solid phases. They also present a solubility model based on the Henry's constant and empirical expressions for the equilibrium compositions at high pressures. Spycher *et al.* (2003) developed an expression for the equilibrium constants for carbon dioxide and water that they used for the phase equilibrium calculations up to 60 MPa and 373 K. Several other solubility models are available, e.g. by Duan and Sun (2003), Crovetto (1991), and Carroll *et al.* (1991). The equation of state by dos Ramos *et al.* (2007a) (see also dos Ramos *et al.* (2007b)) uses the statistical associating fluid theory for potentials of variable range (SAFT-VR), which is a formulation explicit in the Helmholtz free energy, for the description of phase equilibria and excess properties of the carbon dioxide + water system. Islam and Carlson (2012) use a different SAFT approach for the description of phase equilibria for temperatures up to 573 K and pressures up to 60 MPa. However, although their qualitative predictions are correct, even at low temperatures, the equilibrium concentrations calculated

from both SAFT models are not in good agreement with the experimental data. Gallagher *et al.* (1993a) developed a corresponding states model for the high temperature and high pressure region of the carbon dioxide + water system that is able to predict the few available phase equilibrium data at high temperatures qualitatively correct. However, their model is limited to CO₂ mole fractions up to 30 % and temperatures above 400 K. Pappa *et al.* (2009) reviewed the capability of three mixture models based on the Peng-Robinson (PR) cubic equation of state for the description of the phase equilibria of this system over a wide temperature and pressure range. Also Abudour *et al.* (2012) use the PR EOS as basis for their mixture model for the systems water + methane, water + CO₂, and water + nitrogen, together with temperature-dependent binary interaction parameters for the mixing rules of the parameters a and b . Finally, Paulus and Penoncello (2006) suggest a correlation that uses the Helmholtz free energy model by Lemmon and Jacobsen (1999) for the description of the gas phase properties and the PR model for the description of phase equilibria.

The focus of research has been much more limited when it comes to other CO₂-mixtures. Kreglewski and Hall (1983) presented an equation of state for the mixtures of CO₂ with nitrogen and methane, which enables the description of the phase equilibria over the whole pTx range. Other correlations mainly use the established cubic equations of state with adjusted interaction parameters (e.g. Coquelet *et al.* (2008), Li and Yan (2009), Xu *et al.* (1992)).

Although mainly developed for the calculation of natural gas properties, the GERG-2004 or GERG-2008 by Kunz and Wagner (2012) covers all main components of typical CCS mixtures and of technical processes employing humid gases. As mentioned above, the type of multi-parameter equations of state used in the GERG-2008 mixture model is in principle able to describe the whole fluid region of multi-component mixtures up to very high pressures and temperatures, provided sufficient experimental data are available to adjust the mixture parameters appropriately. However, the GERG-2008 was not developed with the focus on humid gases, resulting in considerable deviations and qualitatively wrong predictions when it comes to the solubility of gases in water. However, other mixtures important to the goal of their work (e.g. the binary system carbon dioxide + nitrogen), are modeled with great care and accuracy.

2.2 Applications, Components and Mixtures Considered in the New Mixture Model

The new Helmholtz free energy mixture model was developed with the aim to provide an improved thermodynamic description for processes where highly non-ideal mixtures and states are involved. In order to constrain the desired range of components and mixtures, as well as the temperature and pressure range of interest, some of the possible technical

applications of interest for this model are given in the following section, along with estimated operation ranges for temperature, pressure and mixture components and compositions.

Compressed Air Energy Storage (CAES)

In order to meet the challenges that the fluctuating electricity supply of wind turbines or solar power plants pose to the energy market, a compressed air energy storage process can be used to transform surplus electricity at high-production and low-demand times into compressed air, and produce electricity by expanding the compressed air again in a gas turbine when needed. The CAES process can be separated in two process stages: the charging process in times of electrical power surplus, and the discharging process in times of power shortage. During charging, ambient air is compressed in several stages by motor-driven compressors. The pressurized air is first cooled down to about 320 K and then stored in a cavern. In case of an adiabatic process (A-CAES), the heat of the pressurized air is stored in a separate heat storage unit (e.g. a molten salt tank). During discharging, the air is heated up either by a gas burner or by the heat storage, before it is expanded in a turbine in order to generate power (Figure 2.1).

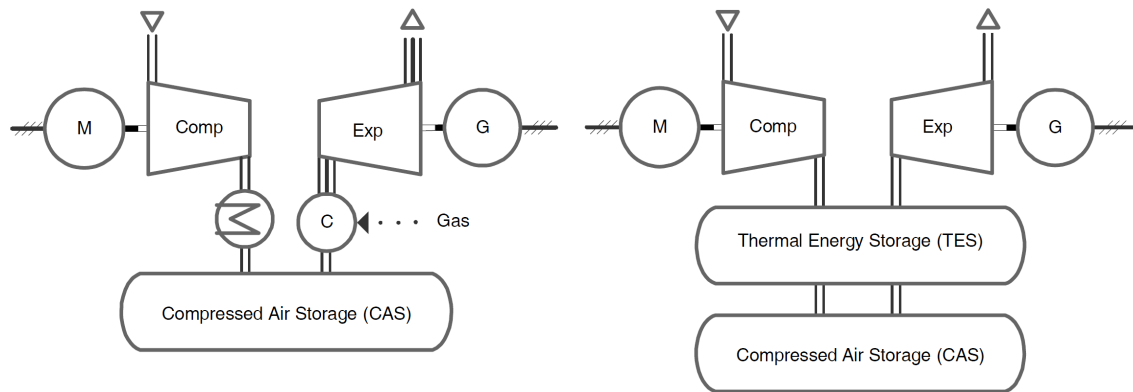


Figure 2.1: Principle of diabatic (left) and adiabatic (right) compressed air energy storage [Wolf (2010)].

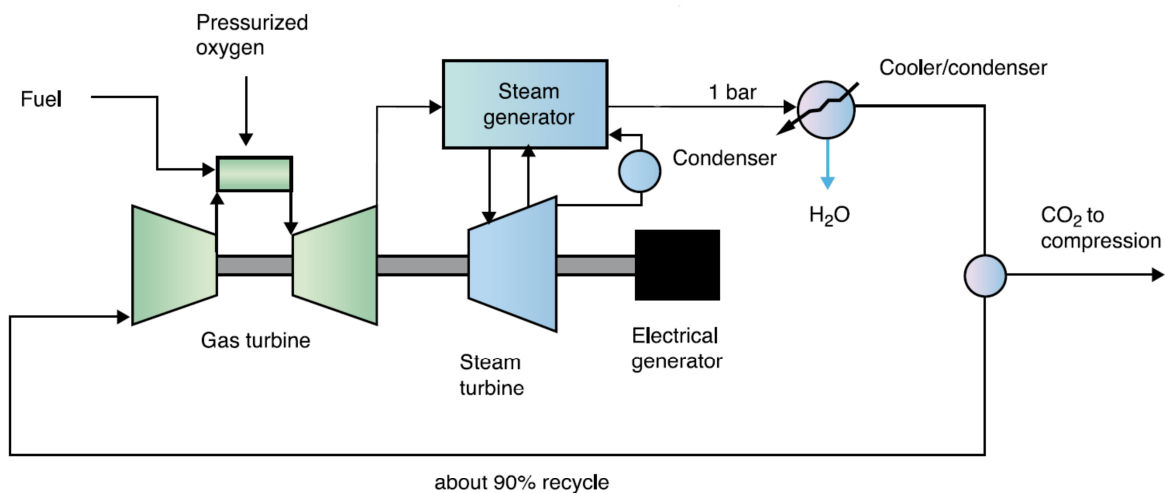
Depending on the plant layout, the storage pressure can reach up to 15 MPa, with compressor exit temperatures of up to 900 K [Wolf (2010)]. Since humid air is used as a working fluid, condensation may occur in the storage unit and possibly in the coolers between compression stages. The boundary conditions of this process are given in Table 2.1.

Table 2.1: Estimated range of compositions, temperatures and pressures in a CAES cycle.

Quantity	Min.	Max.	Quantity	Min.	Max.
<i>Range of compositions [mol-%]</i>			<i>Temperatures and pressures</i>		
Carbon Dioxide (CO ₂)	0	< 0.1	Temperature [K]	270	900
Water (H ₂ O)	0	4	Pressure [MPa]	0.1	15
Nitrogen (N ₂)	75	78			
Oxygen (O ₂)	20	21			
Argon (Ar)	0.9	1			

Oxyfuel Gas Turbine Combined Cycle

This power cycle is based on a conventional gas turbine combined cycle with a few major adjustments (see Figure 2.2). In the combustion chamber, the fuel is burned with (almost) pure oxygen instead of air. The hot combustion gas – which mainly consists of CO₂ and water, due to the oxyfuel combustion – is expanded in a modified gas turbine to produce power. The turbine exhaust gas is lead to the steam generator, where it is used as heat source in a conventional Rankine cycle. Instead of going to the stack, the gas stream is cooled down further, part of the water condenses. The CO₂-rich stream is split, the main part is fed back to the compressor inlet and the other part is lead to compression and transport. The recirculation is necessary to control the combustion temperature without the use of air.

**Figure 2.2:** Principle of an oxyfuel gas turbine combined cycle [Metz *et al.* (2005)]. The main part of the flue gas is recycled to the compressor inlet after cooling.

Assuming natural gas as fuel and complete combustion, the working fluid of the oxyfuel gas turbine is a CO₂-rich mixture with water and the air components as impurities. The operating temperatures reach from ambient to about 1600 K in the combustion chamber. Due to higher optimal pressure ranges compared to conventional gas turbines, a maximum pressure of 3.5 MPa may be expected [Metz *et al.* (2005)]. In Table 2.2 the estimated

ranges of compositions, temperatures and pressures are given for the oxyfuel gas turbine cycle, based on Metz *et al.* (2005) and Johnson *et al.* (2005).

Table 2.2: Estimated range of compositions, temperatures and pressures in an oxyfuel gas turbine cycle.

Quantity	Min.	Max.	Quantity	Min.	Max.
<i>Range of compositions [mol-%]</i>			<i>Temperatures and pressures</i>		
Carbon Dioxide (CO ₂)	80 (0) ^{a)}	> 96	Temperature [K]	290	1600
Water (H ₂ O)	0	15 (> 99) ^{a)}	Pressure [MPa]	0.1	3.5
Nitrogen (N ₂)	0	5			
Oxygen (O ₂)	0	2 (> 95) ^{b)}			
Argon (Ar)	0	5			

^{a)} Value in brackets: If the condensate stream is modeled as well.

^{b)} Value in brackets: If the pressurized oxygen stream is modeled as well.

Compression, Transport and Injection of Separated Carbon Dioxide

The CO₂-rich fluid separated in a power cycle with CO₂ capture will in most cases be a gaseous stream at ambient pressure. The amount and number of impurities vary depending on the capture process, but in all cases the mixture will be (nearly) saturated with water, and inert gases such as argon and nitrogen will be present in small amounts. In order to economically transport and store the separated CO₂, this stream needs to be liquefied by increasing the pressure above ca. 7 to 10 MPa, depending on the amount of impurities in the CO₂ stream. The compression incorporates several compression stages with intercooling after each stage. In each intercooler, water condensate (with dissolved carbon dioxide and other gases) is separated from the fluid stream. In the last compression stage the now liquid CO₂-rich stream is pumped to the designated transport pressure. In case the transport is carried out via pipeline the pressure is raised to 10 to 15 MPa, so the fluid is liquid at ambient temperature. For ship transport lower pressures are favorable in order to save costs on the pressures vessels, and the fluid is transported in a vapor-liquid equilibrium state. In order to have the pressure vessels mostly filled with liquid and thus maximize the transport capacity, the fluid has to be cooled to ca. 220 K and held at pressures between 1 MPa and 4 MPa, depending on the amount of impurities in the mixture.

Several transportation scenarios are conceivable, from pipeline over ship to truck or railroad transport. The most feasible solution however is believed to be the pipeline transport. During transportation the temperature might change depending on the ambient conditions that may cause the appearance of phase equilibria. Pipeline leakage may cause

rapid expansion with the formation of dry ice and/or CO₂ hydrate as a result. However, equilibria with solid phases are not considered in this work.

Table 2.3: Range of compositions, temperatures and pressures in compression, transportation and storage of carbon dioxide.

Quantity	Min.	Max.	Quantity	Min.	Max.
<i>Range of compositions [mol-%]</i>			<i>Temperatures and pressures</i>		
Carbon Dioxide (CO ₂)	89	> 99	Temperature [K]	220	450
Water (H ₂ O)	0	< 0.1	Pressure [MPa]	0.1	30
Nitrogen (N ₂)	0	4			
Oxygen (O ₂)	0	2			
Argon (Ar)	0	5			

Injection of carbon dioxide to underground storage areas (possibly saline aquifers) or at subsea level will lead to contact of the CO₂-rich liquid with water at very high pressures, resulting in liquid-liquid equilibria. Depending on storage depth and rock density the storage pressure can vary between 15 and 30 MPa. Estimated operation ranges for compression, transport and storage of carbon dioxide are given in Table 2.3. A detailed analysis of different processes and their operating conditions with regard to pressure and temperature range as well as relevant components and mixtures is given by Li *et al.* (2011).

Requirements for the New Mixture Model

Derived from the applications discussed above, the range of temperatures, pressures and mixtures in which the new mixture model should be valid in order to serve as a basis for process evaluations in a wide spectrum is given in Table 2.4. For most CCS related applications, the property model needs to cover the whole fluid region, including phase equilibria, for pressures up to 15 MPa and temperatures between 220 K and 500 K and gas phase properties up to 700 K. For gas turbine applications gas phase properties need to be calculated up to ca. 2000 K and 5 MPa. Liquid properties need to be calculated for pressures up to 30 MPa at temperatures below 400 K in order to cover storage scenarios. Thus, although no coverage with accurate experimental data is expected at such high temperatures and pressures, the model should extrapolate reasonably within this temperature and pressure range as well.

This work is focused on the main components of the working fluids in processes such as the ones given above, namely carbon dioxide, water, nitrogen, oxygen, and argon. Additionally, carbon monoxide is included since it may play a minor role as a combustion product in oxyfuel combustion. Other potential combustion gas constituents, such as nitrogen oxide (NO_x), sulfur dioxide (SO₂), or impurities such as hydrogen sulfide (H₂S)

found e.g. in biogas and raw natural gas may be of interest in related processes but are not included in the considerations in this work. Within the extended temperature range introduced here the molecules of some of the substances included in this model start to dissociate. This dissociation and its effect on the thermodynamic properties are however not considered in this model. A simplified dissociation model is e.g. given in the VDI guideline VDI 4670 (2003) for combustion gases.

Table 2.4: Aspired range of validity with regard to components, temperatures and pressures for the new mixture model.

Quantity	Min.	Max.	Quantity	Min.	Max.
<i>Range of compositions [mol-%]</i>			<i>Temperatures and pressures</i>		
Carbon Dioxide (CO ₂)	0	100	Temperature [K]	220	700 (2000)
Water (H ₂ O)	0	100	Pressure [MPa]	0	15 (30)
Nitrogen (N ₂)	0	100			
Oxygen (O ₂)	0	100			
Argon (Ar)	0	100			
Carbon monoxide (CO)	0	100			

2.3 General Structure

The mixture model developed in this work adapts the functional form introduced in the GERG-2004 equation of state by Kunz *et al.* (2007). It is a fundamental equation of state explicit in the Helmholtz free energy a with the independent variables density ρ , temperature T , and molar composition $\bar{x}$. The function $a(\rho, T, \bar{x})$ is split into a part a^0 , which represents the mixture of ideal gases, and a part a^r , which represents the residual mixing behavior. Written in the dimensionless, reduced form $\alpha = a/(RT)$, the basic structure of the model reads

$$\frac{a}{RT} = \alpha(\delta, \tau, \bar{x}) = \alpha^0(\rho, T, \bar{x}) + \alpha^r(\delta, \tau, \bar{x}), \quad 2.25$$

with δ as the reduced mixture density and τ as the inverse reduced mixture temperature according to

$$\delta = \rho / \rho_r(\bar{x}) \quad \text{and} \quad \tau = T_r(\bar{x}) / T. \quad 2.26$$

While the residual part α^r of the reduced Helmholtz free energy model is evaluated at reduced mixture parameters using composition-dependent reducing functions $\rho_r(\bar{x})$ and $T_r(\bar{x})$, the ideal-gas part α^0 given as

$$\alpha^0(\rho, T, \bar{x}) = \sum_{i=1}^N x_i \left[\alpha_{0,i}^0(\delta_{0,i}, \tau_{0,i}) + \ln x_i \right], \quad 2.27$$

where N is the number of components in the mixture and $\alpha_{o,i}^o$ and x_i are the dimensionless ideal-gas part of the Helmholtz free energy and the mole fraction of component i in the mixture, respectively. The sum $x_i \ln x_i$ accounts for the entropy of mixing in the ideal mixture. The contributions of the pure components to the ideal-gas Helmholtz free energy are evaluated at their component specific reduced parameters $\delta_{o,i}$ and $\tau_{o,i}$ that are usually given by

$$\delta_{o,i} = \rho / \rho_{c,i} \quad \text{and} \quad \tau_{o,i} = T_{c,i} / T. \quad 2.28$$

The residual part of the Helmholtz free energy of the mixture is given by

$$\alpha^r(\delta, \tau, \bar{x}) = \sum_{i=1}^N x_i \alpha_{o,i}^r(\delta, \tau) + \Delta \alpha^r(\delta, \tau, \bar{x}), \quad 2.29$$

where $\alpha_{o,i}^r$ is the residual part of the reduced Helmholtz free energy of component i , δ and τ are the reduced density and temperature according to Eqn. 2.26, and $\Delta \alpha^r$ is the so-called *departure function*, which is constituted by

$$\Delta \alpha^r(\delta, \tau, \bar{x}) = \sum_{i=1}^{N-1} \sum_{j=i+1}^N x_i x_j F_{ij} \alpha_{ij}^r(\delta, \tau), \quad 2.30$$

with the binary specific departure function α_{ij}^r for the components i and j and the weighing factor F_{ij} introduced by Lemmon and Jacobsen (1999) for the use of generalized departure functions for a group of binary systems.

The mixture model given in Eqns. 2.25 to 2.30 is thus a combination of pure fluid contributions, namely $\alpha_{o,i}^o$ and $\alpha_{o,i}^r$, and mixture contributions, namely the reducing functions $\rho_r(\bar{x})$ and $T_r(\bar{x})$, and the binary departure functions α_{ij}^r . For the description of the pure fluid contributions Kunz *et al.* (2007) developed new short Helmholtz equations of state specifically designed to work well with mixture models. These equations are slightly less accurate than the respective reference equation of state for the same substance but use considerably less terms, which makes them more suitable for extrapolation and calculations in the two-phase region; two important features for the calculation of mixture properties.

However, in this work the reference equations of state were chosen for the description of the pure fluid contributions. This way the transition from mixture calculations to pure fluid calculations is consistent, always using the best available model. Second, the pure fluid equation of state for water within the GERG-2004 equation of state shows considerable deviations from the IAPWS-95 equation for caloric properties in the liquid region (see Figure 2.3). While this deficiency will hardly be noticeable when calculating properties of natural gas mixtures (which that mixture model was originally designed for), such deviations become much more relevant when calculating properties of gas mixtures with higher water content, or gas solutions in water.

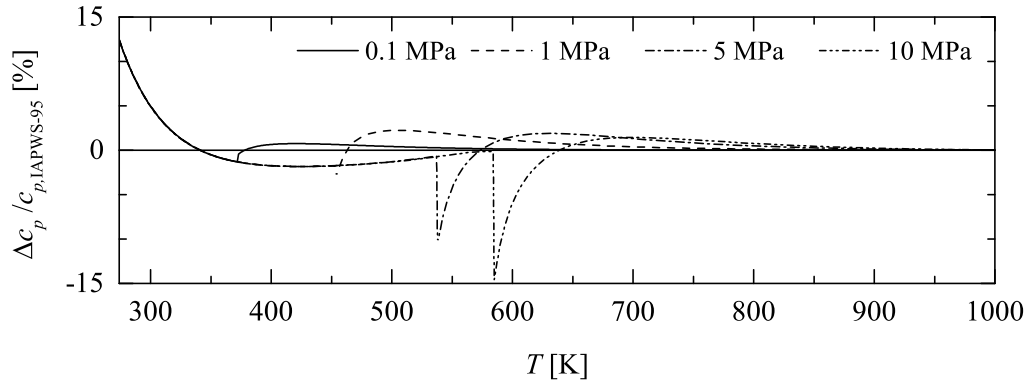


Figure 2.3: Deviations of the isobaric heat capacity calculated with the Helmholtz equation of state for water in the GERG-2004 formulation by Kunz *et al.* (2007) from the IAPWS-95 reference EOS by Wagner and Pruß (1999).

The equations of state used in this work for the description of the pure fluid contributions to the mixture Helmholtz free energy are given in Table 2.5. Details on the structure and development of Helmholtz equations of state for pure fluids can be found in the respective publications and in the comprehensive work by Span (2000).

Table 2.5: Helmholtz equations of state used for the pure components in the EOS-CG mixture model.

Component	Formula	Pure fluid equation used in the EOS-CG mixture model
Carbon dioxide	CO ₂	Reference equation of state by Span and Wagner (1996)
Water	H ₂ O	Reference equation of state by Wagner and Pruß (1999)
Nitrogen	N ₂	Reference equation of state by Span <i>et al.</i> (2000)
Oxygen	O ₂	Reference equation of state by Schmidt and Wagner (1985)
Argon	Ar	Reference equation of state by Tegeler <i>et al.</i> (1999)
Carbon monoxide	CO	Short industrial equation of state by Lemmon and Span (2006)

Based on the formulation by Kunz *et al.* (2007), the reducing functions $\rho_r(\bar{x})$ and $T_r(\bar{x})$ used in this work are given by

$$\frac{1}{\rho_r(\bar{x})} = \sum_{i=1}^N x_i^2 \frac{1}{\rho_{c,i}} + \sum_{i=1}^{N-1} \sum_{j=i+1}^N 2x_i x_j \beta_{v,ij} \gamma_{v,ij} \frac{x_i + x_j}{\beta_{v,ij}^2 x_i + x_j} \frac{1}{8} \left(\frac{1}{\rho_{c,i}^{1/3}} + \frac{1}{\rho_{c,j}^{1/3}} \right)^3, \quad 2.31$$

and

$$T_r(\bar{x}) = \sum_{i=1}^N x_i^2 T_{c,i} + \sum_{i=1}^{N-1} \sum_{j=i+1}^N 2x_i x_j \beta_{T,ij} \gamma_{T,ij} \frac{x_i + x_j}{\beta_{T,ij}^2 x_i + x_j} (T_{c,i} T_{c,j})^{0.5}. \quad 2.32$$

These functions are quadratic mixing rules that form a composition-dependent surface between the critical parameters for density and temperature (indices c) of the pure components in the mixture. The binary parameters β and γ allow for arbitrary symmetric and asymmetric shapes of the functions and are fitted to experimental data. They take into account the deviation of the real mixture behavior from the generalized combining rules by

Lorentz and Berthelot, into which Eqns. 2.31 and 2.32 merge when the binary parameters β and γ are set to unity. The binary parameters obey the following symmetry rules

$$\beta_{T,ij} = \frac{1}{\beta_{T,ji}}, \quad \beta_{v,ij} = \frac{1}{\beta_{v,ji}} \quad \text{and} \quad \gamma_{T,ij} = \gamma_{T,ji}, \quad \gamma_{v,ij} = \gamma_{v,ji}. \quad 2.33$$

The reducing functions used in this work do not fulfill the invariance condition that was first discussed by Michelsen and Kistenmacher (1990). This condition occurs when calculating multi-component mixtures and describes the effect of splitting the composition of a component in several pseudo components with the same properties. A mathematically correct model should be invariant to such splitting and return the same results as before. However, Kunz *et al.* (2007) demonstrated in their work that the effect of invariance is negligible, and the advantages of quadratic mixing rules over an alternative invariant formulation prevail.

The departure function $\Delta\alpha^r$ is introduced for the description of residual mixing effects that cannot be described accurately enough only by the use of adjusted reducing parameters β and γ . This additional empirical correlation function is based on binary departure functions α_{ij}^r and fitted to experimental data of binary mixtures. The mathematical structure is similar to the structure of the established Helmholtz free energy models for pure fluids. In his preliminary mixture model for natural gases Klimeck (2000) used polynomial terms of the form $n_{ij}\delta^{d_{ij}}\tau^{t_{ij}}$ and exponential terms of the form $n_{ij}\delta^{d_{ij}}\tau^{l_{ij}}\exp(-\delta^{l_{ij}})$. Kunz *et al.* (2007), however, replaced the simple exponential terms with a new, *special* exponential term that they found to be more suitable for the description of phase boundaries of binary mixtures of hydrocarbons, especially in the critical region. This new term has the form $n_{ij}\delta^{d_{ij}}\tau^{l_{ij}}\exp[-\eta_{ij}(\delta - \varepsilon_{ij})^2 - \beta_{ij}(\delta - \gamma_{ij})]$. In this work, all three term forms were allowed in the development of the binary departure functions, which result in the general mathematical structure

$$\begin{aligned} \alpha_{ij}^r(\delta, \tau) = & \sum_{k=1}^{K_{\text{pol},ij}} n_{ij,k} \delta^{d_{ij,k}} \tau^{t_{ij,k}} + \sum_{k=K_{\text{pol},ij}+1}^{K_{\text{pol},ij}+K_{\text{exp},ij}} n_{ij,k} \delta^{d_{ij,k}} \tau^{l_{ij,k}} \exp(-\delta^{l_{ij,k}}) \\ & + \sum_{k=K_{\text{pol},ij}+K_{\text{exp},ij}+1}^{K_{\text{pol},ij}+K_{\text{exp},ij}+K_{\text{spec},ij}} n_{ij,k} \delta^{d_{ij,k}} \tau^{l_{ij,k}} \exp\left[-\eta_{ij,k}(\delta - \varepsilon_{ij,k})^2 - \beta_{ij,k}(\delta - \gamma_{ij,k})\right]. \end{aligned} \quad 2.34$$

The coefficients n_{ij} and the exponents d_{ij} , t_{ij} , l_{ij} , η_{ij} , ε_{ij} , β_{ij} , and γ_{ij} are adjustable parameters and fitted to experimental thermodynamic properties of the binary mixture of the components i and j . The parameters η_{ij} , ε_{ij} , β_{ij} , and γ_{ij} in the special term developed by Kunz *et al.* (2007) are not independent, since the expression in the exponent $[-\eta_{ij}(\delta - \varepsilon_{ij})^2 - \beta_{ij}(\delta - \gamma_{ij})]$ can be brought to the form $[A_{ij}\delta^2 + B_{ij}\delta + C_{ij}]$, with $A_{ij} = -\eta_{ij}$, $B_{ij} = 2\varepsilon_{ij} - \beta_{ij}$ and $C_{ij} = \beta_{ij}\gamma_{ij} - \eta_{ij}\varepsilon_{ij}^2$. Therefore they should not be treated as independent parameters in the fitting process. In this work, the parameters ε_{ij} and γ_{ij} were fixed and only η_{ij} and β_{ij} were fitted.

The structure of the Helmholtz free energy mixture model can be summarized as follows:

- The ideal gas part α^0 of the reduced Helmholtz free energy, comprising of the ideal-gas parts of the Helmholtz free energy equations of all pure components considered in the mixture and an additional term due to the entropy of mixing.
- The residual part α^r of the reduced Helmholtz free energy, comprising of the residual parts of the Helmholtz free energy equations of all pure components considered in the mixture, evaluated at common reduced variables for density and temperature, and the departure function $\Delta\alpha^r$.

The mixture model can be tuned to experimental data of thermodynamic binary mixture properties by fitting

- the parameters of the reducing functions $\rho_r(\bar{x})$ and $T_r(\bar{x})$,
- the weight parameter F_{ij} in combination with a generalized departure function, and
- the coefficients and exponents of the binary departure functions α_{ij}^r .

In Figure 2.4 the mixing rules in the GERG-2008 model are given for the 15 binary systems considered in this work (see Kunz *et al.* (2007)). Except for the system nitrogen + carbon dioxide the model is only fitted to experimental mixture data by adjusting the parameters of the reducing functions. For four systems no adjustments were made at all, the reducing function parameters are set to unity and the reducing functions become quadratic combining rules.

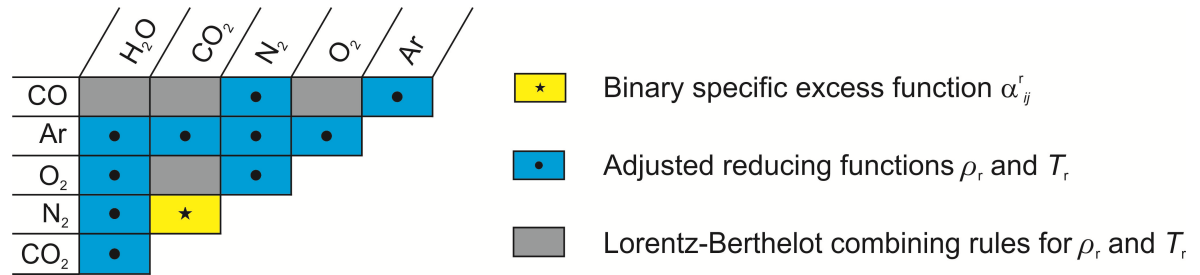


Figure 2.4: The 15 binary systems under consideration in this work and their respective binary mixture parameters and departure functions in the GERG-2008 model.

2.4 Calculation of Thermodynamic Properties from the Mixture Model

The Helmholtz free energy $A(V, T, \bar{n})$ is one of the four fundamental equations of state (or state functions) that contains all information necessary to calculate all thermodynamic properties simply by combinations of its derivatives. The other fundamental equations of state with the same characteristics are the internal energy $U(S, V, \bar{n})$, the Gibbs free energy $G(T, p, \bar{n})$, and the enthalpy $H(p, S, \bar{n})$.

Thermodynamic properties in the homogeneous region (vapor, liquid or supercritical) can be calculated easily from derivatives of $A(V, T, \bar{n})$ or $a(v, T, \bar{x})$ with respect to the volume (or density) and the temperature. As an example, the pressure is related to the Helmholtz free energy by $p = -(\partial a / \partial v)_{T, \bar{x}}$. By applying variable transformation rules, the derivatives can be expressed in terms of the reduced Helmholtz free energy α and the reduced variables δ and τ . The relation between pressure and reduced Helmholtz free energy reads

$$p(\delta, \tau, \bar{x}) = \rho RT (1 + \delta \alpha_\delta^r), \quad 2.35$$

where α_δ^r stands for the first partial derivative of the residual Helmholtz free energy α^r with respect to the reduced density δ according to

$$\alpha_\delta^r = \left(\frac{\partial \alpha^r}{\partial \delta} \right)_{\tau, \bar{x}}. \quad 2.36$$

In this fashion all thermodynamic properties may be calculated. For a more detailed derivation of the relations between the Helmholtz free energy and other thermodynamic properties, see Span (2000). A list of all common thermodynamic properties and their relation to the reduced Helmholtz free energy α is given in Table 2.6. The numerical description of the partial derivatives of the ideal-gas part and the residual part of the Helmholtz free energy mixture model needed for the calculation of all common thermodynamic properties is given in Table 2.7. The partial derivatives of the pure fluid Helmholtz equations of state employed in this mixture model are given in the respective publications (see Table 2.5). The partial derivatives of the binary departure function α_{ij}^r with respect to δ and τ are given in Table 2.8.

Since the Helmholtz free energy is a function of density and temperature as independent thermodynamic variables (plus, for mixtures, the composition), the properties calculated from derivatives of the Helmholtz free energy are also functions of density and temperature. In case the evaluation of thermodynamic properties is required at other given thermodynamic variables, e.g. temperature and pressure or pressure and enthalpy, the calculation from a Helmholtz free energy model involves the iterative determination of the original independent variables density and temperature before the actual property calculation can be performed. More details on the calculation of thermodynamic properties using input parameters other than density and temperature are given in Chapter 3.

The calculation of thermodynamic properties in a system with two (or more) phases in thermodynamic equilibrium requires the solution of the phase equilibrium conditions as given in Section 3.3. Once the density, temperature, and composition of the corresponding phases are determined, the properties of each phase can be calculated the same way as for a homogenous fluid. From the respective phase properties, the bulk properties of the overall system in two-phase equilibrium can be determined by

Table 2.6: Thermodynamic properties and their relation to the reduced Helmholtz free energy α .

Property and definition	Relation to α and its derivatives
Pressure $p(T, \rho, \bar{x}) = -(\partial a / \partial v)_{T, \bar{x}}$	$p(\delta, \tau, \bar{x}) = \rho RT (1 + \delta \alpha_\delta^r)$
Compression factor $Z(T, \rho, \bar{x}) = p / (\rho RT)$	$Z(\delta, \tau, \bar{x}) = 1 + \delta \alpha_\delta^r$
Entropy $s(T, \rho, \bar{x}) = -(\partial a / \partial T)_{v, \bar{x}}$	$s(\delta, \tau, \bar{x}) = R \left[\tau (\alpha_\tau^o + \alpha_\tau^r) - \alpha^o - \alpha^r \right]$
Internal energy $u(T, \rho, \bar{x}) = a + Ts$	$u(\delta, \tau, \bar{x}) = RT \left[\tau (\alpha_\tau^o + \alpha_\tau^r) \right]$
Isochoric heat capacity $c_v(T, \rho, \bar{x}) = (\partial u / \partial T)_{v, \bar{x}}$	$c_v(\delta, \tau, \bar{x}) = R \left[-\tau^2 (\alpha_{\tau\tau}^o + \alpha_{\tau\tau}^r) \right]$
Enthalpy $h(T, p, \bar{x}) = u + pv$	$h(\delta, \tau, \bar{x}) = RT \left[1 + \tau (\alpha_\tau^o + \alpha_\tau^r) + \delta \alpha_\delta^r \right]$
Isobaric heat capacity $c_p(T, p, \bar{x}) = (\partial h / \partial T)_{p, \bar{x}}$	$c_p(\delta, \tau, \bar{x}) = R \left[-\tau^2 (\alpha_{\tau\tau}^o + \alpha_{\tau\tau}^r) + \frac{(1 + \delta \alpha_\delta^r - \delta \tau \alpha_{\delta\tau}^r)^2}{1 + 2\delta \alpha_\delta^r + \delta^2 \alpha_{\delta\delta}^r} \right]$
Gibbs free energy $g(T, p, \bar{x}) = h - Ts$	$g(\delta, \tau, \bar{x}) = RT \left[1 - \alpha^o - \alpha^r + \delta \alpha_\delta^r \right]$
Speed of sound $w(T, p, \bar{x}) = \sqrt{(1/M)(\partial p / \partial \rho)_{s, \bar{x}}}$	$w^2(\delta, \tau, \bar{x}) = \frac{RT}{M} \left[1 + 2\delta \alpha_\delta^r + \delta^2 \alpha_{\delta\delta}^r - \frac{(1 + \delta \alpha_\delta^r - \delta \tau \alpha_{\delta\tau}^r)^2}{\tau^2 (\alpha_{\tau\tau}^o + \alpha_{\tau\tau}^r)} \right]$
Joule-Thomson coefficient $\mu_{JT}(T, p, \bar{x}) = \left(\frac{\partial T}{\partial p} \right)_{h, \bar{x}}$	$\mu_{JT}(\delta, \tau, \bar{x}) = \frac{1}{R\rho} \left[\frac{-(\delta \alpha_\delta^r + \delta^2 \alpha_{\delta\delta}^r + \delta \tau \alpha_{\delta\tau}^r)}{(1 + \delta \alpha_\delta^r - \delta \tau \alpha_{\delta\tau}^r)^2 - \tau^2 (\alpha_{\tau\tau}^o + \alpha_{\tau\tau}^r)(1 + 2\delta \alpha_\delta^r + \delta^2 \alpha_{\delta\delta}^r)} \right]$
Second thermal virial coefficient $B(T, \bar{x}) = \lim_{\rho \rightarrow 0} (\partial Z / \partial \rho)_{T, \bar{x}}$	$B(\tau, \bar{x}) = 1/\rho_r \lim_{\delta \rightarrow 0} \alpha_\delta^r$
Third thermal virial coefficient $C(T, \bar{x}) = \frac{1}{2} \lim_{\rho \rightarrow 0} (\partial^2 Z / \partial \rho^2)_{T, \bar{x}}$	$C(\tau, \bar{x}) = 1/\rho_r^2 \lim_{\delta \rightarrow 0} \alpha_{\delta\delta}^r$
Fugacity coefficient of component i $\ln \varphi_i(T, p, \bar{n}) = \int_0^p \left(\frac{\hat{v}_i}{RT} - \frac{1}{p} \right) dp_{T, \bar{n}}$	$\ln \varphi_i(\delta, \tau, \bar{x}) = (\partial n \alpha^r / \partial n_i)_{T, V, n_{j \neq i}} - \ln Z$
Fugacity of component i $f_i(T, p, \bar{x}) = x_i p \varphi_i(T, p, \bar{x})$	$f_i(\delta, \tau, \bar{x}) = x_i \rho RT \exp(\partial n \alpha^r / \partial n_i)_{T, V, n_{j \neq i}}$
Chemical potential of component i $\mu_i(T, V, \bar{n}) = (\partial A / \partial n_i)_{T, V, n_{j \neq i}}$	$\mu_i(\delta, \tau, \bar{x}) = RT \left[(\partial n \alpha^o / \partial n_i)_{T, V, n_{j \neq i}} + (\partial n \alpha^r / \partial n_i)_{T, V, n_{j \neq i}} \right]$
Pressure derivatives $(\partial p / \partial \rho)_{T, \bar{x}}$	$(\partial p / \partial \rho)_{T, \bar{x}} = RT (1 + 2\delta \alpha_\delta^r + \delta^2 \alpha_{\delta\delta}^r)$
$(\partial p / \partial T)_{\rho, \bar{x}}$	$(\partial p / \partial T)_{\rho, \bar{x}} = R\rho (1 + \delta \alpha_\delta^r - \delta \tau \alpha_{\delta\tau}^r)$

Table 2.7: The reduced Helmholtz free energy mixture model and its first and second order partial derivatives with respect to δ and τ needed for the calculation of common thermodynamic properties.

Selected derivatives of α^o with respect to δ and τ	
$\alpha^o(\rho, T, \bar{x})$	$\alpha^o = \sum_{i=1}^N x_i \left[\alpha_{o,i}^o(\delta_{o,i}, \tau_{o,i}) + \ln x_i \right]$
$\delta \left(\frac{\partial \alpha^o}{\partial \delta} \right)_{\tau, \bar{x}}$	$\delta \alpha_{\delta}^o = \sum_{i=1}^N x_i \delta_{o,i} \left(\frac{\partial \alpha_{o,i}^o(\delta_{o,i}, \tau_{o,i})}{\partial \delta_{o,i}} \right)_{\tau_{o,i}}$
$\delta^2 \left(\frac{\partial^2 \alpha^o}{\partial \delta^2} \right)_{\tau, \bar{x}}$	$\delta^2 \alpha_{\delta\delta}^o = \sum_{i=1}^N x_i \delta_{o,i}^2 \left(\frac{\partial^2 \alpha_{o,i}^o(\delta_{o,i}, \tau_{o,i})}{\partial \delta_{o,i}^2} \right)_{\tau_{o,i}}$
$\tau \left(\frac{\partial \alpha^o}{\partial \tau} \right)_{\delta, \bar{x}}$	$\tau \alpha_{\tau}^o = \sum_{i=1}^N x_i \tau_{o,i} \left(\frac{\partial \alpha_{o,i}^o(\delta_{o,i}, \tau_{o,i})}{\partial \tau_{o,i}} \right)_{\delta_{o,i}}$
$\tau^2 \left(\frac{\partial^2 \alpha^o}{\partial \tau^2} \right)_{\delta, \bar{x}}$	$\tau^2 \alpha_{\tau\tau}^o = \sum_{i=1}^N x_i \tau_{o,i}^2 \left(\frac{\partial^2 \alpha_{o,i}^o(\delta_{o,i}, \tau_{o,i})}{\partial \tau_{o,i}^2} \right)_{\delta_{o,i}}$
$\delta \tau \left(\frac{\partial^2 \alpha^o}{\partial \delta \partial \tau} \right)_{\bar{x}}$	$\delta \tau \alpha_{\delta\tau}^o = 0$
$\delta \tau^2 \left(\frac{\partial^3 \alpha^o}{\partial \delta \partial \tau^2} \right)_{\bar{x}}$	$\delta \tau^2 \alpha_{\delta\tau\tau}^o = 0$
Selected derivatives of α^r with respect to δ and τ	
$\alpha^r(\delta, \tau, \bar{x})$	$\alpha^r = \sum_{i=1}^N x_i \alpha_{o,i}^r(\delta, \tau) + \sum_{i=1}^{N-1} \sum_{j=i+1}^N x_i x_j F_{ij} \alpha_{ij}^r(\delta, \tau)$
$\delta \left(\frac{\partial \alpha^r}{\partial \delta} \right)_{\tau, \bar{x}}$	$\delta \alpha_{\delta}^r = \sum_{i=1}^N x_i \delta \left(\frac{\partial \alpha_{o,i}^r}{\partial \delta} \right)_{\tau} + \sum_{i=1}^{N-1} \sum_{j=i+1}^N x_i x_j F_{ij} \delta \left(\frac{\partial \alpha_{ij}^r}{\partial \delta} \right)_{\tau}$
$\delta^2 \left(\frac{\partial^2 \alpha^r}{\partial \delta^2} \right)_{\tau, \bar{x}}$	$\delta^2 \alpha_{\delta\delta}^r = \sum_{i=1}^N x_i \delta^2 \left(\frac{\partial^2 \alpha_{o,i}^r}{\partial \delta^2} \right)_{\tau} + \sum_{i=1}^{N-1} \sum_{j=i+1}^N x_i x_j F_{ij} \delta^2 \left(\frac{\partial^2 \alpha_{ij}^r}{\partial \delta^2} \right)_{\tau}$
$\tau \left(\frac{\partial \alpha^r}{\partial \tau} \right)_{\delta, \bar{x}}$	$\tau \alpha_{\tau}^r = \sum_{i=1}^N x_i \tau \left(\frac{\partial \alpha_{o,i}^r}{\partial \tau} \right)_{\delta} + \sum_{i=1}^{N-1} \sum_{j=i+1}^N x_i x_j F_{ij} \tau \left(\frac{\partial \alpha_{ij}^r}{\partial \tau} \right)_{\delta}$
$\tau^2 \left(\frac{\partial^2 \alpha^r}{\partial \tau^2} \right)_{\delta, \bar{x}}$	$\tau^2 \alpha_{\tau\tau}^r = \sum_{i=1}^N x_i \tau^2 \left(\frac{\partial^2 \alpha_{o,i}^r}{\partial \tau^2} \right)_{\delta} + \sum_{i=1}^{N-1} \sum_{j=i+1}^N x_i x_j F_{ij} \tau^2 \left(\frac{\partial^2 \alpha_{ij}^r}{\partial \tau^2} \right)_{\delta}$
$\delta \tau \left(\frac{\partial^2 \alpha^r}{\partial \delta \partial \tau} \right)_{\bar{x}}$	$\delta \tau \alpha_{\delta\tau}^r = \sum_{i=1}^N x_i \delta \tau \left(\frac{\partial^2 \alpha_{o,i}^r}{\partial \delta \partial \tau} \right) + \sum_{i=1}^{N-1} \sum_{j=i+1}^N x_i x_j F_{ij} \delta \tau \left(\frac{\partial^2 \alpha_{ij}^r}{\partial \delta \partial \tau} \right)$
$\delta \tau^2 \left(\frac{\partial^3 \alpha^r}{\partial \delta \partial \tau^2} \right)_{\bar{x}}$	$\delta \tau^2 \alpha_{\delta\tau\tau}^r = \sum_{i=1}^N x_i \delta \tau^2 \left(\frac{\partial^3 \alpha_{o,i}^r}{\partial \delta \partial \tau^2} \right) + \sum_{i=1}^{N-1} \sum_{j=i+1}^N x_i x_j F_{ij} \delta \tau^2 \left(\frac{\partial^3 \alpha_{ij}^r}{\partial \delta \partial \tau^2} \right)$

Table 2.8: The binary departure function α_{ij}^r and its derivatives with respect to the reduced mixture variables δ and τ .

$$\alpha_{ij}^r(\delta, \tau) = \sum_{k=1}^{K_{\text{pol},ij}} \alpha_{ij,k,\text{pol}}^r(\delta, \tau) + \sum_{k=K_{\text{pol},ij}+1}^{K_{\text{pol},ij}+K_{\text{exp},ij}} \alpha_{ij,k,\text{exp}}^r(\delta, \tau) + \sum_{k=K_{\text{pol},ij}+K_{\text{exp},ij}+1}^{K_{\text{pol},ij}+K_{\text{exp},ij}+K_{\text{spec},ij}} \alpha_{ij,k,\text{spec}}^r(\delta, \tau), \quad \text{with}$$

$$\alpha_{ij,k,\text{pol}}^r(\delta, \tau) = n_{ij,k} \delta^{d_{ij,k}} \tau^{t_{ij,k}},$$

$$\alpha_{ij,k,\text{exp}}^r(\delta, \tau) = n_{ij,k} \delta^{d_{ij,k}} \tau^{t_{ij,k}} \exp(-\delta^{l_{ij,k}}), \quad \text{and}$$

$$\alpha_{ij,k,\text{spec}}^r(\delta, \tau) = n_{ij,k} \delta^{d_{ij,k}} \tau^{t_{ij,k}} \exp\left[-\eta_{ij,k}(\delta - \varepsilon_{ij,k})^2 - \beta_{ij,k}(\delta - \gamma_{ij,k})\right].$$

$$\delta \left(\frac{\partial \alpha_{ij}^r}{\partial \delta} \right)_{\tau, \bar{x}} = \sum_{k=1}^{K_{\text{pol},ij}} d_{ij,k} \alpha_{ij,k,\text{pol}}^r(\delta, \tau) + \sum_{k=K_{\text{pol},ij}+1}^{K_{\text{pol},ij}+K_{\text{exp},ij}} (d_{ij,k} - l_{ij,k} \delta^{l_{ij,k}}) \alpha_{ij,k,\text{exp}}^r(\delta, \tau)$$

$$+ \sum_{k=K_{\text{pol},ij}+K_{\text{exp},ij}+1}^{K_{\text{pol},ij}+K_{\text{exp},ij}+K_{\text{spec},ij}} \left[d_{ij,k} - \delta (2\eta_{ij,k}(\delta - \varepsilon_{ij,k}) + \beta_{ij,k}) \right] \alpha_{ij,k,\text{spec}}^r(\delta, \tau)$$

$$\delta^2 \left(\frac{\partial^2 \alpha_{ij}^r}{\partial \delta^2} \right)_{\tau, \bar{x}} = \sum_{k=1}^{K_{\text{pol},ij}} d_{ij,k} (d_{ij,k} - 1) \alpha_{ij,k,\text{pol}}^r(\delta, \tau)$$

$$+ \sum_{k=K_{\text{pol},ij}+1}^{K_{\text{pol},ij}+K_{\text{exp},ij}} \left[(d_{ij,k} - l_{ij,k} \delta^{l_{ij,k}}) (d_{ij,k} - 1 - l_{ij,k} \delta^{l_{ij,k}}) - l_{ij,k}^2 \delta^{l_{ij,k}} \right] \alpha_{ij,k,\text{exp}}^r(\delta, \tau)$$

$$+ \sum_{k=K_{\text{pol},ij}+K_{\text{exp},ij}+1}^{K_{\text{pol},ij}+K_{\text{exp},ij}+K_{\text{spec},ij}} \left[2\eta_{ij,k} \delta^2 - d_{ij,k} + (d_{ij,k} - \delta (2\eta_{ij,k}(\delta - \varepsilon_{ij,k}) + \beta_{ij,k}))^2 \right] \alpha_{ij,k,\text{spec}}^r(\delta, \tau)$$

$$\tau \left(\frac{\partial \alpha_{ij}^r}{\partial \tau} \right)_{\delta, \bar{x}} = \sum_{k=1}^{K_{\text{pol},ij}} t_{ij,k} \alpha_{ij,k,\text{pol}}^r(\delta, \tau) + \sum_{k=K_{\text{pol},ij}+1}^{K_{\text{pol},ij}+K_{\text{exp},ij}} t_{ij,k} \alpha_{ij,k,\text{exp}}^r(\delta, \tau) + \sum_{k=K_{\text{pol},ij}+K_{\text{exp},ij}+1}^{K_{\text{pol},ij}+K_{\text{exp},ij}+K_{\text{spec},ij}} t_{ij,k} \alpha_{ij,k,\text{spec}}^r(\delta, \tau)$$

$$\tau^2 \left(\frac{\partial^2 \alpha_{ij}^r}{\partial \tau^2} \right)_{\delta, \bar{x}} = \sum_{k=1}^{K_{\text{pol},ij}} t_{ij,k} (t_{ij,k} - 1) \alpha_{ij,k,\text{pol}}^r(\delta, \tau) + \sum_{k=K_{\text{pol},ij}+1}^{K_{\text{pol},ij}+K_{\text{exp},ij}} t_{ij,k} (t_{ij,k} - 1) \alpha_{ij,k,\text{exp}}^r(\delta, \tau)$$

$$+ \sum_{k=K_{\text{pol},ij}+K_{\text{exp},ij}+1}^{K_{\text{pol},ij}+K_{\text{exp},ij}+K_{\text{spec},ij}} t_{ij,k} (t_{ij,k} - 1) \alpha_{ij,k,\text{spec}}^r(\delta, \tau)$$

$$\delta \tau \left(\frac{\partial^2 \alpha_{ij}^r}{\partial \delta \partial \tau} \right)_{\bar{x}} = \sum_{k=1}^{K_{\text{pol},ij}} d_{ij,k} t_{ij,k} \alpha_{ij,k,\text{pol}}^r(\delta, \tau) + \sum_{k=K_{\text{pol},ij}+1}^{K_{\text{pol},ij}+K_{\text{exp},ij}} (d_{ij,k} - l_{ij,k} \delta^{l_{ij,k}}) t_{ij,k} \alpha_{ij,k,\text{exp}}^r(\delta, \tau)$$

$$+ \sum_{k=K_{\text{pol},ij}+K_{\text{exp},ij}+1}^{K_{\text{pol},ij}+K_{\text{exp},ij}+K_{\text{spec},ij}} \left[d_{ij,k} - \delta (2\eta_{ij,k}(\delta - \varepsilon_{ij,k}) + \beta_{ij,k}) \right] t_{ij,k} \alpha_{ij,k,\text{spec}}^r(\delta, \tau)$$

$$\delta \tau^2 \left(\frac{\partial^3 \alpha_{ij}^r}{\partial \delta \partial \tau^2} \right)_{\bar{x}} = \sum_{k=1}^{K_{\text{pol},ij}} d_{ij,k} t_{ij,k} (t_{ij,k} - 1) \alpha_{ij,k,\text{pol}}^r(\delta, \tau) + \sum_{k=K_{\text{pol},ij}+1}^{K_{\text{pol},ij}+K_{\text{exp},ij}} (d_{ij,k} - l_{ij,k} \delta^{l_{ij,k}}) t_{ij,k} (t_{ij,k} - 1) \alpha_{ij,k,\text{exp}}^r(\delta, \tau)$$

$$+ \sum_{k=K_{\text{pol},ij}+K_{\text{exp},ij}+1}^{K_{\text{pol},ij}+K_{\text{exp},ij}+K_{\text{spec},ij}} \left[d_{ij,k} - \delta (2\eta_{ij,k}(\delta - \varepsilon_{ij,k}) + \beta_{ij,k}) \right] t_{ij,k} (t_{ij,k} - 1) \alpha_{ij,k,\text{spec}}^r(\delta, \tau)$$

$$z(\rho, T, \bar{x}) = \beta z''(\rho'', T, \bar{x}'') + (1 - \beta) z'(\rho', T, \bar{x}'), \quad 2.37$$

where z stands for an arbitrary thermodynamic molar bulk property, z' , z'' , ρ' , ρ'' , $\bar{x}'$, and $\bar{x}''$ are the respective properties, densities and compositions of the two phases in equilibrium, and β is the molar phase fraction of the phase denoted " (usually the vapor phase).

2.5 Parameters

The new Helmholtz energy mixture model consists of six components (see Table 2.5), resulting in 15 binary systems. Depending on the amount and quality of the available experimental data, as well as on the complexity of the mixing behavior, the mixture model was adjusted to experimental data by fitting the binary parameters of the reducing functions given in Eqns. 2.31 and 2.32, by developing binary specific departure functions (Eqn. 2.34) with adjusted coefficients and exponents or by adjusting the weight parameter for a generalized departure function, F_{ij} . In order to summarize the full information on the new mixture model within this chapter, the model parameters are given in the tables below. Details on the fitting procedure are discussed in Chapter 4, and examples of the representation of experimental data by the new mixture model are given in Chapter 5.

Table 2.9: Parameters of the reducing functions given in Eqns. 2.31 and 2.32 for the 15 binary systems of the new mixture model.

Mixture ij	$\beta_{T,ij}$	$\gamma_{T,ij}$	$\beta_{v,ij}$	$\gamma_{v,ij}$	F_{ij}
CO ₂ -H ₂ O	1.030538	0.828472	1.021392	0.895156	1
CO ₂ -N ₂ ^a	0.994140013	1.107654104	1.022709642	1.047578256	1
CO ₂ -O ₂	1.000000	1.031986	1.000000	1.084460	0
CO ₂ -Ar	1.027147	0.968781	1.001378	1.029710	1
CO ₂ -CO	0.993245	1.068392	1.030855	1.245499	0
H ₂ O-N ₂	0.954149	0.805147	1.079628	0.733443	1
H ₂ O-O ₂	0.798046	0.807842	0.972576	0.873460	0.6017
H ₂ O-Ar	0.679104	0.921000	0.940398	1.050952	0
H ₂ O-CO	1.045927	0.823984	1.063348	0.766756	0.9897
N ₂ -O ₂ ^a	0.997190589	0.995157044	0.999521770	0.997082328	0
N ₂ -Ar	0.999442	0.989311	1.006697	1.001549	0
N ₂ -CO	1.002409	0.994100	1.000000	1.001317	0
O ₂ -Ar	0.999039	0.988822	1.006502	1.001341	0
O ₂ -CO ^b	1.000000	1.000000	1.000000	1.000000	0
CO-Ar ^a	1.000000000	0.954215746	1.000000000	1.159720623	0

^a Binary mixture model taken from the GERG-2004 equation of state with no modifications.

^b No fitting of the binary interaction parameters due to lack of data.

Table 2.10: Parameters of the binary departure functions of the new mixture model (Eqn. 2.34).

k	$n_{ij,k}$	$t_{ij,k}$	$d_{ij,k}$	$l_{ij,k}$	$\eta_{ij,k}$	$\varepsilon_{ij,k}$	$\beta_{ij,k}$	$\gamma_{ij,k}$
CO₂–H₂O								
1	3.9440467×10^{-1}	0.880	1	0	–	–	–	–
2	–1.7634732	2.932	1	0	–	–	–	–
3	1.4620755×10^{-1}	2.433	3	0	–	–	–	–
4	8.7522320×10^{-3}	1.330	0	1	–	–	–	–
5	2.0349398	4.416	2	1	–	–	–	–
6	$-9.0350250 \times 10^{-2}$	5.514	3	1	–	–	–	–
7	$-2.1638854 \times 10^{-1}$	5.203	1	2	–	–	–	–
8	3.9612170×10^{-2}	1.000	5	2	–	–	–	–
CO₂–N₂^a								
1	$2.8661625028399 \times 10^{-1}$	1.850	2	–	–	–	–	–
2	$-1.0919833861247 \times 10^{-1}$	1.400	3	–	–	–	–	–
3	–1.1374032082270	3.200	1	–	0.25	0.5	0.75	0.5
4	$7.6580544237358 \times 10^{-1}$	2.500	1	–	0.25	0.5	1.00	0.5
5	$4.2638000926819 \times 10^{-3}$	8.000	1	–	0.00	0.5	2.00	0.5
6	$1.7673538204534 \times 10^{-1}$	3.750	2	–	0.00	0.5	3.00	0.5
CO₂–Ar								
1	2.0483577×10^{-1}	2.194	2	–	–	–	–	–
2	$-1.1465124 \times 10^{-1}$	1.743	3	–	–	–	–	–
3	–2.3151700	2.470	1	–	0.25	0.5	0.75	0.5
4	2.3523617	1.977	1	–	0.25	0.5	1.00	0.5
5	$-6.6835959 \times 10^{-1}$	1.207	1	–	0.00	0.5	1.05	0.5
6	$-5.3016558 \times 10^{-2}$	0.796	2	–	0.00	0.5	3.00	0.5
H₂O–N₂, H₂O–O₂, H₂O–CO								
1	4.0142079	0.547	1	–	–	–	–	–
2	–1.1573939	0.055	1	1	–	–	–	–
3	–7.2102425	1.925	1	1	–	–	–	–
4	–5.3251223	0.552	2	1	–	–	–	–
5	–2.2155867	1.000	4	1	–	–	–	–

^a Binary mixture model taken from the GERG-2004 equation of state with no modifications.

The parameters of the reducing functions for all 15 binary systems are given in Table 2.9; an overview is given in Figure 2.5. For 11 out of the 15 binary systems new parameter sets were developed during this work. For three binary systems (CO₂–N₂, N₂–O₂, and CO–Ar) the reducing parameters were taken from the GERG-2004 equation of state by Kunz *et al.*

(2007) without modification. Based on the data situation for the respective mixtures these parameter sets were found to be the best possible fit.

For one binary system (O_2 -CO) the parameters were not adjusted, since no experimental data could be found in the literature. For this system the reducing function parameters are set to unity, converting the reducing functions into the generalized Lorentz-Berthelot combining rules.

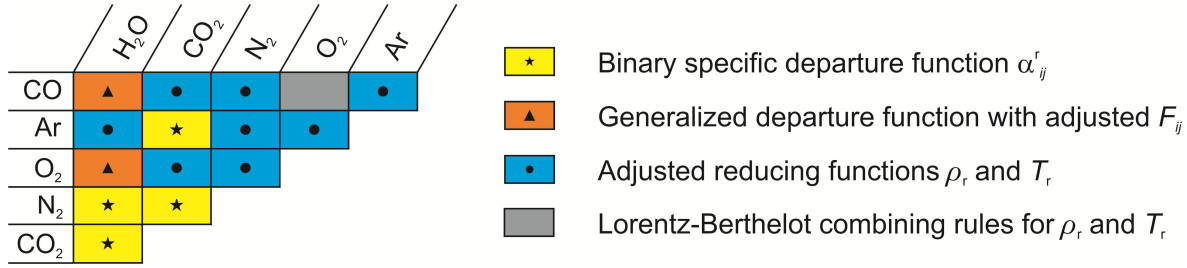


Figure 2.5: The 15 binary systems under consideration in this work and their respective binary mixture parameters and departure functions in the new EOS-CG mixture model.

Beside to the adjusted reducing function parameters, the new mixture model contains binary specific departure functions for four binary systems, namely CO_2 - H_2O , CO_2 - N_2 , CO_2 -Ar, and H_2O - N_2 (see Table 2.10). The binary departure function for the system CO_2 - N_2 was again taken from the GERG-2004 equation of state without modification. Since the system is also of major relevance for natural gas mixtures, it was studied well both experimentally and theoretically, resulting in a binary specific departure function in the GERG-2004 equation that yields accurate results both for the homogeneous phase as well as for the properties on the phase boundaries. For the three systems CO_2 - H_2O , CO_2 -Ar and H_2O - N_2 binary departure functions were developed as part of this work. For the systems H_2O - O_2 and H_2O -CO the departure function developed for H_2O - N_2 is used with an adjusted weight parameter F_{ij} .

3 STABILITY ANALYSIS AND FLASH CALCULATION

As already discussed in Section 2.4, the mathematical structure of the mixture model presented in this work allows for the calculation of all thermodynamic properties by combining derivatives of the reduced Helmholtz free energy. However, a reliable phase stability algorithm is important in order to use the model for the property calculation in the whole fluid region without any previous knowledge about the phase boundaries of the given mixture. Once such an algorithm detects instability (which means that the mixture will split into two or more phases at the given conditions and at thermodynamic equilibrium), the properties of the phases in equilibrium have to be calculated by means of a flash algorithm.

The algorithms for the calculation of the phase stability, phase envelope, flash, and density described in this chapter were developed in cooperation with A. Jäger at the thermodynamics group at the Ruhr-University Bochum. A publication is currently in progress and will be submitted to the *Fluid Phase Equilibria* journal [Gernert *et al.* (2013)].

3.1 Phase Stability Condition

A thermodynamic system as well as other, e.g. mechanical systems, is defined as *stable* if it returns to its original state after being forced into other states in its neighborhood. If the system does not return to its original state after a forced displacement, but moves further away, it is called *unstable*. A system is in a *neutral* state if it stays in its new state after a forced displacement, and a state is called *metastable* if the system returns to its original state after an infinitesimal displacement, but will move to a different state after larger displacements (compare Figure 3.1a-Figure 3.1d). In thermodynamics, as well as in mechanics, all processes are directed towards stability; an unstable state cannot be realized since a system always undergoes small disturbances. [Stephan *et al.* (2010)]

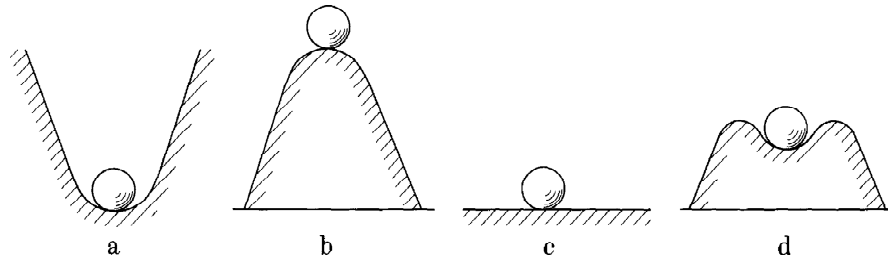


Figure 3.1: Visualization of a thermodynamically stable (a), unstable (b), neutral (c), and metastable (d) state [Stephan *et al.* (2010)].

Derived from the considerations above, thermodynamic equilibrium or a thermodynamically stable state in a closed system is always the result of a minimum of its Gibbs free

energetic potential, in other words, any displacement within a thermodynamically stable system will lead to an increase of the Gibbs free energy:

$$\Delta G(T, p, \bar{n}) > 0 \quad \text{for } T, p, n_i = \text{const.} \quad 3.1$$

By applying the Legendre transformation, this relation can be expressed in other thermodynamic state functions and results in

$$\begin{aligned} \Delta S(U, V, \bar{n}) &< 0 & \text{for } U, V, n_i &= \text{const,} \\ \Delta U(S, V, \bar{n}) &> 0 & \text{for } S, V, n_i &= \text{const,} \\ \Delta A(T, V, \bar{n}) &> 0 & \text{for } T, V, n_i &= \text{const,} \\ \Delta H(S, p, \bar{n}) &> 0 & \text{for } S, p, n_i &= \text{const.} \end{aligned} \quad 3.2$$

This concludes that as a necessary stability criterion all fundamental equations of state, namely $G(T, p, \bar{n})$, $A(T, V, \bar{n})$, $U(S, V, \bar{n})$, and $H(S, p, \bar{n})$, have to be at a minimum. Based on these considerations, more stability criteria can be derived.

Mechanical Stability

Since the Helmholtz free energy A has to have a minimum at stability, the condition

$$\left(\frac{\partial^2 A}{\partial V^2} \right)_{T, \bar{n}} > 0 \quad 3.3$$

has to be fulfilled. With

$$dA = -SdT - pdV + \sum_{i=1}^N \mu_i dn_i \quad 3.4$$

and thus

$$\left(\frac{\partial A}{\partial V} \right)_{T, \bar{n}} = -p \quad 3.5$$

Eqn. 3.3 can be rewritten in the following form:

$$\left(\frac{\partial p}{\partial V} \right)_{T, \bar{n}} < 0. \quad 3.6$$

The mechanical stability condition given in Eqn. 3.6 says that an increase in pressure at constant temperature and amount of substance results in a decrease in volume.

Thermal Stability

As with the mechanical stability, the thermal stability can be derived from the minimum of a fundamental equation of state. From the minimum of the internal energy U at stability, the relation

$$\left(\frac{\partial^2 U}{\partial S^2} \right)_{V, \bar{n}} > 0 \quad 3.7$$

is given. Since the total differential of U can be expressed as

$$dU = TdS - pdV + \sum_{i=1}^N \mu_i dn_i \quad 3.8$$

and thus the partial derivative of U with respect to the entropy S gives

$$\left(\frac{\partial U}{\partial S} \right)_{V, \bar{n}} = T. \quad 3.9$$

Eqn. 3.7 can be transformed to

$$\left(\frac{\partial T}{\partial S} \right)_{V, \bar{n}} > 0. \quad 3.10$$

The expression in Eqn. 3.10 implies that heating a closed system (which results in an increase in entropy) has to lead to an increase in temperature.

Chemical Stability

The third commonly known criterion derived from the minimum condition of the state functions at stability is the chemical stability or the stability concerning the exchange of substance. From the minimum of the Gibbs free energy G , one gets:

$$\left(\frac{\partial^2 G}{\partial n_i^2} \right)_{T, p, n_{k \neq i}} > 0. \quad 3.11$$

From the total differential of the fundamental equation of state

$$dG = -SdT + Vdp + \sum_{i=1}^N \mu_i dn_i \quad 3.12$$

and using the relation between G and the chemical potential μ_i of component i in the mixture

$$\left(\frac{\partial G}{\partial n_i} \right)_{T, p, n_{k \neq i}} = \mu_i, \quad 3.13$$

Eqn. 3.11 can be brought to the form

$$\left(\frac{\partial \mu_i}{\partial n_i} \right)_{T, p, n_{k \neq i}} > 0. \quad 3.14$$

In other words: any transfer of material across the system boundaries at constant temperature and pressure leads to an increase of the chemical potential.

The stability criterion for an N -component system has been generalized by Reid and Beegle (1977) as follows:

$$y_{(k+1)(k+1)}^k > 0, \quad 1 \leq k \leq N, \quad 3.15$$

where y^k is the k^{th} order Legendre transform of the thermodynamic base function (or fundamental equation of state)

$$y^0 = U(S, V, n_1, n_2, \dots, n_N) = f(x_1, x_2, \dots, x_{N+2}) \quad 3.16$$

and $y_{(k+1)(k+1)}^k$ is the second-order partial derivative with respect to the extensive variable x_{k+1} (which, in this context, does not denote a mole fraction). The Legendre transforms can be calculated from the base function using the relation

$$y^k = y^0 - \sum_{i=1}^k \xi_i x_i = f(\xi_1, \dots, \xi_k, x_{k+1}, \dots, x_{N+2}) \quad 3.17$$

where ξ_i denote the partial derivatives of y^0 with respect to x_i according to

$$\xi_i = \left(\frac{\partial y^0}{\partial x_i} \right)_{x_{j \neq i}}. \quad 3.18$$

From this generalized approach, the three stability criteria given in Eqns. 3.3, 3.7 and 3.11 can be derived as well. The Helmholtz energy is the first Legendre transform of U and reads

$$y^1 = A = U - TS = A(\partial U / \partial S, V, n_1, n_2, \dots, n_N) \quad \text{with} \quad \partial U / \partial S = T, \quad 3.19$$

and therefore the general stability criterion can be transformed to the mechanical stability by

$$y_{22}^1 = \left(\frac{\partial^2 A}{\partial V^2} \right)_{T, \bar{n}} > 0. \quad 3.20$$

The second stability criterion – the thermal stability – can be related to the general approach in the same fashion:

$$y_{11}^0 = \left(\frac{\partial^2 U}{\partial S^2} \right)_{V, \bar{n}} > 0. \quad 3.21$$

For the third criterion, the Gibbs free energy needs to be determined from U ; it is the second-order Legendre transform and reads

$$y^2 = G = U - TS + pV = G(\partial U / \partial S, \partial U / \partial V, n_1, n_2, \dots, n_N) \quad \text{with} \quad \partial U / \partial V = -p. \quad 3.22$$

The chemical stability criterion then follows

$$y_{33}^2 = \left(\frac{\partial^2 G}{\partial n_i^2} \right)_{T, p, n_{k \neq i}} > 0. \quad 3.23$$

It can be applied to any component derivative i , since the order of components in the system is irrelevant.

3.2 Stability Calculation

As described above, a thermodynamic system is stable if its state functions ($G(T, p, \bar{n})$, $A(T, V, \bar{n})$, $U(S, V, \bar{n})$, and $H(S, p, \bar{n})$) are at their minima. If this is not the case, the system is unstable and decomposes into two or more coexisting phases. Most commonly, the stability analysis is performed in terms of the Gibbs free energy G . This has the advantage that the Gibbs state function has the temperature T and the pressure p as independent variables. Since both temperature and pressure must have the same value in

coexisting phases, the stability analysis only has to be performed as a function of the composition.

Performing stability tests and calculating phase equilibria for multi-component mixtures has been the focus of much research over the last several decades. The challenge lies in the contradictory goals of developing an efficient yet stable and reliable algorithm. A number of different approaches were developed for the task of finding the global minimum of a multidimensional state function. Originated in the simulation of annealing processes, the simulated annealing algorithm, a stochastic search algorithm applicable to many global optimization problems by Corana *et al.* (1987), was adapted by Zhu [Zhu and Xu (1999), Zhu *et al.* (2000)], and further investigated by Rangaiah (2001) and Henderson *et al.* (2001) to find the global minimum of the Gibbs free energy. Other stochastic search algorithms for the direct global optimization of the Gibbs free energy were suggested by Lee *et al.* (1999) and Nichita *et al.* (2002). For activity coefficient models, McDonald and Floudas (1995, 1996) reformulated the Gibbs free energy minimization problem with UNIFAC and the Wilson equation and used a branch and bound algorithm to solve the set of equations. Hua *et al.* (1996a, 1996b, 1998) used an interval analysis method combined with the Newton iteration to solve the nonlinear set of equations resulting from the Gibbs free energy minimization problem, without the need of initial guesses of phase compositions, and demonstrated the algorithm on cubic equations of state. The area method suggested by Eubank *et al.* (1992) uses the integral of the Gibbs energy function rather than its derivatives, combined with a grid search, to find the approximate location of its solutions.

3.2.1 The Tangent Plane Condition

The phase stability calculation algorithm used in this work is based on the formulation by Michelsen [Michelsen (1982a, 1982b), and Michelsen and Mollerup (2004)] and is also described in detail in the GERG-2004 monograph by Kunz *et al.* (2007), Section 7.5. It uses the tangent plane condition of the Gibbs free energy of mixing as stability criterion, which was first introduced by Baker *et al.* (1982). Consider the total differential of the Gibbs free energy

$$dG = -SdT + Vdp + \sum_{i=1}^N \mu_i dn_i . \quad 3.24$$

At constant T and p , the only way of changing the overall Gibbs free energy is to create a new phase by removing a differential amount of matter $\delta \bar{n}$ from the initial phase². Assuming that the changes in the independent variables of the initial phase are small

² In this context, δ denotes a differential quantity, not the reduced mixture density.

enough that the change of the chemical potentials after the removal of $\delta\bar{n}$ can be neglected, the resulting change in the Gibbs free energy of the initial phase equals

$$\delta G = -\sum_{i=1}^N \mu_i \delta n_i . \quad 3.25$$

At the same time, the Gibbs free energy of the new phase becomes

$$\delta G^+ = \sum_{i=1}^N \mu_i^+ \delta n_i , \quad 3.26$$

with μ_i^+ as the chemical potentials in the new phase. The initial phase is stable if the resulting change in the overall Gibbs free energy by the formation of a new phase is positive:

$$\Delta G = \delta G + \delta G^+ = \sum_{i=1}^N (\mu_i^+ - \mu_i) \delta n_i > 0 . \quad 3.27$$

Eqn. 3.27 can also be written in terms of mole fractions instead of amounts of substance. The initial phase with the composition $\bar{x}$ and the corresponding chemical potentials $\mu_i(\bar{x})$ is stable if the change of the Gibbs free energy is positive after transferring an infinitesimal amount $\delta\bar{n}$ to a new phase with the composition $\bar{w}$:

$$\delta G = \delta n \sum_{i=1}^N w_i [\mu_i(\bar{w}) - \mu_i(\bar{x})] \geq 0 . \quad 3.28$$

This relation leads to the tangent plane condition of Gibbs: A necessary and sufficient condition for stability of the phase of composition $\bar{x}$ is that δG is non-negative for any positive $\delta\bar{n}$ and for any other valid composition $\bar{w}$. Since $\delta\bar{n}$ is always positive, Eqn. 3.28 can be simplified to the tangent plane distance function *TPD*

$$TPD(\bar{w}) = \sum_{i=1}^N w_i [\mu_i(\bar{w}) - \mu_i(\bar{x})] \geq 0 , \quad 3.29$$

which has to be non-negative for any trial phase $\bar{w}$ in order for the initial phase $\bar{x}$ to be stable. Kunz *et al.* (2007) showed that the above expression can be transformed to a more convenient, reduced form that uses the fugacity coefficients ϕ_i rather than the chemical potentials μ_i

$$tpd(\bar{w}) = \frac{TPD(\bar{w})}{RT} = \sum_{i=1}^N w_i [\ln w_i + \ln \phi_i(\bar{w}) - \ln x_i - \ln \phi_i(\bar{x})] . \quad 3.30$$

3.2.2 Stability Calculation Algorithm

Based on the considerations by Michelsen and Mollerup (2004), a stability check can be performed using the following steps.

Step 1: Generation of Initial Estimates

The stability calculation starts with the assumption that two phases are present. For an initial estimate of the phase compositions the *K*-factors are calculated using the correlation suggested by Wilson (1968)

$$\ln K_i = \ln \frac{p_{c,i}}{p} + 5.373(1 + \omega_i) \left(1 - \frac{T_{c,i}}{T} \right), \quad 3.31$$

with the definition of the K -factor being

$$\ln K_i = \ln \frac{x_i''}{x_i'} = \ln \frac{\phi_i'}{\phi_i''}. \quad 3.32$$

In Eqn. 3.32, '' denotes a vapor phase and ' a liquid phase. The Wilson K -factors are used to solve for initial estimates of the phase compositions $\bar{x}''$ and $\bar{x}'$ by applying the Rachford-Rice equation

$$\sum_{i=1}^N (x_i'' - x_i') = 0. \quad 3.33$$

Step 1.1: Rachford-Rice Solver

In order to solve Eqn. 3.33, the following relations between the phase compositions x_i'' and x_i' , the feed composition x_i , the vapor fraction β , and the K -factor K_i are used³:

$$x_i'' = \frac{K_i x_i}{1 - \beta + \beta K_i} \quad \text{and} \quad x_i' = \frac{x_i}{1 - \beta + \beta K_i}, \quad i = 1 \dots N, \quad 3.34$$

with the definition of the molar vapor fraction β being

$$\beta = \frac{n''}{n} = \frac{n''}{n' + n''} = \frac{x_i - x_i'}{x_i'' - x_i'}, \quad i = 1 \dots N. \quad 3.35$$

After combining Eqns. 3.33 and 3.34, the Rachford-Rice equation reads

$$g(\beta) = \sum_{i=1}^N x_i \left(\frac{K_i - 1}{1 - \beta + \beta K_i} \right) = 0. \quad 3.36$$

If the rewritten Rachford-Rice equation (Eqn. 3.36) is evaluated with the Wilson K -Values, the resulting vapor fraction does not necessarily fulfill the condition $0 \leq \beta \leq 1$. Therefore, the following checks are performed:

- The Rachford-Rice equation is solved with the assumption that the mixture is at its bubble point ($\beta = 0$). Eqn. 3.36 then becomes

$$g(0) = \sum_{i=1}^N x_i (K_i - 1) \quad \text{or} \quad \tilde{g}(0) = \sum_{i=1}^N x_i K_i, \quad \text{with} \quad \tilde{g}(0) = g(0) + 1. \quad 3.37$$

If $g(0) \leq 0$ or $\tilde{g}(0) \leq 1$ holds, the mixture is assumed to be at its bubble point or below, and the phase compositions are calculated according to

$$x_i'' = \frac{x_i K_i}{\tilde{g}(0)} \quad \text{and} \quad x_i' = x_i, \quad i = 1 \dots N. \quad 3.38$$

- The Rachford-Rice equation is solved with the assumption that the mixture is at its dew point ($\beta = 1$). Eqn. 3.36 becomes

³ The relations in Eqn. 3.34 are derived from the material balance $x_i = (1 - \beta)x_i' + \beta x_i''$ for each component. A detailed derivation is given by Kunz *et al.* (2007).

$$g(1) = \sum_{i=1}^N x_i \left(1 - \frac{1}{K_i}\right) \quad \text{or} \quad \tilde{g}(1) = \sum_{i=1}^N \frac{x_i}{K_i}, \quad \text{with} \quad \tilde{g}(1) = -g(1) + 1. \quad 3.39$$

If $g(1) \geq 0$ or $\tilde{g}(1) \leq 1$ holds, the mixture is assumed to be at its dew point or above, and the phase compositions are calculated according to

$$x_i'' = x_i \quad \text{and} \quad x_i' = \frac{x_i}{K_i \tilde{g}(1)}, \quad i = 1 \dots N. \quad 3.40$$

- If neither of the first two tests leads to initial phase compositions, the mixture is assumed to be in the two-phase region and Eqn. 3.36 has to be solved iteratively for the vapor fraction β . In order to avoid round-off errors for values of β close to unity, it is useful to replace the vapor fraction β with the liquid fraction $\beta^* = 1 - \beta$ for values of $\beta > 0.5$. This can be checked by calculating Eqn. 3.36 with $\beta = 0.5$; if $g(0.5) > 0$ the vapor fraction is replaced with the liquid fraction. The Rachford-Rice equation can be solved e.g. by the Newton-Raphson method. Here the *regula falsi* or *false position* method is used with a given search interval of $0 \leq \beta \leq 0.5$ or $0 \leq \beta^* \leq 0.5$, respectively. Once β is found, the phase compositions can be calculated from Eqn. 3.34.

Step 2: Successive Substitution Method

Based on the initial estimates of the phase compositions, three steps of successive substitution are performed in order to increase the accuracy of the estimates. The successive substitution is described in detail by Prausnitz and Chueh (1968), it includes the following three steps:

- Using the previous estimates for the phase compositions, the fugacity coefficients φ_i'' and φ_i' are calculated from the equation of state.
- New K -values are calculated using the fugacity coefficients and the relation given in Eqn. 3.32.
- From the K -values new phase compositions x_i' and x_i'' and a new vapor fraction β are calculated by solving the Rachford-Rice equation as given in Eqn. 3.36.

These steps can be repeated for a given number of times or until convergence which means that the differences between the fugacities $f_i' = x_i' \varphi_i' p$ and $f_i'' = x_i'' \varphi_i'' p$ for all components become approximately zero.

Step 3: Tangent Plane Analysis

If the vapor fraction exceeds the bounds $0 \leq \beta \leq 1$ after the successive substitution steps, the algorithm suggests a stable phase and continues with the tangent plane analysis. For $0 \leq \beta \leq 1$, the system is assumed to be unstable and to split into two phases. This needs to be verified by calculating the difference between the Gibbs free energy of the split phases and the feed phase

$$\frac{\Delta G}{nRT} = (1 - \beta) \sum_{i=1}^N x'_i [\ln x'_i + \ln \phi'_i] + \beta \sum_{i=1}^N x''_i [\ln x''_i + \ln \phi''_i] - \sum_{i=1}^N x_i (\ln x_i + \ln \phi_i), \quad 3.41$$

with $\ln \phi'_i = \ln \phi_i(T, p, \bar{x}')$ and $\ln \phi''_i = \ln \phi_i(T, p, \bar{x}'')$. Using the material balance from Eqn. 3.35 to replace the feed mole fractions, Eqn. 3.41 can be written in terms of tangent plane distances tpd :

$$\frac{\Delta G}{nRT} = (1 - \beta) tpd' + \beta tpd'', \quad 3.42$$

where

$$tpd' = tpd(\bar{x}') = \sum_{i=1}^N x'_i (\ln x'_i + \ln \phi'_i - \ln x_i - \ln \phi_i) \quad 3.43$$

and

$$tpd'' = tpd(\bar{x}'') = \sum_{i=1}^N x''_i (\ln x''_i + \ln \phi''_i - \ln x_i - \ln \phi_i) \quad 3.44$$

are the reduced tangent plane distance functions for the feed composition, using the initial liquid and vapor compositions as trial phases. If the change of the Gibbs free energy according to Eqn. 3.42 is negative, the instability of the feed phase is confirmed and the algorithm continues with the isothermal flash calculation (see Section 3.3). Even if the change of the Gibbs free energy with the two trial phases is positive, but one of the tangent plane distance functions tpd' or tpd'' is negative, the feed is proven to be unstable. [Kunz *et al.* (2007)]

In case both tangent plane distance functions tpd' and tpd'' of the initial trial phases and the change in the Gibbs free energy $\Delta G/nRT$ are positive, the algorithm continues with a more detailed stability analysis. In principle, the whole composition range needs to be checked for negative tangent plane distances. Since this is impractical for multi-component mixtures, another more practical approach is used here. From the initial Wilson K -factors and the feed composition, heavy and light trial phase compositions $\bar{x}_{trial,H}$ and $\bar{x}_{trial,L}$ are calculated from

$$x_{i,trial,H} = \frac{x_i}{K_i} \quad \text{and} \quad x_{i,trial,L} = x_i K_i, \quad i = 1 \dots N. \quad 3.45$$

Using each of these trial phase compositions as a starting point, a successive substitution search for the composition with the lowest tangent plane distance value (stationary point) is performed, where the following steps are repeated a given number of times⁴:

- Calculate the tangent plane distance of the current trial phase $tpd(\bar{x}_{trial,n})$. In the first run ($n = 1$), save the tangent plane distance value as $tpd_{\min} = tpd(\bar{x}_{trial,1})$.

⁴ We found a maximum number of 20 iterations useful. In many cases this number is not reached, because other break criteria are fulfilled.

- Compare the values of the tangent plane distances of the current trial phase $tpd(\bar{x}_{trial,n})$ and the minimum trial phase tpd_{min} . If the current value is lower, save it together with the corresponding trial phase composition: $tpd_{min} = tpd(\bar{x}_{trial,n})$, $\bar{x}_{min} = \bar{x}_{trial,n}$.
- Calculate the fugacity coefficients $\varphi_{i,trial,n} = \varphi_i(T, p, \bar{x}_{trial,n})$.
- Calculate a new trial phase composition from

$$x_{i,trial,n+1} = x_i \frac{\varphi_i}{\varphi_{i,trial,n}}, \quad i = 1 \dots N. \quad 3.46$$

Here, the index n denotes the n^{th} step in the iteration process. The iteration process has several break criteria:

- The maximum number of iteration steps is reached.
- The value of tpd_{min} becomes negative and thus the feed composition is found unstable. In this case, three more iterations are performed in order to create more accurate initial values for the following flash calculation given in Section 3.3.
- The change of the trial phase compositions $\bar{x}_{trial,n}$ and $\bar{x}_{trial,n+1}$ becomes very small. This indicates that a local minimum of the tangent plane distance function is found (which does not necessarily have to indicate instability of the feed composition).
- The trial composition $\bar{x}_{trial,n}$ merges with the feed composition $\bar{x}$. This indicates that in the vicinity of the initial trial phase composition the tangent plane distance function has no local minima and no negative values. In this case the system is most likely stable at the original composition.

From the search of stationary points of the tangent plane distance function using both the heavy and the light trial phase compositions as a starting point, two values for tpd_{min} are returned. If one or both of these values are negative, the feed composition is unstable and the algorithm continues with a flash calculation. If both values are positive, the feed composition is assumed to be stable. In each calculation step where the fugacity coefficient is evaluated at a given temperature and pressure, the density has to be calculated first from pressure and temperature in order to generate the original input variables for the Helmholtz free energy model. Since the multi-parameter Helmholtz free energy equations of state used in the new mixture model cannot be solved directly for the density, this calculation process is iterative as well. The density solver plays a crucial role in the stability algorithm since during the iterative search the density has to be calculated at extreme conditions where the system is far from stable. The density solver developed for this task is described in Section 3.7.

In case the stability analysis as described above fails for some reason, the stability of a thermodynamic system at a given T and p can also be checked by calculating the phase

envelope (see Section 3.5) to determine if the T, p point is within or outside the two-phase region.

3.3 The Isothermal Two-Phase Flash

A phase equilibrium calculation at given temperature T , pressure p and feed composition $\bar{x}$ is called an isothermal flash. A thermodynamic N -component system of two or more coexisting phases is in equilibrium when all phases $\alpha, \beta, \dots$ are in thermal, mechanical and chemical equilibrium. These phase equilibrium conditions lead to the following set of equations that has to be satisfied:

$$\text{Equality of temperature in all phases} \quad T^\alpha = T^\beta = \dots = T \quad 3.47$$

$$\text{Equality of pressure in all phases} \quad p^\alpha = p^\beta = \dots = p \quad 3.48$$

$$\text{Equality of chemical potentials in all phases} \quad \mu_i^\alpha = \mu_i^\beta = \dots = \mu_i, \quad i = 1 \dots N. \quad 3.49$$

The equality of chemical potentials for each component in Eqn. 3.49 is commonly replaced by the equality of fugacities (see e.g. Stephan *et al.* (2010), Chapter 7) according to

$$\text{Equality of fugacities in all phases} \quad f_i^\alpha = f_i^\beta = \dots = f_i, \quad i = 1 \dots N. \quad 3.50$$

For a given number of phases P and a mixture with N components, $P \times (N-1)$ unknowns have to be determined, namely the compositions of the first $N-1$ components in each phase of the mixture. The composition of the N^{th} component can be determined by the well-established relation (see e.g. Iglesias-Silva *et al.* (2003))

$$\sum_{i=1}^N x_i = 1 \quad \text{or} \quad x_N = 1 - \sum_{i=1}^{N-1} x_i, \quad 3.51$$

which has to be fulfilled for each phase. In this work, only the isothermal two-phase flash is considered that can be a phase split into a vapor-liquid (VLE) or liquid-liquid (LLE) equilibrium state. In case of the isothermal two-phase flash $2(N-1)$ unknown phase compositions have to be determined by setting up and solving a system of the same number of equations. From the chemical equilibrium condition, the first N equations can be derived

$$F_k = \ln f_i(T, p, \bar{x}') - \ln f_i(T, p, \bar{x}'') = 0, \quad k = i = 1 \dots N. \quad 3.52$$

Note that here the logarithm of the fugacities is used to increase the numerical stability for very small and very large values of f_i . The missing $N-2$ equations can be derived from the material balance. The material balance $n_i = n_i' + n_i''$ has to be fulfilled for both the whole system and each component i . Thus, the molar vapor fraction as given in Eqn. 3.35 can be calculated using the phase compositions of any component in the mixture. Since the vapor fraction has to have the same value independent of the component i that is used for its calculation, this relation can be used to form the missing $N-2$ equations according to

$$F_k = \frac{x_i - x_i'}{x_i'' - x_i'} - \frac{x_{N-1} - x_{N-1}'}{x_{N-1}'' - x_{N-1}'} = 0, \quad i = 1 \dots N-2, k = i + N. \quad 3.53$$

The resulting set of $2(N-1)$ nonlinear equations $\bar{F}(\bar{X})=0$ with the same number of unknowns $\bar{X}$ can only be solved numerically by iterative methods. In this case, the Newton-Raphson method was chosen due to its good rate of convergence, but other methods are conceivable, too. From the Taylor series expansion around the point $\bar{F}(\bar{X}_0)$ one gets

$$\bar{F}(\bar{X}) = \mathbf{J}_{\bar{F}}(\bar{X})\Delta\bar{X} + \bar{F}(\bar{X}_0) = 0, \quad 3.54$$

which leads to the more common formulation of the Newton-Raphson method

$$(\bar{X}_{n+1} - \bar{X}_n) = \Delta\bar{X}_n = -\mathbf{J}_{\bar{F}}^{-1}(\bar{X}_n) \cdot \bar{F}(\bar{X}_n), \quad 3.55$$

where the solution vector $\Delta\bar{X}_n$ is the vector of changes between iteration steps n and $n+1$ in all the unknowns X_i

$$\Delta\bar{X}_n = \begin{pmatrix} x'_{1,n+1} - x'_{1,n} \\ \vdots \\ x'_{N-1,n+1} - x'_{N-1,n} \\ x''_{1,n+1} - x''_{1,n} \\ \vdots \\ x''_{N-1,n+1} - x''_{N-1,n} \end{pmatrix}, \quad 3.56$$

$\bar{F}(\bar{X}_n)$ is the system of equations according to Eqns. 3.52 and 3.53, evaluated at $\bar{X}_n$, and $\mathbf{J}_{\bar{F}}(\bar{X}_n)$ represents the Jacobian matrix of $\bar{F}(\bar{X}_n)$ according to

$$\mathbf{J}_{\bar{F}}(\bar{X}_n) = \begin{pmatrix} \frac{\partial F_1}{\partial x'_1} & \cdots & \frac{\partial F_1}{\partial x'_{N-1}} & \frac{\partial F_1}{\partial x''_1} & \cdots & \frac{\partial F_1}{\partial x''_{N-1}} \\ \vdots & & \vdots & \vdots & & \vdots \\ \frac{\partial F_{2N-2}}{\partial x'_1} & \cdots & \frac{\partial F_{2N-2}}{\partial x'_{N-1}} & \frac{\partial F_{2N-2}}{\partial x''_1} & \cdots & \frac{\partial F_{2N-2}}{\partial x''_{N-1}} \end{pmatrix}. \quad 3.57$$

In the special case of a binary mixture the number of unknowns (x'_i and x''_i) equals the number of components N . Thus, the set of equations needed to solve for the unknowns only comprises of the N objective functions given in Eqn. 3.52.

All derivatives of the $2(N-1)$ objective functions F_k necessary to set up the Jacobian matrix $\mathbf{J}_{\bar{F}}$ can be calculated analytically from the equation of state presented in this work. The derivatives of the fugacities f_k with respect to any of the first $N-1$ mole fractions x_i (which are needed for the derivatives of the first N objective functions) are discussed in detail in Section 3.6. The derivatives of the remaining $N-2$ equations (Eqn. 3.53) with respect to the first $N-2$ mole fractions of the liquid and vapor phase are

$$\frac{\partial F_k}{\partial x'_i} = \frac{x_i - x''_i}{(x''_i - x'_i)^2}, \quad i = 1 \dots N-2 \quad \text{and} \quad k = i + N \quad 3.58$$

and

$$\frac{\partial F_k}{\partial x''_i} = -\frac{x_i - x'_i}{(x''_i - x'_i)^2}, \quad i = 1 \dots N-2 \quad \text{and} \quad k = i + N \quad 3.59$$

respectively. The derivatives of Eqn. 3.53 with respect to the mole fraction of component $N-1$ in the liquid and vapor phase are

$$\frac{\partial F_k}{\partial x'_{N-1}} = -\frac{x_{N-1} - x''_{N-1}}{(x''_{N-1} - x'_{N-1})^2}, \quad k = N + 1 \dots 2N - 2 \quad 3.60$$

and

$$\frac{\partial F_k}{\partial x''_{N-1}} = \frac{x_{N-1} - x'_{N-1}}{(x''_{N-1} - x'_{N-1})^2}, \quad k = N + 1 \dots 2N - 2, \quad 3.61$$

respectively. All other partial derivatives $\partial F_k / \partial x_j$ for $k = N + 1 \dots 2N + 2$ are zero.

To ensure that the Newton-Raphson method converges, the iteration has to start with reasonable initial estimates for the unknown phase compositions $\bar{x}'$ and $\bar{x}''$. Since for a “blind” calculation of thermophysical properties the flash calculation is preceded by the stability analysis, the final heavy and light trial phase compositions deliver sufficiently accurate initial estimates $\bar{x}'_{start}$ and $\bar{x}''_{start}$. Additionally, some boundary conditions have to be met during the iteration process:

- The molar vapor fraction β (see Eqn. 3.33), which is derived from the material balance $n_i = n'_i + n''_i$, has to fulfill the condition $0 \leq \beta \leq 1$. This leads to the expression

$$\beta(\beta - 1) \leq 0 \quad \text{or} \quad (x_i - x'_i)(x_i - x''_i) \leq 0, \quad i = 1 \dots N. \quad 3.62$$

- Assuming that each component is present in all coexisting phases, the condition $0 < x_i < 1$ leads to the expressions⁵

$$x'_i x''_i > 0, \quad i = 1 \dots N \quad 3.63$$

and

$$(x'_i - 1)(x''_i - 1) > 0, \quad i = 1 \dots N. \quad 3.64$$

If one or more of these three boundary conditions are not fulfilled, a step reduction of the solution vector in the form of $\Delta \bar{X}^* = \Delta \bar{X} / k$ with $k > 1$ can be applied. The reduction factor k has to be chosen suitably large, so that the boundary conditions are met when they are calculated with the corrected solution vector $\Delta \bar{X}^*$.

3.4 The Isenthalpic and Isentropic Stability Analysis and Two-Phase Flash

The calculation of fluid properties of mixtures at a given feed composition $\bar{x}$, enthalpy h or entropy s , with the pressure p as an independent variable is of special importance in process calculations. Since in these cases neither of the natural input variables T or ρ of the

⁵ Note that Eqns. 3.63 and 3.64 do not cover the cases of both vapor and liquid compositions of component i exceeding the bounds $0 < x_i < 1$. However, in this case the first condition given in Eqn. 3.62 would be violated, assuming that the feed composition is valid.

equation of state is known, they both need to be determined in a two-dimensional iterative search. Furthermore, the system needs to be checked for stability. Finally, if the system is found to be unstable, a flash calculation has to be performed to find compositions of the coexisting stable phases.

The algorithm described in this section is based on the work by Michelsen (1987), who developed and tested it for use with cubic equations of state. The adaption to Helmholtz-energy models has not yet been published. In a first step, the temperature T is calculated by solving the objective function

$$F_T = z(T, p, \bar{x}) - z_{spec} = 0, \quad 3.65$$

with p and $\bar{x}$ held constant over the whole temperature search range and z being either the enthalpy h or the entropy s . In order to evaluate Eqn. 3.65 using a Helmholtz equation of state, the density needs to be calculated first as a function of temperature and pressure (see also Section 3.7). Eqn. 3.65 becomes

$$F_T = z(T, \rho_{Tp}, \bar{x}) - z_{spec} = 0, \quad \text{with} \quad \rho_{Tp} = \rho(T, p_{spec}, \bar{x}). \quad 3.66$$

In a first step the mixture is treated as a homogeneous phase, no stability checks are performed. When calculating the function $z(T)$ at constant p and $\bar{x}$, two cases may occur. If the pressure is above the maximum pressure at which two phases occur (*cricondenbar*), the function $z(T)$ is continuously increasing and differentiable, and the solution of Eqn. 3.65 already represents the correct temperature associated with the given pressure and enthalpy or entropy (see Figure 3.2 at $p = 10$ MPa for an example).

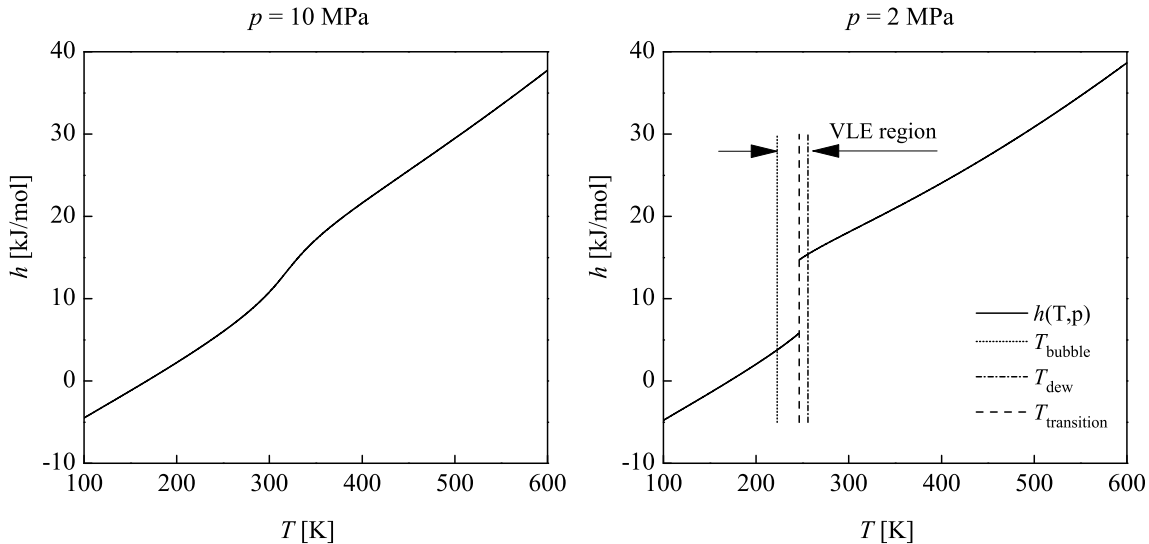


Figure 3.2: The molar enthalpy as a function of temperature at constant pressure and composition (no phase stability is considered) for the system methane – ethane (20 % methane) at 10 MPa and 2 MPa.

In the case where the given pressure is below the cricondenbar, the function $z(T)$ passes a region where the feed phase is unstable and decomposes into two or more phases. Within this region the function passes a point of inconsistency where it jumps to a higher value

that corresponds to the point where the density solver jumps from a liquid like density to a vapor like density (see Figure 3.2 at $p = 2$ MPa)⁶.

For the solution of the objective function F_T in Eqn. 3.66 the *regula falsi* method is applied, which does not need any derivatives of F_T . Since this method is an interval search algorithm, a range for z has to be defined that can be derived from the temperature range of validity of the property model. This search method is advantageous in this application over second-order methods like the Newton-Raphson method, since it can handle functions that are not defined over the whole search range. In the example below (Figure 3.2, $p = 2$ MPa) the enthalpy is not defined for values between 5.8 kJ/mol and 14.7 kJ/mol. For specified enthalpies h_{spec} within this range, the algorithm returns the transition temperature $T_{transition}$ (the point where the density jump occurs) as a solution. Once the temperature is found, the system is checked for stability using the algorithm described in Section 3.2. If it is found to be unstable, the algorithm continues with a flash calculation, using the results of the temperature search and the stability analysis as initial values.

For the calculation of two-phase equilibria at a given feed composition, enthalpy h or entropy s , and pressure p the number of unknowns to be determined by the algorithm increases by one, namely the temperature T . The resulting set of $2N - 1$ unknowns is

$$\bar{X} = \begin{pmatrix} x'_1 \\ \vdots \\ x'_{N-1} \\ x''_1 \\ \vdots \\ x''_{N-1} \\ T \end{pmatrix}. \quad 3.67$$

In order to solve this set of unknowns a set of the same number of objective functions is needed, i.e. an additional objective function has to be added to the set of equations given in Eqns. 3.52 and 3.53, namely

$$F_{2N-1} = z(T, p, \bar{x}', \bar{x}'') - z_{spec} = 0, \quad 3.68$$

where z_{spec} denotes the value of the specified property (either h or s) and $z(T, p, \bar{x}', \bar{x}'')$ the same property calculated from the equation of state at the current flash conditions according to

$$z(T, p, \bar{x}', \bar{x}'') = \beta \cdot z(T, p, \bar{x}'') + (1 - \beta) \cdot z(T, p, \bar{x}'). \quad 3.69$$

⁶ This point does not correspond to the phase equilibrium temperature. It only indicates the point where the one of the two valid density solutions calculated for the overall composition that results in a lower Gibbs free energy $g(T, \rho_p, \bar{x})$ changes from a liquid like to a vapor like density (see Section 3.7 for more details).

The linear system of equations can be solved with the Newton-Raphson method in the same fashion as suggested in Section 3.3. The new solution vector now reads

$$\Delta \bar{X}_n = \begin{pmatrix} x'_{1,n+1} - x'_{1,n} \\ \vdots \\ x'_{N-1,n+1} - x'_{N-1,n} \\ x''_{1,n+1} - x''_{1,n} \\ \vdots \\ x''_{N-1,n+1} - x''_{N-1,n} \\ T_{n+1} - T_n \end{pmatrix}, \quad 3.70$$

and the Jacobian matrix for this system is

$$\mathbf{J}_{\bar{F}}(\bar{X}_n) = \begin{pmatrix} \frac{\partial F_1}{\partial x'_1} & \dots & \frac{\partial F_1}{\partial x'_{N-1}} & \frac{\partial F_1}{\partial x''_1} & \dots & \frac{\partial F_1}{\partial x''_{N-1}} & \frac{\partial F_1}{\partial T} \\ \vdots & & \vdots & \vdots & & \vdots & \vdots \\ \frac{\partial F_{2N-1}}{\partial x'_1} & \dots & \frac{\partial F_{2N-1}}{\partial x'_{N-1}} & \frac{\partial F_{2N-1}}{\partial x''_1} & \dots & \frac{\partial F_{2N-1}}{\partial x''_{N-1}} & \frac{\partial F_{2N-1}}{\partial T} \end{pmatrix}. \quad 3.71$$

The same boundary conditions apply as for the isothermal two-phase flash (Eqns. 3.62-3.64) with the additional condition

$$T > 0, \quad 3.72$$

which can be adapted to $T/T^* - 1 > 0$ with T^* being the lower temperature limit of the range of validity of the mixture model. This criterion becomes important if the mixture model does not extrapolate well to low temperatures. Even if the final value of the equilibrium temperature is not close to the lower limit, its value can change drastically in the first iteration steps.

3.5 Phase Envelope Calculation

The plot of the phase boundaries of a mixture in a p, T diagram at a given composition is called the phase envelope. It is useful to give a quick overview on the most important characteristics of a mixture with regard to its two-phase region, e.g.:

- Does the mixture have a subcooled liquid region (closed / open phase envelope)?
- What are the highest temperature / pressure values at which phase equilibrium can occur (cricondenthem / cricondenbar)?
- Where is the critical point located?
- At what temperature does the mixture start to condense / boil at a given pressure?

The calculation of the phase envelope can also be used within a property calculation algorithm to determine the phase stability of a given mixture. Since such a routine is considerably slower than the stability analysis algorithm presented in Section 3.2.2, it should only be applied if the much faster Michelsen algorithm fails for some reason.

3.5.1 Phase Envelope Characteristics

For the development of a reliable phase envelope algorithm, a detailed knowledge of the phase behavior of mixtures is essential. For many mixtures of lower hydrocarbons, e.g. in natural gas, the phase envelope describes the two-phase region that separates the homogeneous liquid phase at low temperatures from the homogeneous vapor phase at high temperatures. For these so-called “usual” or “closed” phase envelopes both the bubble and the dew lines (which indicate the formation of the first vapor bubble and the first droplet of liquid, respectively) increase from low pressures until they reach the critical point, which is located close to the pressure maximum (see Figure 3.3, left). The dew line passes a temperature maximum T_{CCT} (cricondentherm); the pressure maximum p_{CCB} (cricondenbar) can be located on the dew line or on the bubble line.

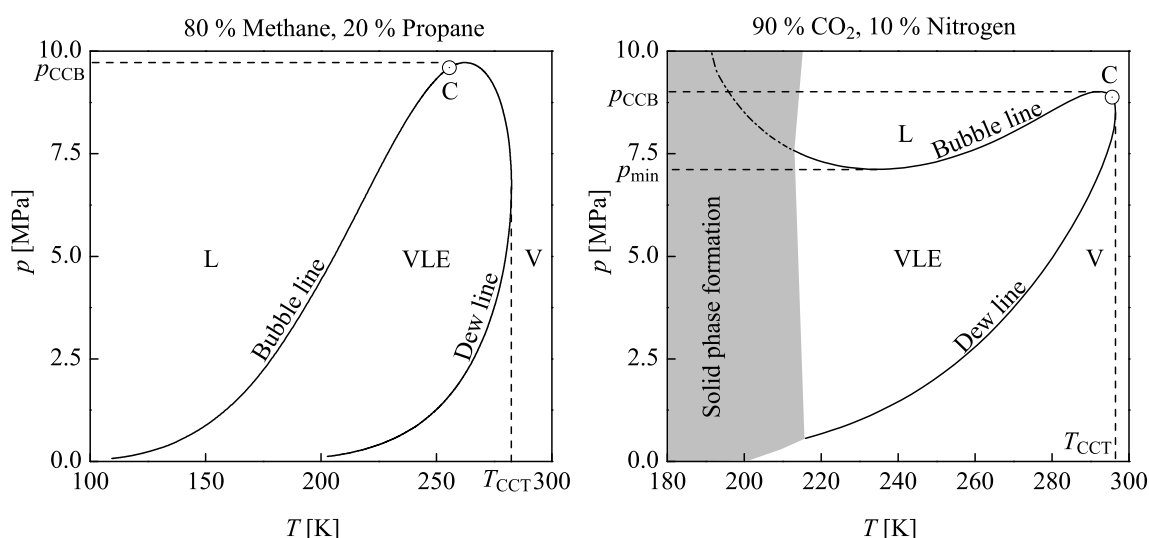


Figure 3.3: Examples for a closed (left) and open (right) phase envelope with the critical point (C), the pressure maximum (p_{CCB}) and the temperature maximum (T_{CCT}) as the main characteristic features.

For mixtures of components with large differences in critical temperatures, the phase envelope may show a more complex behavior. In such a case of an “unusual” or “open” phase envelope, the bubble line does not decrease with decreasing temperatures but increases instead to infinite pressures (see Figure 3.3, right). This behavior indicates a low solubility of the lighter component(s) in the heavier component and results in a liquid-liquid equilibrium (LLE) at higher pressures (or the existence of two immiscible liquid-like supercritical phases). In addition to a pressure and temperature maximum, an open phase envelope may also show a pressure minimum p_{min} . Even two temperature maxima may occur (see Kunz *et al.* (2007), p. 154 for an example). Unusual phase envelopes may show several critical points or no critical point at all. The phase equilibrium may change from vapor-liquid to liquid-liquid equilibrium or even equilibria of fluid phases with a solid phase. The different two-phase equilibrium regions are separated by three-phase

equilibrium lines (in case of a binary mixture) or regions. For more examples on unusual phase envelopes, see also Michelsen and Møllerup (2004), Chapter 11.

3.5.2 Saturation Point Calculation

Saturation points are points on the phase envelope, i.e. the points where a single vapor or liquid phase reaches its stability limit and a second coexisting phase emerges. Since at a saturation point only one phase of the composition $\bar{z}$ is present (the emerging phase still has a phase fraction of zero), the degree of freedom reduces by one, compared to a point in the two-phase region. Therefore only one state variable has to be set and the other one will be determined. With e.g. T and p as state variables, either T or p can be fixed, while the respective other variable is determined and must be calculated. Together with the composition of the incipient phase $\bar{x}$ a set of N independent variables has to be determined, namely $N - 1$ mole fractions x_i of the emerging phase (the last mole fraction is again determined by the relation given in Eqn. 3.51) and T or p . It will be shown in Section 3.5.3 that it may be preferable to fix one of the mole fractions of the incipient phase instead of T or p when calculating the phase envelope. In this case, the N unknowns that have to be solved for are $N - 2$ mole fractions x_i , T and p . The equality of the fugacities of all N components (compare Eqn. 3.52) serves as the system of equations that is set up to solve for the N unknowns. The derivatives necessary to solve the problem using the Newton-Raphson method by setting up the Jacobian matrix are given in Section 3.6.

3.5.3 Phase Envelope Calculation Algorithm

In order to account for the different types of phase envelopes, the phase envelope calculation algorithm suggested here follows a combined strategy. In a first step, an attempt is made to calculate an initial bubble point at low pressure.

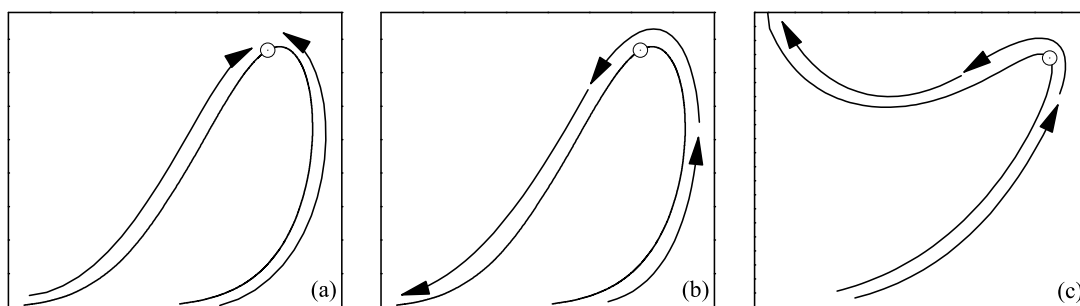


Figure 3.4: Phase envelope calculation strategies. (a): separate calculation of the dew and bubble lines up to the critical point (O); (b) and (c): calculation of the whole phase envelope in one single loop with a jump over the critical point for both a closed (b) and open (c) phase envelope.

If the calculation succeeds, the bubble line is calculated until very close to the critical point. In the second step, the dew line (which exists in every mixture) is calculated, starting at low pressures as well until the critical point is reached. If the calculation of the bubble

line in the first step failed, the algorithm now tries to continue past the critical point to calculate the bubble line until a specified maximum (or minimum) pressure is reached (see Figure 3.4).⁷ The construction of the bubble line and the dew line follow exactly the same routine, so here the description is done for the dew line only.

Calculation of the first saturation points

The construction of the phase envelope always starts with the calculation of a low-pressure saturation point, since for low pressures the initial estimates for the unknown variables – which are needed to solve the flash problem using the Newton-Raphson method – can be generated from the Wilson K -factors (see Section 3.5.2). The pressure for the first saturation point is initially set to 0.1 MPa, but is raised accordingly for mixtures with higher sublimation pressures (e.g. with CO₂ as the main component). Since usually the sublimation pressure of a mixture is unknown, an estimated triple point pressure p_{test} is generated using the triple point pressures of the pure components according to

$$p_{\text{test}} = \sum_{i=1}^N z_i p_{\text{tp},i} . \quad 3.73$$

This artificial mixture triple point pressure is used for the calculation of the first point if $p_{\text{test}} > 0.1$ MPa (e.g. for mixtures with high CO₂ content). In case the calculation of the first point fails using initial estimates from the Wilson K -factors, more accurate initial estimates of the unknowns have to be generated by finding a point in the two-phase region close to the phase boundary and using its phase densities and compositions as initial estimates for the dew point. Such a point in the two-phase region is found by fixing the pressure and reducing the temperature stepwise while each time performing the stability analysis (see Section 3.2.2) until the system is found unstable. Then the p, T -flash is calculated (see Section 3.3) and the resulting phase compositions and densities are used as initial estimates for a saturation point calculation. Once the first saturation point is found, three more saturation points are calculated at low pressures, where $p_{n+1} = 1.1p_n$ using the results of the previous point as initial estimates for the unknown variables.

Initial estimates and step size control

After the calculation of the first four saturation points a more sophisticated step control and generation of initial estimates for the Newton-Raphson solver is applied in order to speed up the phase envelope calculation. This strategy is based on the extrapolation of the next point on the phase envelope from the previous points. All variables necessary to describe the system on the phase boundary, namely T , p , ρ_z , ρ_x , and $\bar{x}$ (with ρ_z as the density of the

⁷ For two reasons this second step is not done directly without trying to calculate the bubble line first. First, the calculation of the bubble line is much faster when beginning at low pressures. Second, the step over the critical point does not always succeed.

original phase with the composition $\bar{z}$ and ρ_x and $\bar{x}$ as the density and composition of the incipient phase) are estimated using cubic extrapolations from the four previously calculated points. For this extrapolation procedure, one of these variables must be set as the independent variable u , and the others become the dependent variables w_i according to

$$w(u) = Au^3 + Bu^2 + Cu + D. \quad 3.74$$

In order for the function $w(u)$ to be well-defined for all u , the independent variable u has to be monotonously increasing or decreasing along the whole phase boundary line (starting at low pressures). The only variable that fulfills this condition is the density of the original phase ρ_z . For a closed phase envelope (Figure 3.4a) this density equals the saturated vapor density on the dew line up to the critical point, and the saturated liquid density on the bubble line. Also for an open phase envelope (Figure 3.4c) this density increases monotonously, even beyond the critical point, where the system either decomposes into a vapor-liquid (in this case the liquid is the original phase) or liquid-liquid equilibrium (in this case the densities of both phases increase with pressure). With the density of the original phase ρ_z as the independent variable u , all other variables (T , p , ρ_x , and x_i) are extrapolated as cubic functions of ρ_z . The coefficients of the cubic functions A_w , B_w , C_w , and D_w are determined from the respective values of the last four points on the phase envelope by solving for each dependent variable w the linear set of equations

$$w_{n-i}(\rho_{z,n-i}) = A_w \rho_{z,n-i}^3 + B_w \rho_{z,n-i}^2 + C_w \rho_{z,n-i} + D, \quad i = 0 \dots 3. \quad 3.75$$

In order to calculate the initial estimates for a new point $n+1$ on the phase envelope, the value for $\rho_{z,n+1}$ has to be chosen. This is done by determining a density step $\Delta\rho_z$ and adding it to the density value of the last point. The step size selection for $\Delta\rho_z$ has to be done carefully. If $\Delta\rho_z$ is chosen too large, the resulting estimates $w_{n+1}(\rho_{n+1})$ may not be accurate enough and the flash calculation fails. On the other hand, if $\Delta\rho_z$ is chosen too small, the phase envelope calculation is slowed down unnecessarily. The step size calculation is based on the distance between the phase densities of the last point n on the phase envelope and the estimated critical density – which is yet unknown and estimated as the arithmetic average of the two phase densities of the last point.

$$\Delta\rho_z = \left[\frac{1}{2}(\rho_{z,n} + \rho_{x,n}) - \rho_{z,n} \right] \cdot SR^{-1}. \quad 3.76$$

This step size definition results in smaller density steps in the proximity of the critical point, which is reasonable since the calculation of saturation points becomes more challenging in the critical region. Therefore small steps, which are more likely to produce more accurate initial estimates, are favored. On the other hand, this step size definition will never lead to a step over the critical point. This topic, however, is discussed later on in this section. The step reduction factor SR indicates a fraction of the distance to the estimated critical point that should be covered by the next step. This factor can initially be set to a

fixed value (e.g. 2.0, which means the new density is $\frac{1}{2}$ closer to the estimated critical density than the previous one) but is adapted depending on the number of iterations necessary for the calculation of the previous point. If for the calculation of the previous saturation point more than e.g. 4 iterations were needed, the initial estimates were obviously not accurate enough. Therefore for the next point, the step reduction factor SR is increased. In this way the step size $\Delta\rho_z$ is directly controlled by the quality of the initial estimates for the previous point.

Furthermore, the step size $\Delta\rho_z$ is limited by the maximum allowed step size $\Delta\rho_{z,\max}$, which is related to the sensitivities of the independent variables with respect to ρ_z . The sensitivities S_w are expressed by the slopes of the cubic extrapolation functions, namely

$$S_w = \frac{\partial w}{\partial \rho_z} = 3A_w \rho_z^2 + 2B_w \rho_z + C_w, \quad w = T, p, x_1 \dots x_{n-1}. \quad 3.77$$

The variable with the largest sensitivity is used to determine a maximum step size which $\Delta\rho_z$ should not exceed. It is furthermore set to the given variable in the next Newton iteration (see Section 3.5.2). Although the sensitivities of pressure, temperature and compositions have different units and orders of magnitude and therefore in principle cannot be compared, a practical approach used here is the reduction of the temperature and pressure sensitivity by

$$S_T^* = \frac{S_T}{T_n} \quad \text{and} \quad S_p^* = \frac{S_p}{p_n}. \quad 3.78$$

The maximum allowed density step $\Delta\rho_{z,\max}$ is related to the variable with the largest (reduced) sensitivity $S_{\max}$ and a maximum allowed step size $\Delta w_{\max}$ of this variable by

$$\Delta\rho_{z,\max} = \frac{\Delta w_{\max}}{S_{\max}} \quad \text{for} \quad S_{\max} = \max \left\{ |S_{x_i}|, |S_T^*|, |S_p^*| \right\}, \quad i = 1 \dots N-1. \quad 3.79$$

The maximum allowed step sizes $\Delta x_{\max}$, $\Delta T_{\max}$, and $\Delta p_{\max}$ do not have any actual thermodynamic relevance. However, they limit the number and the distance of points on the phase envelope. Moreover, the larger these values are set, the larger becomes the deviation of the cubic estimates from the equation of state, where the choice of large values may result in the algorithm failing. In our case, values of $\Delta x_{\max} = 0.05$, $\Delta T_{\max} = 5$ K, and $\Delta p_{\max} = 0.5$ MPa proved to be reasonable for a large variety of mixtures⁸.

In case of $\Delta\rho_z > \Delta\rho_{z,\max}$, the step size $\Delta\rho_z$ is set to maximum step size $\Delta\rho_{z,\max}$. Finally, the initial estimate for $\rho_{z,n+1}$ of the next point $n+1$ on the phase envelope can be calculated from the density of the previous point n and $\Delta\rho_z$

⁸ The maximum allowed step sizes are only used with regard to the sensitivities of the cubic extrapolation functions and are only very rough estimates. The actual step sizes might differ considerably from these values.

$$\rho_{z,n+1} = \rho_{z,n} + \Delta\rho_z, \quad 3.80$$

and the initial estimates for all other variables are calculated according to Eqn. 3.74 from $w_{i,n+1}(\rho_{z,n+1})$.

Critical point calculation

The critical point of a mixture at a given composition is the set of variables (e.g. T and p) at which the densities and compositions of the phases in equilibrium have identical values:

$$\begin{aligned} \rho''_{\text{crit}} &= \rho'_{\text{crit}} \quad \text{and} \\ \bar{x}''_{\text{crit}} &= \bar{x}'_{\text{crit}}. \end{aligned} \quad 3.81$$

When calculating points on the phase envelope the approach to the critical point is indicated by the composition and density of the incipient phase becoming more and more identical to the properties of the original phase. Thus the critical point can be regarded as a saturation point where the incipient phase has exactly the same properties as the original phase.

As already discussed in Section 3.1, Beegle *et al.* (1974) showed that the stability criteria for a stable phase can be reduced to one necessary and sufficient stability criterion that reads in the generalized fashion with regards to the Legendre transform of the internal energy u :

$$y_{(N+1)(N+1)}^N > 0. \quad 3.82$$

For a system of N components, the second-order partial derivative of the N^{th} -order Legendre transform of U with respect to its last variable (in the $N+1$ position) is the first to become zero. The limit of stability, i.e. the formation of a new phase (or a saturation point), is reached when

$$y_{(N+1)(N+1)}^N = 0. \quad 3.83$$

Based on this observation, Reid and Beegle (1977) showed that in addition to the stability limit, which indicates the formation of a new phase and thus marks the critical point as a saturation point, the necessary and sufficient criteria for a mixture at a critical condition are

$$y_{(N+1)(N+1)(N+1)}^N = 0 \quad 3.84$$

and

$$y_{(N+1)(N+1)(N+1)(N+1)}^N \geq 0. \quad 3.85$$

Although the critical point conditions are expressed in the simplest form as given in Eqns. 3.83 to 3.85, it may be more convenient for computational purposes to use lower order Legendre transforms instead of the N^{th} order transform. Beegle *et al.* (1974) developed an equivalent expression to Eqn. 3.83, where the determinant

$$L_i = 0, \quad 3.86$$

with

$$L_i = \begin{vmatrix} y_{(i+1)(i+1)}^i & \cdots & y_{(i+1)(N+1)}^i \\ \vdots & & \vdots \\ y_{(N+1)(i+1)}^i & \cdots & y_{(N+1)(N+1)}^i \end{vmatrix} \quad \text{for any } 0 \leq i \leq N. \quad 3.87$$

For the second critical point criterion from Eqn. 3.84 Reid and Beegle (1977) give the equivalent expression in terms of the determinant

$$M_i = 0, \quad 3.88$$

with

$$M_i = \begin{vmatrix} y_{(i+1)(i+1)}^i & \cdots & y_{(i+1)(N+1)}^i \\ \vdots & & \vdots \\ y_{(N+1)(i+1)}^i & \cdots & y_{(N+1)(N+1)}^i \\ \partial L_i / \partial x_{i+1} & \cdots & \partial L_i / \partial x_{N+1} \end{vmatrix} \quad \text{for any } 0 \leq i \leq N. \quad 3.89$$

Akasaka (2008) used this approach to calculate the critical point of mixtures with mixture models based on Helmholtz energy equations of state. The Helmholtz free energy A is the first Legendre transform of the base function $y^0 = U(S, V, n_1, n_2, \dots, n_N)$, which means $i = 1$ for Eqns. 3.86 to 3.89. He reorganized the order of the independent variables of the function $A(T, V, n_1, n_2, \dots, n_N)$ so that the partial derivatives needed for the determinants L_1 and M_1 become exclusive derivatives with respect to the mole numbers, instead of mixed derivatives with respect to volume and mole numbers, thus creating a numerically more stable set of equations. However, even with the approach by Akasaka (2008), third partial derivatives of the Helmholtz energy with respect to mole numbers are needed in order to evaluate Eqns. 3.86 to 3.89. If the Newton-Raphson method is used for the solution of the set of equations, fourth-order derivatives are needed. These derivatives can be obtained numerically, as is suggested by Akasaka; however, the use of numerical derivatives may pose numerical problems, especially for mixtures where very small amounts of one (or more) of the components occur in one (or both) of the phases. On the other hand the development and programming of analytical third- and fourth-order derivatives of Helmholtz energy equations of state becomes very complex.

For phase envelope calculations, the critical value of the composition is already known since it equals the composition of the original phase. The critical density and temperature are unknown and could in principle be determined by the method described above. However, in this context a more practical method is used, where the critical point is estimated accurately instead of calculated exactly. When approaching the critical point on the phase envelope, the step size is reduced automatically by the algorithm described above, allowing for the calculation of dew or bubble points very close to the critical point. Using these points, the critical density and temperature can be interpolated using a cubic interpolation function with the density of the original phase as the independent variable. From the relation

$$x_i(\rho_{\text{crit}}) - z_i = A_{x_i} \rho_{\text{crit}}^3 + B_{x_i} \rho_{\text{crit}}^2 + C_{x_i} \rho_{\text{crit}} + D_{x_i} - z_i = 0, \quad 1 \leq i \leq N \quad 3.90$$

the critical density ρ_{crit} can be calculated using standard cubic root finding methods. The coefficients A , B , C , and D of the cubic equation have to be determined from four points on the phase boundary surrounding the critical locus. In the next step, the critical temperature and pressure can be calculated in the same fashion from cubic interpolation functions of the density, using the critical density ρ_{crit} as the input.

The step over the critical point

In the case of a mixture with an open phase envelope, the bubble line cannot be calculated starting at low pressures, but has to be derived from successive calculations over the critical point. Thus, the algorithm has to “jump” over the critical point in order to continue the calculation of the saturation line. This jump over the critical point is attempted when the phase densities and the phase compositions become very close. Once a defined threshold is reached the initial estimates for the next point on the phase envelope are generated by using the composition with the largest sensitivity with respect to ρ_z as an independent variable for the extrapolation functions (see also Eqn. 3.77). The new value for this composition is calculated by

$$x_{i,n+1} = 2x_{i,\text{crit}} - x_{i,n}, \quad 1 \leq i \leq N \quad 3.91$$

thus creating a new point on the other side of the critical point with the same distance to it as the previous point (see Figure 3.5). All other initial estimates are calculated from *linear* extrapolation functions using the composition x_i as independent variable and the values of the last two points on the phase envelope for the extrapolation.

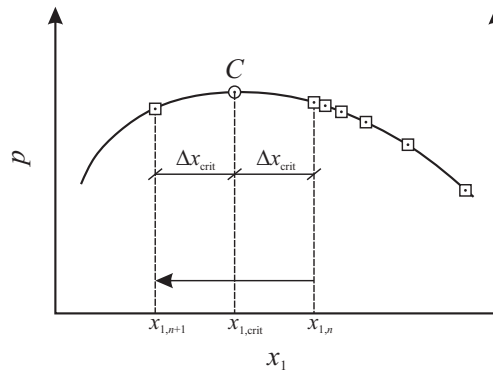


Figure 3.5: The step over the critical point for a binary mixture, controlled by the composition x_1 .

Cricondentherm and cricondenbar

As mentioned before, the temperature and pressure maxima on a normal phase envelope (see Figure 3.3) – also called the cricondentherm and cricondenbar – may be of interest in the process layout when using a specified mixture in a temperature and pressure range close to the phase boundaries. They are defined by the conditions

$$\frac{dT_{sat}}{dp_{sat}} = 0 \quad \text{cricondentherm} \quad 3.92$$

and

$$\frac{dp_{sat}}{dT_{sat}} = 0 \quad \text{cricondenbar.} \quad 3.93$$

A method for the direct calculation of these points was first suggested by Michelsen (1985), who used the modified tangent plane distance function

$$Q = 1 - \sum_{i=1}^N x_i + \sum_{i=1}^N y_i \left[\ln x_i + \ln \varphi_i(\bar{x}) - \ln z_i + \ln \varphi_i(\bar{z}) \right] = 0 \quad 3.94$$

and derived its relation to the slope of the phase boundary curve

$$\frac{dT_{sat}}{dp_{sat}} = - \left(\frac{\partial Q}{\partial p_{sat}} \right) / \left(\frac{\partial Q}{\partial T_{sat}} \right) \quad \text{and} \quad \frac{dp_{sat}}{dT_{sat}} = - \left(\frac{\partial Q}{\partial T_{sat}} \right) / \left(\frac{\partial Q}{\partial p_{sat}} \right). \quad 3.95$$

At the temperature and pressure maxima, the relations of Eqn. 3.95 read

$$\frac{dT_{sat}}{dp_{sat}} = 0 \rightarrow \left(\frac{\partial Q}{\partial p_{sat}} \right)_{T_{sat}, \bar{x}} = \sum_{i=1}^N x_i \left[\left(\frac{\partial \ln \varphi_i(\bar{x})}{\partial p} \right)_{T, \bar{x}} - \left(\frac{\partial \ln \varphi_i(\bar{z})}{\partial p} \right)_{T, \bar{z}} \right] = 0 \quad 3.96$$

and

$$\frac{dp_{sat}}{dT_{sat}} = 0 \rightarrow \left(\frac{\partial Q}{\partial T_{sat}} \right)_{p_{sat}, \bar{x}} = \sum_{i=1}^N x_i \left[\left(\frac{\partial \ln \varphi_i(\bar{x})}{\partial T} \right)_{p, \bar{x}} - \left(\frac{\partial \ln \varphi_i(\bar{z})}{\partial T} \right)_{p, \bar{z}} \right] = 0, \quad 3.97$$

respectively. Eqns. 3.96 and 3.97 provide the additional equations necessary to calculate a saturation point with an additional unknown, namely the maximum temperature or the maximum pressure. For more details on the set of equations necessary for the calculation of saturation points, see Section 3.5.2. As for the critical point calculation, the use of Eqns. 3.96 and 3.97 in a Newton-Raphson method requires higher order derivatives, which become highly complex when using Helmholtz equations of state. Therefore, again a more practical approach is used here, using cubic interpolation functions to find the estimated temperature and pressure maxima in the fashion

$$\frac{dT}{d\rho_z} = 0 \quad \text{cricondentherm, with} \quad T(\rho_z) = A_T \rho_z^3 + B_T \rho_z^2 + C_T \rho_z + D_T \quad 3.98$$

and

$$\frac{dp}{d\rho_z} = 0 \quad \text{cricondenbar, with} \quad p(\rho_z) = A_p \rho_z^3 + B_p \rho_z^2 + C_p \rho_z + D_p \quad 3.99$$

respectively. Since the density ρ_z is monotonously increasing along the whole phase boundary, the criteria in Eqns. 3.98 and 3.99 equal the definitions of Eqns. 3.92 and 3.93. The coefficients of the cubic functions are generated from four points on the phase envelope surrounding the temperature or pressure maximum. From the maximum conditions the density ρ_z at the pressure or temperature maximum is determined and then used to calculate estimates of all other unknown properties at this point. The initial

estimates are then used to calculate a saturation point at given $p(T_{\max})$ or $T(p_{\max})$, respectively.

3.6 Derivatives of the Helmholtz Energy Mixture Model Required for Flash Calculations

For the calculation of phase equilibria using the Newton-Raphson method, the derivatives of the objective functions F_k with respect to temperature T , pressure p and the mole fraction x_i of component i are needed to set up the Jacobian matrix (see Section 3.3 and 3.4). The first N objective functions are

$$F_k = \ln f_i(T, p, \bar{x}') - \ln f_i(T, p, \bar{x}'') = 0, \quad k = i = 1 \dots N, \quad 3.100$$

and their derivatives read

$$\frac{\partial F_k}{\partial T} = \left(\frac{\partial \ln f_i(T, p, \bar{x}')}{\partial T} \right)_{p, \bar{x}'} - \left(\frac{\partial \ln f_i(T, p, \bar{x}'')}{\partial T} \right)_{p, \bar{x}''}, \quad 3.101$$

$$\frac{\partial F_k}{\partial p} = \left(\frac{\partial \ln f_i(T, p, \bar{x}')}{\partial p} \right)_{T, \bar{x}'} - \left(\frac{\partial \ln f_i(T, p, \bar{x}'')}{\partial p} \right)_{T, \bar{x}''}, \quad \text{and} \quad 3.102$$

$$\frac{\partial F_k}{\partial x_j'} = \left(\frac{\partial \ln f_i(T, p, \bar{x}')}{\partial x_j'} \right)_{T, p, x_{k \neq j}'} \quad \text{and} \quad \frac{\partial F_k}{\partial x_j''} = - \left(\frac{\partial \ln f_i(T, p, \bar{x}'')}{\partial x_j''} \right)_{T, p, x_{k \neq j}''} \quad 3.103$$

3.6.1 Derivatives of the Fugacity Coefficient

Using the definition of the fugacity coefficient of component i in the mixture

$$\varphi_i(T, p, \bar{x}) = \frac{f_i(T, p, \bar{x})}{px_i}, \quad 3.104$$

the derivatives of the fugacity necessary to evaluate Eqns. 3.101 and 3.102 can be simplified to

$$\left(\frac{\partial \ln f_i(T, p, \bar{x})}{\partial T} \right)_{p, \bar{x}} = \left(\frac{\partial \ln \varphi_i(T, p, \bar{x})}{\partial T} \right)_{p, \bar{x}} \quad \text{and} \quad 3.105$$

$$\left(\frac{\partial \ln f_i(T, p, \bar{x})}{\partial p} \right)_{T, \bar{x}} = \left(\frac{\partial \ln \varphi_i(T, p, \bar{x})}{\partial p} \right)_{T, \bar{x}} + \frac{1}{p}. \quad 3.106$$

For the calculation of the derivatives of $\ln f_i$ with respect to the mole fractions, the mole fraction x_N of the last component has to be replaced by

$$x_N = 1 - \sum_{k=1}^{N-1} x_k \quad 3.107$$

in order to create $N - 1$ independent variables x_j . When applying Eqns. 3.104 and 3.107 to Eqn. 3.103, three cases have to be considered. For the first $N - 1$ components, the derivative of $\ln f_i$ with respect to x_j and for $i \neq j$ is simplified to

$$\left(\frac{\partial \ln f_i(T, p, \bar{x})}{\partial x_j} \right)_{T, p, x_{k \neq j}} = \left(\frac{\partial \ln \varphi_i(T, p, \bar{x})}{\partial x_j} \right)_{T, p, x_{k \neq j}} \quad i \neq j, i=1 \dots N-1, j=1 \dots N-1. \quad 3.108$$

For the case $i = j$, the fugacity derivative in Eqn. 3.103 becomes

$$\left(\frac{\partial \ln f_i(T, p, \bar{x})}{\partial x_i} \right)_{T, p, x_{k \neq i}} = \frac{1}{x_i} + \left(\frac{\partial \ln \varphi_i(T, p, \bar{x})}{\partial x_i} \right)_{T, p, x_{k \neq i}} \quad i=1 \dots N-1. \quad 3.109$$

The derivative of the fugacity of the N^{th} component with respect to any other mole fraction x_j reads

$$\left(\frac{\partial \ln f_N(T, p, \bar{x})}{\partial x_j} \right)_{T, p, x_{k \neq j}} = -\frac{1}{x_N} + \left(\frac{\partial \ln \varphi_N(T, p, \bar{x})}{\partial x_j} \right)_{T, p, x_{k \neq j}}. \quad 3.110$$

The logarithm of the fugacity coefficient can be expressed in terms of the reduced Helmholtz free energy α from the relation

$$\ln \varphi_i = \left(\frac{\partial n \alpha^r}{\partial n_i} \right)_{T, V, n_{j \neq i}} - \ln Z, \quad 3.111$$

with the compressibility factor Z as

$$Z = \frac{pV}{nRT} = 1 + \delta \alpha_\delta^r. \quad 3.112$$

From this relation, the derivatives of $\ln \varphi_i$ with respect to temperature T , pressure p and mole fraction x_j can be obtained:

$$\left(\frac{\partial \ln \varphi_i}{\partial T} \right)_{p, \bar{x}} = \left(\frac{\partial^2 n \alpha^r}{\partial T \partial n_i} \right)_{V, \bar{n}} + \frac{1}{T} + \frac{\left(\frac{\partial p}{\partial n_i} \right)_{T, V, n_{j \neq i}} \left(\frac{\partial p}{\partial T} \right)_{V, \bar{n}}}{RT \left(\frac{\partial p}{\partial V} \right)_{T, \bar{n}}}, \quad 3.113$$

$$\left(\frac{\partial \ln \varphi_i}{\partial p} \right)_{T, \bar{x}} = -\frac{\left(\frac{\partial p}{\partial n_i} \right)_{T, V, n_{j \neq i}}}{RT \left(\frac{\partial p}{\partial V} \right)_{T, \bar{n}}} - \frac{1}{p}, \quad \text{and} \quad 3.114$$

$$\left(\frac{\partial \ln \varphi_i}{\partial x_j} \right)_{T, p, x_{k \neq j}} = \left(\frac{\partial^2 n \alpha^r}{\partial x_j \partial n_i} \right)_{T, V} + \frac{1}{RT} \frac{\left(\frac{\partial p}{\partial n_i} \right)_{T, V, n_{k \neq i}} \left(\frac{\partial p}{\partial x_j} \right)_{T, V, x_{k \neq j}}}{\left(\frac{\partial p}{\partial V} \right)_{T, \bar{n}}}. \quad 3.115$$

In the following, the derivatives needed to calculate Eqns. 3.113 to 3.115 are described successively, using the thermodynamic relations between the Helmholtz free energy and the other thermodynamic properties (see Section 2.4) as well as several variable transformations. As a result, the above equations can be calculated directly by combinations of derivatives of the reduced Helmholtz free energy α as it is presented in the mixture model used in this work, with respect to its natural variables δ , τ and x_j . Part of

these relations has already been published by Kunz *et al.* (2007), with the exception of the derivative of the fugacity coefficient with respect to x_j (which is needed for building the Jacobian matrix when the flash calculation is solved with the Newton-Raphson method). In their work, Kunz *et al.* approximate the mole fraction derivative using derivatives with respect to amounts of substance n_j , whereas in this work, the actual mole fraction derivatives were developed, using the relation given in Eqn. 3.107.

The second mixed derivative of $n\alpha^r$ with respect to mole number n_i and temperature T , which is needed in the first part of Eqn. 3.113, can be expressed after a first transformation step by

$$\left(\frac{\partial^2 n\alpha^r}{\partial T \partial n_i} \right)_{V, \bar{n}} = -\frac{1}{T} \left[\tau \alpha_\tau^r + \tau \left(\frac{\partial}{\partial \tau} \left(n \left(\frac{\partial \alpha^r}{\partial n_i} \right)_{T, V, n_{j \neq i}} \right) \right)_{\delta, \bar{x}} \right]. \quad 3.116$$

In order to solve Eqn. 3.115, the second mixed derivative of $n\alpha^r$ with respect to mole number n_i and mole fraction x_j is required. It can be split into two terms:

$$\left(\frac{\partial^2 n\alpha^r}{\partial x_j \partial n_i} \right)_{T, V} = \left(\frac{\partial}{\partial x_j} \left(n \left(\frac{\partial \alpha^r}{\partial n_i} \right)_{T, V, n_{j \neq i}} \right) \right)_{T, V, x_{k \neq j}} + \left(\frac{\partial \alpha^r}{\partial x_j} \right)_{T, V, x_{k \neq j}}. \quad 3.117$$

In order to transform from T and V as independent variables to τ and δ , the first term of Eqn. 3.117 becomes

$$\begin{aligned} \left(\frac{\partial}{\partial x_j} \left(n \left(\frac{\partial \alpha^r}{\partial n_i} \right)_{T, V, n_{j \neq i}} \right) \right)_{T, V, x_{k \neq j}} &= \left(\frac{\partial}{\partial x_j} \left(n \left(\frac{\partial \alpha^r}{\partial n_i} \right)_{T, V, n_{j \neq i}} \right) \right)_{\tau, \delta, x_{k \neq j}} \\ &+ \left(\frac{\partial \delta}{\partial x_j} \right)_{T, V, x_{k \neq j}} \left(\frac{\partial}{\partial \delta} \left(n \left(\frac{\partial \alpha^r}{\partial n_i} \right)_{T, V, n_{j \neq i}} \right) \right)_{\tau, \bar{x}} \\ &+ \left(\frac{\partial \tau}{\partial x_j} \right)_{T, V, x_{k \neq j}} \left(\frac{\partial}{\partial \tau} \left(n \left(\frac{\partial \alpha^r}{\partial n_i} \right)_{T, V, n_{j \neq i}} \right) \right)_{\delta, \bar{x}}. \end{aligned} \quad 3.118$$

Also, the second term of Eqn. 3.117 needs to be transformed to τ and δ as independent variables. After a first variable transformation step, it reads⁹:

$$\left(\frac{\partial \alpha^r}{\partial x_j} \right)_{T, V, x_{i \neq j}} = \alpha_\delta^r \cdot \left(\frac{\partial \delta}{\partial x_j} \right)_{T, V, x_{i \neq j}} + \alpha_\tau^r \cdot \left(\frac{\partial \tau}{\partial x_j} \right)_{T, V, x_{i \neq j}} + \alpha_{x_j}^r. \quad 3.119$$

⁹ In this context, the indices δ , τ , x_i , or x_j of α^r denote partial derivatives of the reduced Helmholtz free energy with respect to these variables. While the derivatives with respect to x_i are given in this section, the derivatives with respect to δ and τ were already introduced in Section 2.4.

The first expression on the right hand side of Eqn. 3.118 can be expanded further by transforming the independent variables of the inner derivative to τ and δ as well. The term then reads:

$$\begin{aligned}
 \left(\frac{\partial}{\partial x_j} \left(n \left(\frac{\partial \alpha^r}{\partial n_i} \right)_{T,V,n_{j \neq i}} \right) \right)_{\tau,\delta,x_{k \neq j}} &= \delta \alpha_{\delta x_j}^r \left(1 - \frac{1}{\rho_r} n \left(\frac{\partial \rho_r}{\partial n_i} \right)_{n_{j \neq i}} \right) + \tau \alpha_{\tau x_j}^r \frac{1}{T_r} n \left(\frac{\partial T_r}{\partial n_i} \right)_{n_{j \neq i}} \\
 &\quad - \delta \alpha_{\delta}^r \frac{1}{\rho_r} \left[\left(\frac{\partial}{\partial x_j} \left(n \left(\frac{\partial \rho_r}{\partial n_i} \right)_{n_{j \neq i}} \right) \right)_{x_{k \neq j}} - \frac{1}{\rho_r} \left(\frac{\partial \rho_r}{\partial x_j} \right)_{x_{k \neq j}} \cdot n \left(\frac{\partial \rho_r}{\partial n_i} \right)_{n_{j \neq i}} \right] \\
 &\quad + \tau \alpha_{\tau}^r \frac{1}{T_r} \left[\left(\frac{\partial}{\partial x_j} \left(n \left(\frac{\partial T_r}{\partial n_i} \right)_{n_{j \neq i}} \right) \right)_{x_{k \neq j}} - \frac{1}{T_r} \left(\frac{\partial T_r}{\partial x_j} \right)_{x_{k \neq j}} \cdot n \left(\frac{\partial T_r}{\partial n_i} \right)_{n_{j \neq i}} \right] \\
 &\quad + \alpha_{x_j x_j}^r - \alpha_{x_j}^r - \sum_{k=1}^{N-1} x_k \alpha_{x_j x_k}^r.
 \end{aligned} \tag{3.120}$$

The derivatives of the reduced parameters τ and δ with respect to the mole fractions can be expressed more conveniently by derivatives of the reducing functions T_r and ρ_r , using the relations $\tau = T_r/T$ and $\delta = \rho/\rho_r$, which lead to

$$\left(\frac{\partial \delta}{\partial x_j} \right)_{T,V,x_{k \neq j}} = \rho \left(\frac{\partial (1/\rho_r)}{\partial x_j} \right)_{T,V,x_{k \neq j}} = -\rho \frac{1}{\rho_r^2} \left(\frac{\partial \rho_r}{\partial x_j} \right)_{T,V,x_{k \neq j}} \tag{3.121}$$

and

$$\left(\frac{\partial \tau}{\partial x_j} \right)_{T,V,x_{k \neq j}} = \frac{1}{T} \left(\frac{\partial T_r}{\partial x_j} \right)_{T,V,x_{k \neq j}}. \tag{3.122}$$

The two mixed derivatives of α^r with respect to δ and n_i , and τ and n_i , given in Eqn. 3.118, can also be expressed in terms of derivatives that can be directly calculated from the equation of state and the reducing functions:

$$\begin{aligned}
 \left(\frac{\partial}{\partial \tau} \left(n \left(\frac{\partial \alpha^r}{\partial n_i} \right)_{T,V,n_{j \neq i}} \right) \right)_{\delta,\bar{x}} &= \delta \alpha_{\delta \tau}^r \left(1 - \frac{1}{\rho_r} n \left(\frac{\partial \rho_r}{\partial n_i} \right)_{n_{j \neq i}} \right) + (\alpha_{\tau}^r + \tau \alpha_{\tau \tau}^r) \frac{1}{T_r} n \left(\frac{\partial T_r}{\partial n_i} \right)_{n_{j \neq i}} \\
 &\quad + \alpha_{\tau x_i}^r - \sum_{k=1}^{N-1} x_k \alpha_{\tau x_k}^r
 \end{aligned} \tag{3.123}$$

and

$$\begin{aligned}
 \left(\frac{\partial}{\partial \delta} \left(n \left(\frac{\partial \alpha^r}{\partial n_i} \right)_{T,V,n_{j \neq i}} \right) \right)_{\tau,\bar{x}} &= (\alpha_{\delta}^r + \delta \alpha_{\delta \delta}^r) \left(1 - \frac{1}{\rho_r} n \left(\frac{\partial \rho_r}{\partial n_i} \right)_{n_{j \neq i}} \right) + \tau \alpha_{\delta \tau}^r \frac{1}{T_r} n \left(\frac{\partial T_r}{\partial n_i} \right)_{n_{j \neq i}} \\
 &\quad + \alpha_{\delta x_i}^r - \sum_{k=1}^{N-1} x_k \alpha_{\delta x_k}^r.
 \end{aligned} \tag{3.124}$$

The derivatives of the reducing functions with respect to the amounts of substance needed here can be determined from the derivatives with respect to the mole fractions as follows:

$$n \left(\frac{\partial T_r}{\partial n_i} \right)_{n_{j \neq i}} = \left(\frac{\partial T_r}{\partial x_i} \right)_{x_{j \neq i}} - \sum_{k=1}^{N-1} x_k \left(\frac{\partial T_r}{\partial x_k} \right)_{x_{j \neq k}} \quad 3.125$$

and

$$n \left(\frac{\partial \rho_r}{\partial n_i} \right)_{n_{j \neq i}} = \left(\frac{\partial \rho_r}{\partial x_i} \right)_{x_{j \neq i}} - \sum_{k=1}^{N-1} x_k \left(\frac{\partial \rho_r}{\partial x_k} \right)_{x_{j \neq k}}, \quad \text{with} \quad \left(\frac{\partial \rho_r}{\partial x_i} \right)_{x_{j \neq i}} = -\rho_r^2 \left(\frac{\partial (1/\rho_r)}{\partial x_i} \right)_{x_{j \neq i}}. \quad 3.126$$

Note that the above functions in Eqns. 3.123 to 3.126 have only $N-1$ derivatives with respect to the mole fractions x_k but N derivatives with respect to the amounts of substance n_i . For the derivative with respect to the last amount of substance n_N , the respective derivative with respect to x_N vanishes, but the sum over derivatives with respect to all other x_k remains. This also holds true for the second derivatives of the reducing functions that are needed for Eqn. 3.120:

$$\left(\frac{\partial}{\partial x_j} \left(n \left(\frac{\partial T_r}{\partial n_i} \right)_{n_{j \neq i}} \right) \right)_{x_{i \neq j}} = \left(\frac{\partial^2 T_r}{\partial x_j \partial x_i} \right)_{x_{k \neq j \neq i}} - \left(\frac{\partial T_r}{\partial x_i} \right)_{x_{j \neq i}} - \sum_{k=1}^{N-1} x_k \left(\frac{\partial^2 T_r}{\partial x_k \partial x_j} \right)_{x_{m \neq k \neq j}} \quad 3.127$$

and

$$\left(\frac{\partial}{\partial x_j} \left(n \left(\frac{\partial \rho_r}{\partial n_i} \right)_{n_{j \neq i}} \right) \right)_{x_{i \neq j}} = \left(\frac{\partial^2 \rho_r}{\partial x_j \partial x_i} \right)_{x_{k \neq j \neq i}} - \left(\frac{\partial \rho_r}{\partial x_i} \right)_{x_{j \neq i}} - \sum_{k=1}^{N-1} x_k \left(\frac{\partial^2 \rho_r}{\partial x_k \partial x_j} \right)_{x_{m \neq k \neq j}}. \quad 3.128$$

With the set of equations above, the derivatives given in Eqns. 3.116 and 3.117 can be fully described by a combination of derivatives of α^r with respect to τ , δ and x_j and derivatives of T_r and ρ_r with respect to x_j . The derivatives of the pressure p with respect to the amount of substance n_i , the mole fraction x_j , the temperature T and the total volume V needed to evaluate Eqns. 3.113 to 3.115 have to be developed in the same fashion. They read

$$n \left(\frac{\partial p}{\partial n_i} \right)_{T, V, n_{j \neq i}} = \rho R T \left[1 + \delta \alpha_\delta^r \left(2 - \frac{1}{\rho_r} n \left(\frac{\partial \rho_r}{\partial n_i} \right)_{n_{j \neq i}} + \delta \cdot n \left(\frac{\partial}{\partial n_i} \left(\frac{\partial \alpha^r}{\partial \delta} \right)_{\tau, \bar{x}} \right)_{T, V, n_{j \neq i}} \right) \right], \quad 3.129$$

$$\left(\frac{\partial p}{\partial x_j} \right)_{T, V, x_{k \neq j}} = \rho R T \left[-\frac{1}{\rho_r} \left(\frac{\partial \rho_r}{\partial x_j} \right)_{x_{k \neq j}} \delta \alpha_\delta^r + \delta \left(\frac{\partial}{\partial x_j} \left(\left(\frac{\partial \alpha^r}{\partial \delta} \right)_{\tau, \bar{x}} \right) \right)_{T, V, x_{k \neq j}} \right], \quad 3.130$$

$$\left(\frac{\partial p}{\partial T} \right)_{V, \bar{x}} = \rho R (1 + \delta \alpha_\delta^r - \delta \tau \alpha_{\delta \tau}^r) \quad 3.131$$

and

$$n \left(\frac{\partial p}{\partial V} \right)_{T, \bar{x}} = -\rho^2 R T (1 + 2\delta \alpha_\delta^r + \delta^2 \alpha_{\delta \delta}^r). \quad 3.132$$

All derivatives needed to evaluate Eqns. 3.129 to 3.132 have already been described above, except for the expressions in the second term of Eqns. 3.129 and 3.130. These derivatives can be rewritten in the form

$$\begin{aligned}
n \left(\frac{\partial}{\partial n_i} \left(\frac{\partial \alpha^r}{\partial \delta} \right) \right)_{\tau, \bar{x}} \bigg|_{T, V, n_{j \neq i}} &= \delta \alpha_{\delta \delta}^r \left(1 - \frac{1}{\rho_r} n \left(\frac{\partial \rho_r}{\partial n_i} \right)_{n_{j \neq i}} \right) + \tau \alpha_{\delta \tau}^r \frac{1}{T_r} n \left(\frac{\partial T_r}{\partial n_i} \right)_{n_{j \neq i}} \\
&+ \alpha_{\delta x_i}^r - \sum_{k=1}^{N-1} x_k \alpha_{\delta x_k}^r
\end{aligned} \tag{3.133}$$

and

$$\left(\frac{\partial}{\partial x_j} \left(\left(\frac{\partial \alpha^r}{\partial \delta} \right) \right) \right)_{\tau, \bar{x}} \bigg|_{T, V, x_{k \neq j}} = \alpha_{\delta \delta}^r \left(\frac{\partial \delta}{\partial x_j} \right)_{T, V, x_{k \neq j}} + \alpha_{\delta \tau}^r \left(\frac{\partial \tau}{\partial x_j} \right)_{T, V, x_{k \neq j}} + \alpha_{\delta x_j}^r. \tag{3.134}$$

While the derivatives of α^r with respect to τ and δ are given elsewhere (see Section 2.4) the partial derivatives with respect to x_i are described here, since they are chiefly needed for the description of phase equilibria. According to the mixture model used in this work, the residual part α^r of the reduced Helmholtz free energy is given by

$$\alpha^r(\tau, \delta, \bar{x}) = \sum_{k=1}^N x_k \alpha_{o,k}^r(\tau, \delta) + \sum_{k=1}^{N-1} \sum_{m=k+1}^N x_k x_m F_{km} \alpha_{km}^r(\tau, \delta), \tag{3.135}$$

with the residual parts $\alpha_{o,k}^r$ of the pure fluid Helmholtz equations of state, the binary departure functions α_{km}^r and the weighing factor F_{km} . Using again the relation given in Eqn. 3.107 to replace the last mole fraction x_N , the first derivative of α^r with respect to x_i follows

$$\left(\frac{\partial \alpha^r}{\partial x_i} \right)_{\tau, \delta, x_{k \neq i}} = \alpha_{x_i}^r = \alpha_{o,i}^r - \alpha_{o,N}^r + (1 - 2x_i) F_{iN} \alpha_{iN}^r + \sum_{\substack{k=1 \\ k \neq i}}^{N-1} x_k (F_{ik} \alpha_{ik}^r - F_{iN} \alpha_{iN}^r - F_{kN} \alpha_{kN}^r). \tag{3.136}$$

The second derivative of α^r with respect to x_i and x_j reads

$$\left(\frac{\partial^2 \alpha^r}{\partial x_i \partial x_j} \right)_{\delta, \tau} = \alpha_{x_i x_j}^r = F_{ij} \alpha_{ij}^r - F_{iN} \alpha_{iN}^r - F_{jN} \alpha_{jN}^r, \tag{3.137}$$

with the special case $i = j$

$$\left(\frac{\partial^2 \alpha^r}{\partial x_i^2} \right)_{\delta, \tau} = \alpha_{x_i^2}^r = -2F_{iN} \alpha_{iN}^r. \tag{3.138}$$

The second mixed derivatives of α^r with respect to τ and x_i , and δ and x_i are

$$\begin{aligned}
\delta \left(\frac{\partial^2 \alpha^r}{\partial \delta \partial x_i} \right)_{\tau, x_{k \neq i}} &= \delta \alpha_{\delta x_i}^r = \delta \left(\frac{\partial \alpha_{o,i}^r}{\partial \delta} \right)_{\tau, \bar{x}} - \delta \left(\frac{\partial \alpha_{o,N}^r}{\partial \delta} \right)_{\tau, \bar{x}} + (1 - 2x_i) F_{iN} \delta \left(\frac{\partial \alpha_{iN}^r}{\partial \delta} \right)_{\tau, \bar{x}} \\
&+ \sum_{\substack{k=1 \\ k \neq i}}^{N-1} x_k \left(F_{ik} \delta \left(\frac{\partial \alpha_{ik}^r}{\partial \delta} \right)_{\tau, \bar{x}} - F_{iN} \delta \left(\frac{\partial \alpha_{iN}^r}{\partial \delta} \right)_{\tau, \bar{x}} - F_{kN} \delta \left(\frac{\partial \alpha_{kN}^r}{\partial \delta} \right)_{\tau, \bar{x}} \right)
\end{aligned} \tag{3.139}$$

and

$$\begin{aligned} \tau \left(\frac{\partial^2 \alpha^r}{\partial \tau \partial x_i} \right)_{\delta, x_{k \neq i}} &= \tau \alpha_{\tau x_i}^r = \tau \left(\frac{\partial \alpha_{o,i}^r}{\partial \tau} \right)_{\delta, \bar{x}} - \tau \left(\frac{\partial \alpha_{o,N}^r}{\partial \tau} \right)_{\delta, \bar{x}} + (1 - 2x_i) F_{iN} \tau \left(\frac{\partial \alpha_{iN}^r}{\partial \tau} \right)_{\delta, \bar{x}} \\ &+ \sum_{\substack{k=1 \\ k \neq i}}^{N-1} x_k \left(F_{ik} \tau \left(\frac{\partial \alpha_{ik}^r}{\partial \tau} \right)_{\delta, \bar{x}} - F_{iN} \tau \left(\frac{\partial \alpha_{iN}^r}{\partial \tau} \right)_{\delta, \bar{x}} - F_{kN} \tau \left(\frac{\partial \alpha_{kN}^r}{\partial \tau} \right)_{\delta, \bar{x}} \right). \end{aligned} \quad 3.140$$

Finally, the derivatives of the reducing functions T_r and ρ_r with respect to the mole fraction x_i are needed. The general form of the reducing functions used in this mixture model is given by

$$\begin{aligned} Y_r(\bar{x}) &= \sum_{k=1}^N x_k^2 Y_{c,k} + \sum_{k=1}^{N-1} \sum_{m=k+1}^N c_{Y,km} f_{Y,km}(x_k, x_m), \quad \text{with} \\ f_{Y,km}(x_k, x_m) &= x_k x_m \frac{x_k + x_m}{\beta_{Y,km}^2 x_k + x_m} \quad \text{and} \quad c_{Y,km} = 2\beta_{Y,km} \gamma_{Y,km} Y_{c,km}, \quad \text{with} \\ \frac{1}{\rho_{c,km}} &= \frac{1}{8} \left(\frac{1}{\rho_{c,k}^{1/3}} + \frac{1}{\rho_{c,m}^{1/3}} \right)^3 \quad \text{for } Y = v \quad \text{and} \quad T_{c,km} = (T_{c,k} \cdot T_{c,m})^{0.5} \quad \text{for } Y = T, \end{aligned} \quad 3.141$$

for $Y_r = 1/\rho_r$ and $Y_r = T_r$. Again, the mole fraction x_N of the last component needs to be replaced according to Eqn. 3.107 in order to generate independent variables x_i . Thus, Eqn. 3.141 becomes

$$\begin{aligned} Y_r(\bar{x}) &= \sum_{k=1}^{N-1} x_k^2 Y_{c,k} + \sum_{k=1}^{N-2} \sum_{m=k+1}^{N-1} c_{Y,km} f_{Y,km}(x_k, x_m) + \sum_{k=1}^{N-1} c_{Y,kN} f_{Y,kN}(x_k, x_N) + x_N^2 Y_{c,N} \\ \text{with } x_N &= 1 - \sum_{k=1}^{N-1} x_k. \end{aligned} \quad 3.142$$

When deriving Y_r with respect to x_i one has to consider that the derivative of x_N with respect to any other x_i does not disappear, since x_N is now a dependent variable. With this in mind, the necessary derivatives of the reducing functions are given in Table 3.1.

Table 3.1: Derivatives of the reducing functions T_r and ρ_r with respect to the mole fractions x_i .

$$\begin{aligned} \left(\frac{\partial Y_r}{\partial x_i} \right)_{x_{j \neq i}} &= 2x_i Y_{c,i} - 2x_N Y_{c,N} + \sum_{k=1}^{i-1} c_{Y,ki} \frac{\partial f_{Y,ki}(x_k, x_i)}{\partial x_i} + \sum_{k=i+1}^{N-1} c_{Y,ik} \frac{\partial f_{Y,ik}(x_i, x_k)}{\partial x_i} \\ &+ c_{Y,iN} \left(x_N \frac{x_i + x_N}{\beta_{Y,iN}^2 x_i + x_N} + (1 - \beta_{Y,iN}^2) x_i \frac{x_N^2}{(\beta_{Y,iN}^2 x_i + x_N)^2} \right) \\ &+ \sum_{k=1}^{N-1} c_{Y,kN} \left(-x_k \frac{x_k + x_N}{\beta_{Y,kN}^2 x_i + x_N} + (1 - \beta_{Y,kN}^2) x_N \frac{x_k^2}{(\beta_{Y,kN}^2 x_k + x_N)^2} \right) \end{aligned}$$

$$\begin{aligned}
\left(\frac{\partial^2 Y_r}{\partial x_i^2} \right)_{x_{j \neq i}} &= 2(Y_{c,i} + Y_{c,N}) + \sum_{k=1}^{i-1} c_{Y,ki} \frac{\partial^2 f_{Y,ki}(x_k, x_i)}{\partial x_i^2} + \sum_{k=i+1}^{N-1} c_{Y,ik} \frac{\partial^2 f_{Y,ik}(x_i, x_k)}{\partial x_i^2} \\
&+ 2c_{Y,iN} \left(-\frac{x_i + x_N}{\beta_{Y,iN}^2 x_i + x_N} + (1 - \beta_{Y,iN}^2) \left(\frac{x_N^2}{(\beta_{Y,iN}^2 x_i + x_N)^2} + \frac{(1 - \beta_{Y,iN}^2) x_i x_N^2 - \beta_{Y,iN}^2 x_i^2 x_N}{(\beta_{Y,iN}^2 x_i + x_N)^3} \right) \right) \\
&+ \sum_{k=1}^{N-1} 2c_{Y,kN} x_k^2 \frac{1 - \beta_{Y,kN}^2}{(\beta_{Y,kN}^2 x_i + x_N)^2} \left(\frac{x_N}{(\beta_{Y,kN}^2 x_k + x_N)} - 1 \right)
\end{aligned}$$

Table 3.1 (continued)

$$\begin{aligned}
\left(\frac{\partial^2 Y_r}{\partial x_i \partial x_j} \right)_{x_{k \neq i, j}} &= 2Y_{c,N} + c_{Y,ij} \frac{\partial^2 f_{Y,ij}(x_i, x_j)}{\partial x_i \partial x_j} + \sum_{k=1}^{N-1} 2c_{Y,kN} x_k^2 \frac{1 - \beta_{Y,kN}^2}{(\beta_{Y,kN}^2 x_i + x_N)^2} \left(\frac{x_N}{(\beta_{Y,kN}^2 x_k + x_N)} - 1 \right) \\
&+ c_{Y,iN} \left((1 - \beta_{Y,iN}^2) \left(\frac{2x_i x_N^2}{(\beta_{Y,iN}^2 x_i + x_N)^3} - \frac{x_i x_N}{(\beta_{Y,iN}^2 x_i + x_N)^2} \right) - \frac{x_i + x_N}{\beta_{Y,iN}^2 x_i + x_N} \right) \\
&+ c_{Y,jN} \left((1 - \beta_{Y,jN}^2) \left(\frac{2x_j^2 x_N}{(\beta_{Y,jN}^2 x_j + x_N)^3} + \frac{x_j x_N}{(\beta_{Y,jN}^2 x_j + x_N)^2} \right) - \frac{x_j + x_N}{\beta_{Y,jN}^2 x_j + x_N} \right) \\
\left(\frac{\partial f_{Y,ki}(x_k, x_i)}{\partial x_i} \right)_{x_{k \neq i}} &= x_k \frac{x_k + x_i}{\beta_{Y,ki}^2 x_k + x_i} + \frac{x_k x_i}{\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} + \frac{x_i x_k}{\beta_{Y,ik}^2 x_i + x_k} \left(1 - \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 \neq 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(2x_k - \frac{2x_k x_i}{\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 - \frac{2x_i x_k \beta_{Y,ik}^2}{\beta_{Y,ik}^2 x_i + x_k} \right) \\
\left(\frac{\partial^2 f_{Y,ki}(x_k, x_i)}{\partial x_i \partial x_j} \right)_{x_{k \neq i, j}} &= \frac{x_i + x_j}{\beta_{Y,ij}^2 x_i + x_j} + \frac{x_j}{\beta_{Y,ij}^2 x_i + x_j} \left(1 - \frac{x_i + x_j}{\beta_{Y,ij}^2 x_i + x_j} \right) \\
&+ \frac{x_i}{\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) - \frac{x_i x_j}{(\beta_{Y,ij}^2 x_i + x_j)^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}$$

3.6.2 Derivatives of Enthalpy and Entropy

For the calculation of the p, h and p, s flash as described in Section 3.3, the derivatives of the enthalpy h and the entropy s with respect to the mole fraction x_i and the temperature T are needed in addition to the derivatives of the fugacity described above.

Enthalpy Derivatives

In the same fashion as for the fugacity coefficient, the derivative of the enthalpy h with respect to temperature T at constant pressure p and composition $\bar{x}$ has to be converted to the natural variables τ , δ and $\bar{x}$ of the mixture model. In a first step, the pressure as an independent variable is replaced by the total volume V :

$$\left(\frac{\partial h}{\partial T}\right)_{p,\bar{x}} = \left(\frac{\partial h}{\partial V}\right)_{T,\bar{x}} \left(\frac{\partial V}{\partial T}\right)_{p,\bar{x}} + \left(\frac{\partial h}{\partial T}\right)_{V,\bar{x}}. \quad 3.143$$

Now the individual terms of Eqn. 3.143 have to be transformed further. The first term reads

$$\left(\frac{\partial h}{\partial V}\right)_{T,\bar{x}} = \left(\frac{\partial h}{\partial \delta}\right)_{\tau,\bar{x}} \left(\frac{\partial \delta}{\partial V}\right)_{T,\bar{x}}, \quad \text{with} \quad \left(\frac{\partial \delta}{\partial V}\right)_{T,\bar{x}} = -\delta \frac{\rho}{n} \quad 3.144$$

and

$$\frac{1}{n} \left(\frac{\partial V}{\partial T}\right)_{p,\bar{x}} = \frac{-\left(\frac{\partial p}{\partial T}\right)_{V,\bar{x}}}{n \left(\frac{\partial p}{\partial V}\right)_{T,\bar{x}}}. \quad 3.145$$

The derivatives of p with respect to T and V are already known and are given in Eqns. 3.131 and 3.132. The second part of Eqn. 3.143, the derivative of h with respect to T at constant V , can be transformed according to

$$\left(\frac{\partial h}{\partial T}\right)_{V,\bar{x}} = \left(\frac{\partial h}{\partial \tau}\right)_{\delta,\bar{x}} \left(\frac{\partial \tau}{\partial T}\right)_{V,\bar{x}} \quad \text{with} \quad \left(\frac{\partial \tau}{\partial T}\right)_{V,\bar{x}} = -\frac{\tau}{T}. \quad 3.146$$

The only unknown terms left are the derivatives of h with respect to δ and τ . The enthalpy h expressed in terms of the reduced Helmholtz free energy α reads

$$h(\delta, \tau, \bar{x}) = RT \left(1 + \tau (\alpha_{\tau}^0 + \alpha_{\tau}^r) + \delta \alpha_{\delta}^r \right). \quad 3.147$$

From this expression, the derivatives can be determined directly, they are

$$\left(\frac{\partial h}{\partial \delta}\right)_{\tau,\bar{x}} = RT \left(\tau (\alpha_{\delta\tau}^0 + \alpha_{\delta\tau}^r) + \alpha_{\delta}^r + \delta \alpha_{\delta\delta}^r \right), \quad 3.148$$

where the derivative $\alpha_{\delta\tau}^0$ is always zero, and

$$\begin{aligned} \left(\frac{\partial h}{\partial \tau}\right)_{\delta,\bar{x}} &= R \left(\frac{\partial T}{\partial \tau}\right)_{\delta,\bar{x}} \left(1 + \tau (\alpha_{\tau}^0 + \alpha_{\tau}^r) + \delta \alpha_{\delta}^r \right) + RT (\alpha_{\tau}^0 + \alpha_{\tau}^r + \tau (\alpha_{\tau\tau}^0 + \alpha_{\tau\tau}^r) + \delta \alpha_{\delta\tau}^r), \\ \text{with} \quad \left(\frac{\partial T}{\partial \tau}\right)_{\delta,\bar{x}} &= -\frac{T}{\tau}. \end{aligned} \quad 3.149$$

With the above equations, the derivative of h with respect to T at constant p and $\bar{x}$ is conveniently described in terms of derivatives of α with respect to δ and τ .

The derivative of h with respect to the mole fraction x_i has to be transformed in the same way. First, the pressure is replaced by the total volume again, which leads to

$$\left(\frac{\partial h}{\partial x_i}\right)_{p,T,x_{k \neq i}} = \left(\frac{\partial h}{\partial V}\right)_{T,\bar{x}} \left(\frac{\partial V}{\partial x_i}\right)_{p,T,x_{k \neq i}} + \left(\frac{\partial h}{\partial x_i}\right)_{T,V,x_{k \neq i}} \quad 3.150$$

The first term on the right side of Eqn. 3.150, the derivative of h with respect to V , was already introduced in Eqn. 3.144. The derivative of V with respect to x_i can be obtained by combining two already known derivatives (Eqns. 3.130 and 3.132)

$$\frac{1}{n} \left(\frac{\partial V}{\partial x_i}\right)_{T,p,x_{k \neq i}} = \frac{-\left(\frac{\partial p}{\partial x_i}\right)_{T,V,x_{k \neq i}}}{n \left(\frac{\partial p}{\partial V}\right)_{T,\bar{x}}} \quad 3.151$$

The last term on the right side of Eqn. 3.150 is converted further:

$$\left(\frac{\partial h}{\partial x_i}\right)_{T,V,x_{k \neq i}} = \left(\frac{\partial h}{\partial \delta}\right)_{\tau,\bar{x}} \left(\frac{\partial \delta}{\partial x_i}\right)_{T,V,x_{k \neq i}} + \left(\frac{\partial h}{\partial \tau}\right)_{\delta,\bar{x}} \left(\frac{\partial \tau}{\partial x_i}\right)_{T,V,x_{k \neq i}} + \left(\frac{\partial h}{\partial x_i}\right)_{\delta,\tau,x_{k \neq i}} \quad 3.152$$

The derivatives of δ and τ with respect to x_i are already given in Eqns. 3.121 and 3.122. Also, the derivatives of h with respect to δ and τ are already known (Eqns. 3.148 and 3.149). For the missing derivative of h with respect to x_i at constant δ and τ , the expression in terms of the Helmholtz free energy given in Eqn. 3.147 leads to

$$\begin{aligned} \left(\frac{\partial h}{\partial x_i}\right)_{\delta,\tau,x_{k \neq i}} &= R \left(\frac{\partial T}{\partial x_i}\right)_{\delta,\tau,x_{k \neq i}} \left(1 + \tau(\alpha_\tau^o + \alpha_\tau^r) + \delta \alpha_\delta^r\right) \\ &+ RT \left[\tau \left(\frac{\alpha_\tau^o}{\partial x_i}\right)_{\delta,\tau,x_{k \neq i}} + \tau \left(\frac{\alpha_\tau^r}{\partial x_i}\right)_{\delta,\tau,x_{k \neq i}} + \delta \left(\frac{\alpha_\delta^r}{\partial x_i}\right)_{\delta,\tau,x_{k \neq i}} \right] \end{aligned} \quad 3.153$$

with

$$\left(\frac{\partial T}{\partial x_i}\right)_{\delta,\tau,x_{k \neq i}} = \frac{1}{\tau} \left(\frac{\partial T_r}{\partial x_i}\right)_{\delta,\tau,x_{k \neq i}} \quad 3.154$$

The second mixed derivatives of the residual part of the reduced Helmholtz free energy α^r with respect to τ and x_i , and δ and x_i , have already been introduced (Eqns. 3.139 and 3.140). The unknown derivative of the ideal gas part of the Helmholtz free energy

$$\alpha^o(T, \rho, \bar{x}) = \sum_{k=1}^N x_k \left(\alpha_{o,k}^o(\tau_{o,k}, \delta_{o,k}) + \ln x_k \right) \quad 3.155$$

with respect to τ and x_i has to be evaluated at constant δ and τ . Similar to the mixture model, each pure fluid Helmholtz equation of state $\alpha_{o,k}$ is evaluated and derived with respect to reduced variables, $\delta_{o,k}$ and $\tau_{o,k}$. These variables use the critical temperature and density $T_{c,k}$ and $\rho_{c,k}$ as reducing parameters and are related to the reducing parameters δ and τ of the mixture by:

$$\begin{aligned} \tau_{o,k} &= \frac{T_{c,k}}{T} = \tau \frac{T_{c,k}}{T_r(\bar{x})} \quad \text{with} \quad \tau = \frac{T_r(\bar{x})}{T} \quad \text{and} \\ \delta_{o,k} &= \frac{\rho}{\rho_{c,k}} = \delta \frac{\rho_r(\bar{x})}{\rho_{c,k}} \quad \text{with} \quad \delta = \frac{\rho}{\rho_r(\bar{x})}. \end{aligned} \quad 3.156$$

Consider first the derivative of α^o with respect to τ . This equation can be related to the pure fluid derivatives with respect to the reduced variables of each pure component as follows:

$$\left(\frac{\partial \alpha^o}{\partial \tau}\right)_{\delta, \bar{x}} = \alpha_\tau^o = \frac{1}{\tau} \sum_{k=1}^N x_k \tau_{o,k} \left(\frac{\partial \alpha_{o,k}^o}{\partial \tau_{o,k}}\right)_{\delta_{o,k}} = \sum_{k=1}^N x_k \frac{T_{c,k}}{T_r} \left(\frac{\partial \alpha_{o,k}^o}{\partial \tau_{o,k}}\right)_{\delta_{o,k}}. \quad 3.157$$

Replacing the mole fraction x_N in the usual way, the second derivative of α^o with respect to τ and x_i becomes

$$\left(\frac{\partial}{\partial x_i} \left(\frac{\partial \alpha^o}{\partial \tau}\right)\right)_{\delta, \bar{x}} = \frac{\partial}{\partial x_i} \left[\frac{1}{T_r} \left(\sum_{k=1}^{N-1} x_k \left(T_{c,k} \frac{\partial \alpha_{o,k}^o}{\partial \tau_{o,k}} - T_{c,N} \frac{\partial \alpha_{o,N}^o}{\partial \tau_{o,N}} \right) + T_{c,N} \frac{\partial \alpha_{o,N}^o}{\partial \tau_{o,N}} \right) \right]_{\delta, \tau, x_{k \neq i}}. \quad 3.158$$

After applying the product rule to the derivative on the right hand side, it reads

$$\begin{aligned} \left(\frac{\partial}{\partial x_i} \left(\frac{\partial \alpha^o}{\partial \tau}\right)\right)_{\delta, \bar{x}} &= -\frac{1}{T_r^2} \left(\frac{\partial T_r}{\partial x_i}\right)_{\delta, \tau, x_{k \neq i}} \left[\sum_{k=1}^{N-1} x_k \left(T_{c,k} \frac{\partial \alpha_{o,k}^o}{\partial \tau_{o,k}} - T_{c,N} \frac{\partial \alpha_{o,N}^o}{\partial \tau_{o,N}} \right) + T_{c,N} \frac{\partial \alpha_{o,N}^o}{\partial \tau_{o,N}} \right] \\ &\quad + \frac{1}{T_r} \left[T_{c,i} \frac{\partial \alpha_{o,i}^o}{\partial \tau_{o,i}} - T_{c,N} \frac{\partial \alpha_{o,N}^o}{\partial \tau_{o,N}} + T_{c,N} \left(\frac{\partial}{\partial x_i} \left(\frac{\partial \alpha_{o,N}^o}{\partial \tau_{o,N}} \right) \right)_{\delta, \tau, x_{k \neq i}} \right] \\ &\quad + \frac{1}{T_r} \sum_{k=1}^{N-1} x_k \left[T_{c,k} \left(\frac{\partial}{\partial x_i} \left(\frac{\partial \alpha_{o,k}^o}{\partial \tau_{o,k}} \right) \right)_{\delta, \tau, x_{k \neq i}} - T_{c,N} \left(\frac{\partial}{\partial x_i} \left(\frac{\partial \alpha_{o,N}^o}{\partial \tau_{o,N}} \right) \right)_{\delta, \tau, x_{k \neq i}} \right], \end{aligned} \quad 3.159$$

with the second derivative of the ideal-gas part of the Helmholtz free energy of each pure fluid $\alpha_{o,k}^o$ with respect to $\tau_{o,k}$ and x_i

$$\left(\frac{\partial}{\partial x_i} \left(\frac{\partial \alpha_{o,k}^o}{\partial \tau_{o,k}}\right)\right)_{\delta, \tau, x_{k \neq i}} = \left(\frac{\partial^2 \alpha_{o,k}^o}{\partial \tau_{o,k}^2}\right)_{\delta_{o,k}} \left(\frac{\partial \tau_{o,k}}{\partial x_i}\right)_{\delta, \tau, x_{k \neq i}} + \left(\frac{\partial^2 \alpha_{o,k}^o}{\partial \delta_{o,k} \partial \tau_{o,k}}\right)_{\tau_{o,k}} \left(\frac{\partial \delta_{o,k}}{\partial x_i}\right)_{\delta, \tau, x_{k \neq i}}. \quad 3.160$$

The derivatives of the ideal-gas parts of the pure fluid Helmholtz free energy equations of state with respect to $\delta_{o,k}$ and $\tau_{o,k}$ are not discussed in this work. They can be found e.g. in the work of Span (2000). Finally, the derivatives of the pure fluid reduced variables $\tau_{o,k}$ and $\delta_{o,k}$ with respect to x_i are related to the already known mixture reducing function derivatives (see Table 3.1) by

$$\left(\frac{\partial \tau_{o,k}}{\partial x_i}\right)_{\delta, \tau, x_{k \neq i}} = \tau_{o,k} T_r \left(\frac{\partial (1/T_r)}{\partial x_i}\right)_{\delta, \tau, x_{k \neq i}} = -\frac{\tau_{o,k}}{T_r} \left(\frac{\partial T_r}{\partial x_i}\right)_{\delta, \tau, x_{k \neq i}} \quad 3.161$$

and

$$\left(\frac{\partial \delta_{o,k}}{\partial x_i}\right)_{\delta, \tau, x_{k \neq i}} = \frac{\delta_{o,k}}{\rho_r} \left(\frac{\partial \rho_r}{\partial x_i}\right)_{\delta, \tau, x_{k \neq i}}. \quad 3.162$$

Entropy Derivatives

In order to obtain the derivatives of the entropy s with respect to T at constant p and $\bar{x}$ the same steps are followed as for the enthalpy. First, the pressure is converted to the total volume by

$$\left(\frac{\partial s}{\partial T}\right)_{p,\bar{x}} = \left(\frac{\partial s}{\partial V}\right)_{T,\bar{x}} \left(\frac{\partial V}{\partial T}\right)_{p,\bar{x}} + \left(\frac{\partial s}{\partial T}\right)_{V,\bar{x}}, \quad 3.163$$

then, the first term of the right hand side of Eqn. 3.163 is broken down into

$$\left(\frac{\partial s}{\partial V}\right)_{T,\bar{x}} = \left(\frac{\partial s}{\partial \delta}\right)_{\tau,\bar{x}} \left(\frac{\partial \delta}{\partial V}\right)_{T,\bar{x}}, \quad \text{with} \quad \left(\frac{\partial \delta}{\partial V}\right)_{T,\bar{x}} = -\delta \frac{\rho}{n}. \quad 3.164$$

The derivative of the total volume V with respect to T at constant p is already given in Eqn. 3.145. The last term on the right hand side of Eqn. 3.163 is transformed into

$$\left(\frac{\partial s}{\partial T}\right)_{V,\bar{x}} = \left(\frac{\partial s}{\partial \tau}\right)_{\delta,\bar{x}} \left(\frac{\partial \tau}{\partial T}\right)_{V,\bar{x}}, \quad \text{with} \quad \left(\frac{\partial \tau}{\partial T}\right)_{V,\bar{x}} = -\frac{\tau}{T}. \quad 3.165$$

Now only the two derivatives of s with respect to δ and τ are left unknown. From the relation between the reduced Helmholtz free energy α and the entropy s we get

$$s(\delta, \tau, \bar{x}) = R \left[\tau (\alpha_{\tau}^o + \alpha_{\tau}^r) - \alpha^o - \alpha^r \right]. \quad 3.166$$

Again, the derivatives of s with respect to δ and τ can be determined directly from this relation, they are

$$\left(\frac{\partial s}{\partial \delta}\right)_{\tau,\bar{x}} = R \left[\tau (\alpha_{\delta\tau}^o + \alpha_{\delta\tau}^r) - \alpha_{\delta}^o - \alpha_{\delta}^r \right], \quad 3.167$$

with the partial derivative $\alpha_{\delta\tau}^o$ again being zero, and

$$\left(\frac{\partial s}{\partial \tau}\right)_{\delta,\bar{x}} = R \tau (\alpha_{\tau\tau}^o + \alpha_{\tau\tau}^r). \quad 3.168$$

Thus, the entropy derivative given in Eqn. 3.163 can be fully described in terms of derivatives of α with respect to δ and τ .

The derivative of s with respect to x_i at constant T and p can be split up according to

$$\left(\frac{\partial s}{\partial x_i}\right)_{T,p,x_{k \neq i}} = \left(\frac{\partial s}{\partial V}\right)_{T,\bar{x}} \left(\frac{\partial V}{\partial x_i}\right)_{T,p,x_{k \neq i}} + \left(\frac{\partial s}{\partial x_i}\right)_{T,V,x_{k \neq i}}. \quad 3.169$$

The first two terms on the right hand side of Eqn. 3.169 are already known and given in Eqns. 3.164 and 3.151. The last term is converted in the familiar fashion to

$$\left(\frac{\partial s}{\partial x_i}\right)_{T,V,x_{k \neq i}} = \left(\frac{\partial s}{\partial \delta}\right)_{\tau,\bar{x}} \left(\frac{\partial \delta}{\partial x_i}\right)_{T,V,x_{k \neq i}} + \left(\frac{\partial s}{\partial \tau}\right)_{\delta,\bar{x}} \left(\frac{\partial \tau}{\partial x_i}\right)_{T,V,x_{k \neq i}} + \left(\frac{\partial s}{\partial x_i}\right)_{\delta,\tau,x_{k \neq i}}. \quad 3.170$$

While the first four terms have already been introduced (from left to right: Eqns. 3.167, 3.121, 3.168 and 3.122), the last term has to be converted further:

$$\left(\frac{\partial s}{\partial x_i}\right)_{\delta, \tau, x_{k \neq i}} = R \left[\tau \left(\frac{\partial \alpha_{\tau}^o}{\partial x_i}\right)_{\delta, \tau, x_{k \neq i}} + \tau \left(\frac{\partial \alpha_{\tau}^r}{\partial x_i}\right)_{\delta, \tau, x_{k \neq i}} - \left(\frac{\partial \alpha^o}{\partial x_i}\right)_{\delta, \tau, x_{k \neq i}} - \left(\frac{\partial \alpha^r}{\partial x_i}\right)_{\delta, \tau, x_{k \neq i}} \right]. \quad 3.171$$

In the above equation, all terms on the right hand side are already known, except one. The first term is described in Eqns. 3.159 to 3.162, the second in Eqn. 3.140 and the last term in Eqn. 3.136. The remaining third term, the derivative of α^o with respect to x_i at constant δ and τ needs some more conversion. First, the ideal gas part of the Helmholtz free energy as given in Eqn. 3.155 needs to be converted to $N - 1$ independent mole fractions x_i ; it then reads

$$\alpha^o(\rho, T, \bar{x}) = \sum_{k=1}^{N-1} x_k (\alpha_{o,k}^o + \ln x_k) + \left(1 - \sum_{j=1}^{N-1} x_j\right) \left[\alpha_{o,N}^o + \ln \left(1 - \sum_{j=1}^{N-1} x_j\right) \right]. \quad 3.172$$

The derivative of α^o in this converted expression with respect to x_i is

$$\begin{aligned} \left(\frac{\partial \alpha^o}{\partial x_i}\right)_{\delta, \tau, x_{k \neq i}} &= \alpha_{oi}^o - \alpha_{o,N}^o + \ln \left(\frac{x_i}{x_N}\right) + \sum_{k=1}^{N-1} x_k \left[\left(\frac{\partial \alpha_{o,k}^o}{\partial x_i}\right)_{\delta, \tau, x_{k \neq i}} - \left(\frac{\partial \alpha_{o,N}^o}{\partial x_i}\right)_{\delta, \tau, x_{k \neq i}} \right] \\ &\quad + \left(\frac{\partial \alpha_{o,N}^o}{\partial x_i}\right)_{\delta, \tau, x_{k \neq i}}. \end{aligned} \quad 3.173$$

With the same considerations as for the enthalpy derivative and the relations between the pure fluid reduced variables and the mixture reduced variables given in Eqn. 3.156, the derivative of the pure fluid Helmholtz equations $\alpha_{o,k}^o$ with respect to x_i at constant δ and τ is given by

$$\left(\frac{\partial \alpha_{o,k}^o}{\partial x_i}\right)_{\delta, \tau, x_{j \neq i}} = \left(\frac{\partial \alpha_{o,k}^o}{\partial \tau_{o,k}}\right)_{\delta_{o,k}, \bar{x}} \left(\frac{\partial \tau_{o,k}}{\partial x_i}\right)_{\delta, \tau, x_{j \neq i}} + \left(\frac{\partial \alpha_{o,k}^o}{\partial \delta_{o,k}}\right)_{\tau_{o,k}, \bar{x}} \left(\frac{\partial \delta_{o,k}}{\partial x_i}\right)_{\delta, \tau, x_{j \neq i}}. \quad 3.174$$

As mentioned earlier, the derivatives of the pure fluid Helmholtz equations $\alpha_{o,k}^o$ with respect to $\delta_{o,k}$ and $\tau_{o,k}$ can be found in Span (2000). The derivatives of the reduced variables $\delta_{o,k}$ and $\tau_{o,k}$ with respect to x_i are given in Eqns. 3.161 and 3.162.

3.7 Density Solver

The independent variables of the Helmholtz free energy fundamental equation of state are temperature, density (or volume) and mole fractions or mole numbers of the mixture components, yielding the function $A(T, V, \bar{n})$ or $a(T, \rho, \bar{x})$. For the calculation of thermodynamic properties, it is often more convenient to use input variables other than temperature and density, e.g. temperature and pressure, pressure and enthalpy, or pressure and entropy. In all these cases the density corresponding to the given input values needs to be determined first, before the actual property requested by the user can be calculated from combinations of derivatives of the Helmholtz function. Since for all other combinations of input variables a transformation to the variables T and p is first carried out (see Section 3.4), the problem can be reduced to the objective function

$$F_\rho = p_{\text{spec}} - p(T_{\text{spec}}, \rho, \bar{x}_{\text{spec}}) = p_{\text{spec}} - \rho RT \left(1 + \delta \left(\frac{\partial \alpha^r(\delta, \tau, \bar{x})}{\partial \delta} \right)_{\tau, \bar{x}} \right) = 0, \quad 3.175$$

with the specified variables p_{spec} , T_{spec} , and $\bar{x}_{\text{spec}}$, and with ρ as the unknown. For cubic equations of state this function can be solved analytically, but for multi-parameter equations of state explicit in the reduced Helmholtz free energy, the objective function F_ρ has to be solved numerically using an iterative method.

3.7.1 The Problem of Multiple Density Roots

When using pressure-explicit van-der-Waals type cubic equations of state, the determination of the density ρ from the function $p(T, \rho)$ at given T and p is relatively simple and can be done analytically. The root finding algorithm distinguishes three cases: 1) Three real roots are found; in this case the root with the lowest value represents a vapor density and the root with the highest value a liquid-like density, while the inner root represents a thermodynamically meaningless solution. Whether the vapor or the liquid-like density root represent a thermodynamically stable solution has to be determined by a stability analysis. 2) Two real roots with the same value are found (a double root). This particular case represents the critical point (in case of a pure fluid). 3) Only one real root is found, which means that the fluid is stable in a single vapor or liquid-like phase.

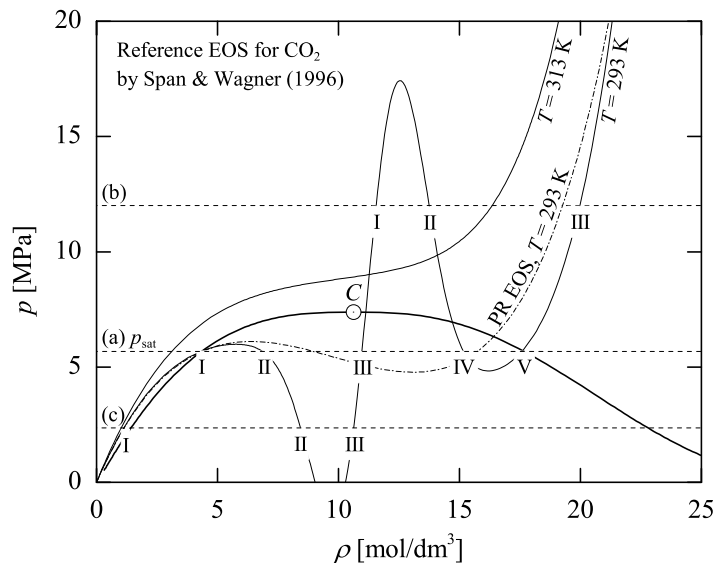


Figure 3.6: The problem of multiple density roots at a given T and p , using the reference EOS of CO_2 by Span and Wagner (1996) as an example, compared to the cubic Peng-Robinson equation (PR EOS).

For multi-parameter equations of state the situation becomes more complicated. One major weakness of van-der-Waals type EOS is the lack in accuracy in the liquid region with density deviations up to 30%. In real fluids, the slope of subcritical isotherms in the liquid region of a p - ρ diagram is much steeper than can be represented by any cubic equation (see Figure 3.6). This problem was overcome with the introduction of multi-parameter

equations of state using higher order density exponents that allowed a much more flexible shaping of the model to highly accurate experimental $p\rho T$ data. However, this considerable gain in accuracy came at a price: While the subcritical isotherms of a van-der-Waals type EOS *always* have one pressure maximum and one pressure minimum which *always* lie within the two-phase region, the Helmholtz-type EOS often have two pressure maxima and minima of which the inner ones increase (and decrease) to very large (positive and negative) pressures at low reduced temperatures.¹⁰

This behavior results in a much more complex situation with regard to the density search at a given p and T (see Figure 3.6):

- (a) At pressures close to the saturation pressure p_{sat} , the equation of state returns five densities corresponding to one pressure and one temperature. The two outermost solutions (I and V) are the two physically correct phase densities. For $p = p_{\text{sat}}$ both density I and V correspond to the densities of the coexisting vapor and liquid phase densities; for $p > p_{\text{sat}}$ only the liquid density (V) is stable and for $p < p_{\text{sat}}$ the vapor density (I) corresponds to the stable phase.
- (b) For pressures further above the saturation pressure, three density solutions corresponding to one pressure at a given temperature are possible. In this case the density with the highest value (III) corresponds to the physically correct solution.
- (c) For pressures well below the saturation pressure, three density solutions corresponding to one pressure at a given temperature are possible. In this case the density with the lowest value (I) corresponds to the physically correct solution.

3.7.2 Advanced Root Finding Algorithm

In case more than one density root is present at a specified temperature, pressure and composition, the challenge for the density solver is to find and identify the physically most reasonable root. If a good initial estimate is available (e.g. from the previous iterations step in a flash or phase envelope calculation), this estimate can be used to generate a density interval for the *regula falsi* method used as a root finding algorithm. In case no such estimate is available, an initial estimate is generated from the Redlich-Kwong-Soave cubic EOS [Soave (1972)]. In most cases such an estimate is accurate enough to create a density interval containing the correct root. However, as mentioned before, in some cases results from the cubic EOS differ considerably from the ones from the Helmholtz EOS, e.g. in the liquid phase or close to the critical point. In such a case a more elaborate search procedure is mandatory. Since an interval search algorithm is used for root finding, the most crucial part is to determine an appropriate search interval. It has to contain one, but only one root. In case a vapor density is needed, this is the root to the left of the “first” maximum of the

¹⁰ This behavior is not inherent in the Helmholtz-type models and can be avoided by careful fitting.

isotherm in a p - ρ diagram (at the lowest density), in case of a liquid density it is the root to the right of the “last” minimum (at the highest density, see Figure 3.6).

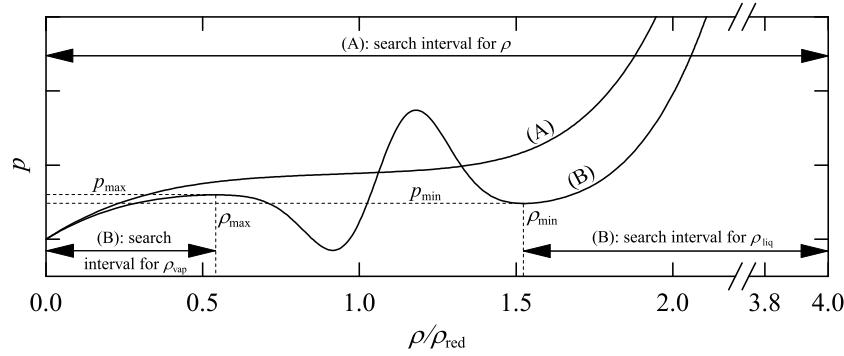


Figure 3.7: Determination of search intervals for the density root finding algorithm. (A): isotherm with only one density root, (B): isotherm with multiple density roots at given p and T .

The advanced root finding algorithm developed in the course of this work uses the following steps to determine the phase density of a pure fluid or mixture at a given temperature, pressure and composition.

1. *Initial root search:* Use an estimated density value (either passed by the calling routine or generated using the SRK) to create a density interval for an initial density search using the *regula falsi* method. In case a root is found, continue with step 4.
2. *Stationary point search:* In case a liquid density is required, search for the pressure minimum at the highest density, in case a vapor density is required, search for the pressure maximum at the lowest density, using the Newton-Raphson method and the necessary criterion

$$\left(\frac{\partial p}{\partial \rho} \right)_{T, \bar{x}} = 0, \quad 3.176$$

as the definition of a stationary point. In order to test the result, the sufficient criteria

$$\left(\frac{\partial^2 p}{\partial \rho^2} \right)_{T, \bar{x}} > 0, \quad 3.177$$

for a minimum, and

$$\left(\frac{\partial^2 p}{\partial \rho^2} \right)_{T, \bar{x}} < 0, \quad 3.178$$

for a maximum, are applied. The start values for the maximum and minimum search are set to a density close to zero and a very large density (e.g. $4\rho_{\text{red}}$), respectively, in order to guarantee convergence.

3. *Phase density root search:* Compare the pressures at the stationary points, p_{max} and p_{min} , to the given pressure p_{spec} . For $p_{\text{spec}} < p_{\text{max}}$ a vapor phase density is present at the given temperature, and for $p_{\text{spec}} > p_{\text{min}}$ a liquid phase density exists. The density at the stationary point, $\rho(p_{\text{max}})$ or $\rho(p_{\text{min}})$, is used as the limit for the search interval, since

the following conditions apply that can be derived directly from the stability criteria (see Eqn. 3.6):

$$0 < \rho(T_{\text{spec}}, p_{\text{spec}}, \bar{x}_{\text{spec}}) < \rho(p_{\text{max}}) \quad 3.179$$

for a vapor phase density, and

$$\rho(T_{\text{spec}}, p_{\text{spec}}, \bar{x}_{\text{spec}}) > \rho(p_{\text{min}}) \quad 3.180$$

for a liquid phase density. While Eqn. 3.179 can be used as the search interval for a vapor phase density without further modifications, the upper limit of the search interval for liquid densities is not defined by physical limits since for increasing pressures the liquid density goes towards infinity. The limiting factor is the physically correct extrapolation behavior of the equation of state. Therefore, a user defined maximum density (or maximum pressure) has to be chosen as a limit.

With the density search interval determined by this method it is guaranteed that only one physically correct density root exists within the interval. The algorithm continues with the root search using the *regula falsi* method.

4. *Thermodynamic tests*: A number of tests are performed to make sure that the density root shows physically correct characteristics. In case a liquid like density was searched for, the following conditions have to be fulfilled:

$$\left(\frac{\partial p}{\partial \rho} \right)_{T, \bar{x}} > 0, \quad \text{and} \quad \left(\frac{\partial^2 p}{\partial \rho^2} \right)_{T, \bar{x}} > 0. \quad 3.181$$

However, roots on the middle branch of a typical subcritical isotherm may also fulfill these conditions, although they are physically meaningless. Only for a correct liquid density these conditions are fulfilled for all densities larger than the root. Therefore this check is performed a number of times with increasing densities until a defined maximum density is reached.

All vapor densities must fulfill the following conditions:

$$\left(\frac{\partial p}{\partial \rho} \right)_{T, \bar{x}} > 0, \quad \text{and} \quad \left(\frac{\partial^2 p}{\partial \rho^2} \right)_{T, \bar{x}} < 0. \quad 3.182$$

Therefore, in order to check if a root is really a vapor density, the root itself and all densities on the same isotherm below this root must fulfill these conditions.

This root search algorithm returns the physically correct density, as long as the numerical search methods converge (the Newton-Raphson method for the stationary point search and the *regula falsi* method for the root search) and as long as a physically correct root exists. For both pure fluids and especially mixtures the equation of state may not behave physically correct over the whole fluid region if such a behavior is not explicitly enforced during the development of a Helmholtz equation of state (see Figure 3.8 for an example).

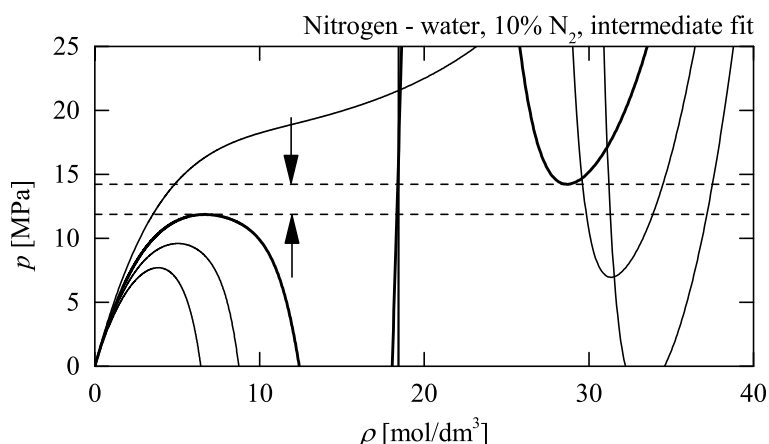


Figure 3.8: Physically incorrect behavior of an intermediate mixture model for nitrogen-water. The marked pressure range does not contain a physically correct density root.

3.7.3 Density Search Strategy

When the density of a certain mixture at a given composition, temperature and pressure needs to be determined, e.g. as part of the stability analysis, the phase in which this mixture is stable is usually not known in advance. Consequently, the density solver has to locate all valid density roots and, in case two roots were found, determine the more likely solution. The search strategy for the correct (or more stable) density root includes the following steps (see Figure 3.9):

1. *Liquid phase density search:* The advanced root finding algorithm described in Section 3.7.2 is used to determine a density root with liquid like characteristics.
2. *Vapor phase density search:* The advanced root finding algorithm described in Section 3.7.2 is used to determine a density root with vapor like characteristics.

For both phases, the search may fail at several points in the search algorithm: The stationary point search fails, no liquid density root exists or the *regula falsi* method fails, or the density root does not pass the thermodynamic test. If two densities were found, the algorithm continues with step 4 below; if only one density was found due to a failure, the algorithm continues with step 3.a) below; if no density was found it continues with step 3.b) below.

- 3.a) *Second root search:* If only one stationary point was found (i.e. the Newton-Raphson method failed) the second stationary point is determined using the *regula falsi* method. Once the second stationary point is found, the second phase density is determined as described in Section 3.7.2 (steps 3 and 4). If this search also fails, only one correct root exists and the algorithm is completed.

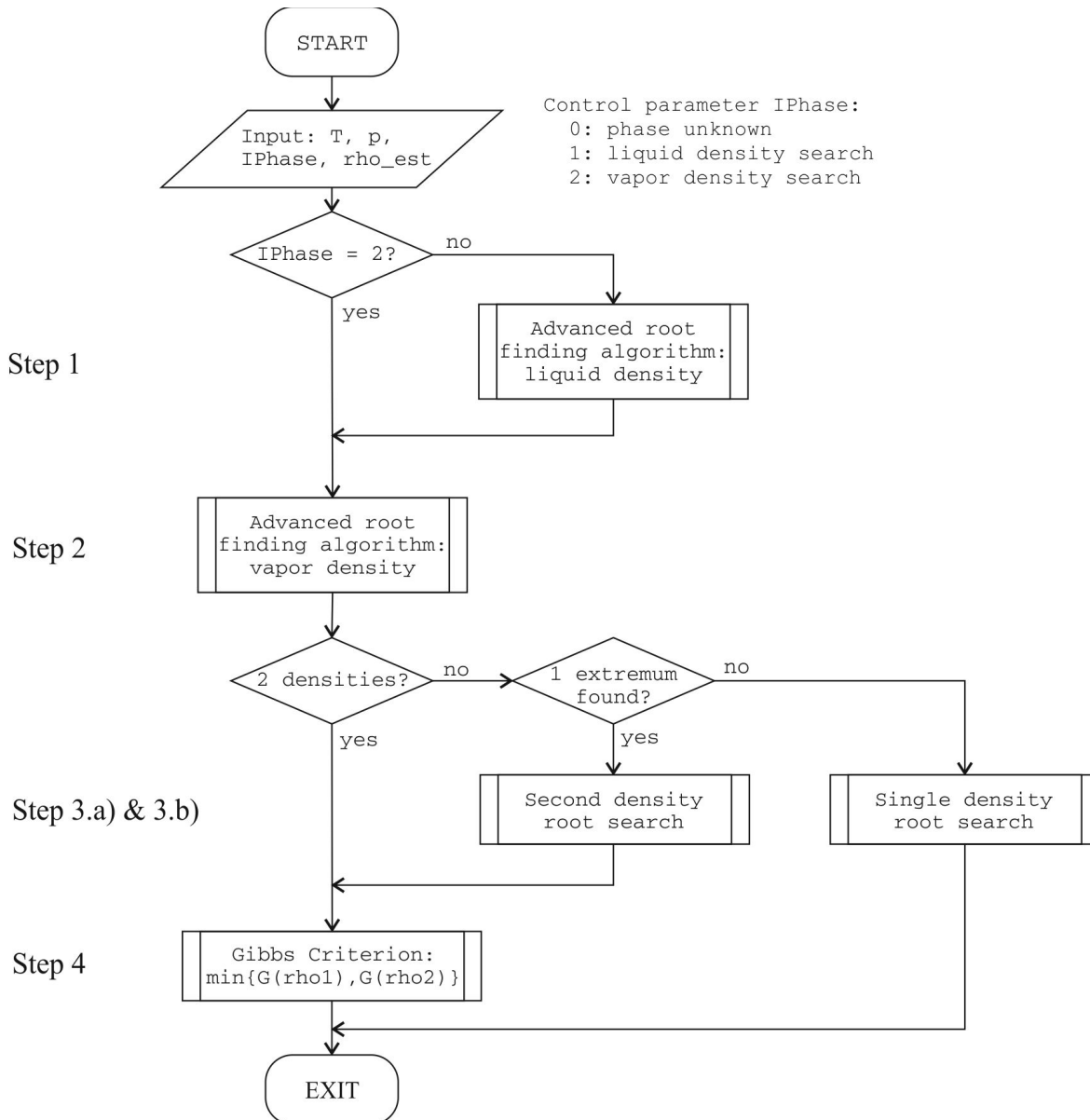


Figure 3.9: Simplified flowchart of the density search strategy.

3.b) *Single root search*: In case both searches for the pressure minimum and maximum fail, the isotherm of the specified mixture is assumed to be a monotonously increasing function (i.e. supercritical for pure fluids, see Figure 3.7).¹¹ In this case only one density solution exists for a given set of temperature, pressure and composition and the search interval for the density search includes the whole density range up to a user defined maximum density. Once the correct density interval is determined, the actual density search is performed using the *regula falsi* method.

¹¹ For pure fluids, the change from subcritical to supercritical isotherms goes along with a change from functions showing local extrema to monotonously increasing functions in the p - ρ diagram and the critical isotherm marks the transition with a saddle point. For mixtures, also subcritical isotherms may also be monotonously increasing.

4. *Two density values - Gibbs Energy Criterion:* In case two densities were found in the previous steps, only one density represents a thermodynamically stable phase while the other density represents a metastable or unstable state. In this case, the Gibbs free energy stability criterion (see Section 3.1) is applied to choose the correct density: The density resulting in a lower Gibbs free energy (at constant temperature and composition) represents the stable phase and is chosen by the algorithm.¹²

¹² During an iterative flash calculation, none of the densities found by the algorithm actually represents a stable phase. However, here the Gibbs criterion leads to the “more likely” density value.

4 PARAMETER FITTING

In statistical thermodynamics the characteristics of a real fluid or mixture are described by modeling a potential surface. Like for Helmholtz energy EOS, this surface can be split in a contribution of the ideal gas and a residual part. The latter is modeled by describing the intermolecular forces, e.g. van-der-Waals forces using physically based potential functions, e.g. the Lennard-Jones potential. The resulting macroscopic potential surface can be translated directly into any of the fundamental equations of state, e.g. the Helmholtz free energy. In the empirical approach used in this work the same potential surface is modeled, but without any direct information on its shape, since the Helmholtz free energy cannot be measured. Instead, this surface is shaped only by fitting its derivatives (which are linked to measurable thermodynamic properties, as given in Table 2.6) to experimental data. Such an approach is only valid if partial derivatives of the state function with respect to all independent variables are fitted; and it becomes more accurate with higher order derivatives included in the fitting process.

The Helmholtz equations of state in reference quality, introduced mainly by the Wagner group in the 1980s and 1990s with the GERG-2008 as the latest publication, were developed using a combination of linear and nonlinear fitting methods, together with a sophisticated combinatory algorithm based on the work by Setzmann and Wagner (1989) to determine the optimal mathematical structure of the equation using a bank of terms from which to choose. In such an algorithm the exponents of a function like the binary departure function α_{ij}^r given in Eqn. 2.34 are not fitted directly but chosen from a bank of terms. The coefficients $n_{ij,k}$ of each term are fitted using first a linear optimization algorithm and linearized data (with temperature and precorrelated density as independent variables, instead of temperature and pressure), and finally, a (much slower) nonlinear algorithm. For more details on these fitting methods see Wagner and Pruß (1999) or Span (2000).

The fitting algorithm and software used in this work for the development of the new mixture model for humid gases and CCS mixtures was provided and has been developed by Dr. Eric W. Lemmon at the National Institute of Standards and Technology (NIST) in Boulder, Colorado. It has been used for the development of many of the highly accurate Helmholtz equations of state for pure fluids published over the last decade (e.g. the equation of state for R125 by Lemmon and Jacobsen (2005), the reference equation for propane by Lemmon *et al.* (2009) or the equation of state for benzene by Thol *et al.* (2012)). It has been extended to mixture models of the GERG-2004 type (the same type of mixture model used in this work, see Section 2.3), resulting in some unpublished adjusted binary reducing parameters and also an unpublished mixture model for the system ethanol + water by Lemmon in 2008, which are available in REFPROP 9.1 by Lemmon *et al.* (2013). This algorithm is a purely nonlinear minimizer with the ability to adjust both

coefficients and exponents of an equation of state at the same time. It is also capable of fitting all types of thermodynamic data at the same time without any previous linearization or precorrelations.

4.1 Building the Sum of Squares

The objective function for which the global minimum has to be determined is the sum of squares (*SOS*) of the (weighted) deviations between the experimental data points considered in the fit and their equivalents calculated from the equation of state. Additionally, the sum of squares can be extended to contributions by constraints that can be added to force the equation of state to show certain characteristics, as will be explained in more detail later in this section. The independent variables of the objective function *SOS* can be explicitly chosen by the user, but generally consist of the reducing function parameters given in Eqns. 2.31 and 2.32 and the coefficients and exponents of the binary departure function α_{ij}^r given in Eqn. 2.34.¹³ Thus, the *SOS* is given by

$$\begin{aligned} SOS &= SOS(\beta_{T,ij}, \gamma_{T,ij}, \beta_{v,ij}, \gamma_{v,ij}, n_{ij,k}, d_{ij,k}, t_{ij,k}, l_{ij,k}, \eta_{ij,k}, \beta_{ij,k}) \\ &= \sum_i W_{p,i} F_{p,i}^2 + \sum_i W_{c,i} F_{c,i}^2, \end{aligned} \quad 4.1$$

where W_i are the individual weights assigned to each data point and constraint, and F_i are the contributions of the deviations between the model and experimental properties and constraints. In this context the indices p and c describe weights and deviations assigned to properties and constraints, respectively. Usually, the contribution of an experimental data point of the property z to the sum of squares is given by the relative deviation between the experimental value z_{exp} and the value z_{calc} according to

$$F_z = \frac{z_{\text{exp}} - z_{\text{calc}}(p_{\text{exp}}, T_{\text{exp}}, \bar{x}_{\text{exp}})}{z_{\text{exp}}}, \quad 4.2$$

where z_{calc} is calculated from the model using the independent variables of the experimental data point (usually temperature and pressure, or temperature and density, plus composition) as input. Exceptions are the contributions of phase equilibrium data (VLE) and density data (see Table 4.1).

¹³ Note that the parameters $\varepsilon_{ij,k}$ and $\gamma_{ij,k}$ in the special exponential term developed by Kunz *et al.* (2007) were not fitted here as independent variables, since at least one of them is not independent from the other parameters in this exponent. See Section 2.3 for an explanation.

Table 4.1: Common experimental mixture data used for fitting mixture models and their contribution to the sum of squares.

Property	Contribution to the sum of squares (<i>SOS</i>)
Density $\rho(p, T, \bar{x})$	$F_{\rho}^2 = \left[\frac{p_{\text{exp}} - p_{\text{calc}}(\rho, T, \bar{x})}{\rho_{\text{exp}}} \left(\frac{\partial p}{\partial \rho} \right)^{-1}_{T, \bar{x}} \right]^2$
Pressure $p(\rho, T, \bar{x})$	$F_p^2 = \left(\frac{p_{\text{exp}} - p_{\text{calc}}(\rho, T, \bar{x})}{p_{\text{exp}}} \right)^2$
VLE data, $p, T, \bar{x}', \bar{x}''$ given	$F_{pT\bar{x}\bar{x}''}^2 = \sum_{i=1}^2 \left(\frac{f_i'(p, T, \bar{x}') - f_i''(p, T, \bar{x}'')}{1 + f_i'(p, T, \bar{x}')} \right)^2$
VLE data, $p, T, \bar{x}'$ or $p, T, \bar{x}''$ given	$F_{pT\bar{x}'}^2 = \sum_{i=1}^2 (x'_{i,\text{calc}} - x'_{i,\text{exp}})^2 + \left(\frac{p_{\text{exp}} - p_{\text{calc}}(\rho', T, \bar{x}')}{p_{\text{exp}}} \right)^2$ or $F_{pT\bar{x}''}^2 = \sum_{i=1}^2 (x''_{i,\text{calc}} - x''_{i,\text{exp}})^2 + \left(\frac{p_{\text{exp}} - p_{\text{calc}}(\rho'', T, \bar{x}'')}{p_{\text{exp}}} \right)^2$
Isobaric heat capacity $c_p(p, T, \bar{x})$	$F_{c_p}^2 = \left(\frac{c_{p,\text{exp}} - c_{p,\text{calc}}(p, T, \bar{x})}{c_{p,\text{exp}}} \right)^2$
Isochoric heat capacity $c_v(\rho, T, \bar{x})$	$F_{c_v}^2 = \left(\frac{c_{v,\text{exp}} - c_{v,\text{calc}}(\rho, T, \bar{x})}{c_{v,\text{exp}}} \right)^2$
Speed of sound $w(p, T, \bar{x})$	$F_w^2 = \left(\frac{w_{\text{exp}} - w_{\text{calc}}(p, T, \bar{x})}{w_{\text{exp}}} \right)^2$
Joule-Thomson coefficient $\mu_{JT}(p, T, \bar{x})$	$F_{JT}^2 = \left(\frac{\mu_{JT,\text{exp}} - \mu_{JT,\text{calc}}(p, T, \bar{x})}{\mu_{JT,\text{exp}}} \right)^2$
Excess enthalpy $h^E(p, T, \bar{x})$	$F_{h^E}^2 = \left(\frac{h_{\text{exp}}^E - h_{\text{calc}}^E(p, T, \bar{x})}{h_{\text{exp}}^E} \right)^2$
2 nd virial coefficient $B(T, \bar{x})$	$F_B^2 = \left(\frac{B_{\text{exp}} - B_{\text{calc}}(T, \bar{x})}{B_{\text{exp}}} \right)^2$
2 nd cross virial coefficient $B_{12}(T)$	$F_{B_{12}}^2 = \left(\frac{B_{12,\text{exp}} - B_{12,\text{calc}}(T)}{B_{12,\text{exp}}} \right)^2$

Thermodynamic constraints

As mentioned before, the nonlinear fitting technique allows the use of constraints in order to shape the equation of state to show physically correct behavior in regions where no experimental data are available, and to ensure reasonable extrapolation. These constraints are also added to the sum of squares. Constraints are used to force a certain shape of an arbitrary thermodynamic property along an isoline, which means along one of the input properties while all other input properties (two in case of binary mixtures) are kept constant. The shape can be formed by defining the basic behavior of the property itself, its slope, curvature and third and fourth derivatives. As an example, in the homogeneous gas phase the pressure as a function of density at constant temperature and composition is a monotonously increasing function with the following characteristics (see Table 4.2): It increases from zero density up to the phase boundary while showing a positive slope and negative curvature.

Table 4.2: Example for the description of a thermodynamic property along an isoline (pressure along an isotherm) and the resulting constraints for the property itself, its slope and curvature.

Thermodynamic property characteristics	Resulting constraint
The pressure p is positive.	$p(\rho)_{T,\bar{x}} > 0$
The slope of p along an isotherm is positive.	$(\partial p / \partial \rho)_{T,\bar{x}} > 0$
<i>In the gas phase</i> the curvature p along an isotherm is negative.	$(\partial^2 p / \partial \rho^2)_{T,\bar{x}} < 0, \text{ for } 0 \leq \rho \leq \rho''$

A list of thermodynamic properties commonly used as constraints when fitting mixture models is given in Table 4.3. As shown in the example for a thermodynamic constraint in Table 4.2, a certain characteristic of a thermodynamic property used as a constraint in the fitting procedure is always evaluated as a function of one of its state variables, while the other state variables are kept constant. A list of properties that can be used as variables and properties that can be kept constant is given in Table 4.4. Several attributes of the property used as a constraint can be manipulated. Beside the function values all partial derivatives with respect to the variable parameter up to the fourth derivative can be controlled. The control parameters that can be assigned to the function value or its derivative include the conditions *positive* and *negative*, *zero* and *one sign change only*.

Table 4.3: Properties and derivatives commonly used as thermodynamic constraints for fitting mixture models.

Constraint	Constraint
Density ρ	Joule-Thomson coefficient μ_{JT}
Pressure p	Phase identifier parameter Π^*
Temperature T	2 nd cross virial coefficient B_{12}
Isobaric heat capacity c_p	Excess volume v^E
Isochoric heat capacity c_v	Excess enthalpy h^E
Speed of sound w	Excess entropy s^E
2 nd / 3 rd / 4 th virial coeff. $B/C/D$	Excess Gibbs energy g^E
Fugacity of 1 st / 2 nd component f_1/f_2	Derivative $(\partial p/\partial \rho)_{T,\bar{x}}$
Grüneisen coeff. $Gr = (\rho c_v^r)^{-1} (\partial p/\partial T)_{\rho,\bar{x}}$	Derivative $(\partial^2 p/\partial \rho^2)_{T,\bar{x}}$
Reduced residual Helmholtz free energy α^r	Derivative $(\partial p/\partial T)_{\rho,\bar{x}}$
Compressibility factor Z	Derivative $(\partial^2 p/\partial T^2)_{\rho,\bar{x}}$

* The phase identification parameter was introduced by Venkatarathnam and Oellrich (2011) for the determination of a liquid-like phase ($\Pi > 1$) or a vapor phase ($\Pi < 1$) without any knowledge necessary of the critical parameters of a fluid or mixture. Its definition is given in Eqn. 4.8.

A thermodynamic constraint is passed to the fitter together with numerical values for the two constant parameters, a range for the variable parameter q (start value q_{start} , end value q_{end} , and step size Δq), and a weight $W_{c,i}$. The derivatives of the property z with respect to q are calculated numerically from property values of the previous steps by

$$\begin{aligned}
 \left(\frac{\partial z}{\partial q}\right) &= \frac{z(q) - z(q - \Delta q)}{\Delta q}, \\
 \left(\frac{\partial^2 z}{\partial q^2}\right) &= \frac{z(q) - 2z(q - \Delta q) + z(q - 2\Delta q)}{\Delta q^2}, \\
 \left(\frac{\partial^3 z}{\partial q^3}\right) &= \frac{z(q) - 3z(q - \Delta q) + 3z(q - 2\Delta q) - z(q - 3\Delta q)}{\Delta q^3}, \\
 \left(\frac{\partial^4 z}{\partial q^4}\right) &= \frac{z(q) - 4z(q - \Delta q) + 6z(q - 2\Delta q) - 4z(q - 3\Delta q) + z(q - 4\Delta q)}{\Delta q^4}.
 \end{aligned} \tag{4.3}$$

The constraint is evaluated within the given range at each step, and for each step its contribution to the *SOS* is checked. In case the constraint is violated, the contribution to the *SOS* is given by the exponential of the value of the respective constraint. For the example given above the constraint imposes a negative curvature of the pressure with respect to density over a particular range, such as from 0 to 10 with a step size of 1 (arbitrary values,

units are irrelevant to this example), which means it is evaluated nine times. If it is positive instead of negative at three of these evaluation points, the squared value of the slope at these points is added to the *SOS*. Thus, the step size Δq has to be chosen in accordance to the range over which the constraint is evaluated and the derivative order used as a constraint (e.g. a minimum of five steps is required for one evaluation of the fourth derivative). More examples for the use of thermodynamic constraints in the development of equations of state for mixtures are given in Section 4.3.

Table 4.4: Constant and variable input parameters for an arbitrary thermodynamic constraint.

Property used as isoline	Property to be varied
Temperature T	Temperature T
Density ρ	Density ρ
Pressure p	Pressure p
Composition x_1 of component 1	Composition x_1 of component 1

Other Constraints

Beside the selection and weighing of experimental property data and thermodynamic constraints, the fitting process can be controlled by a number of other constraints that directly control the adjustable parameters of the mixture model. These constraints include:

- fitting only reducing parameters / only the departure function,
- fitting only selected coefficients or exponents of the binary departure function,
- forcing the reducing parameters, the coefficients, temperature exponents, density exponents, and exponents in the exponential term of the binary departure function to stay within a given range,
- forcing a selected coefficient, temperature exponent, density exponent, or exponent in the exponential term to be larger or smaller than a given value,
- Forcing the temperature exponents of the departure function to stay apart and not assume almost similar values (thus avoiding intercorrelation of terms).

4.2 The Nonlinear Minimization Algorithm

As mentioned before, the algorithm used in this work for fitting the parameters of the mixture model was developed and provided by Dr. Eric W. Lemmon at NIST. However, since it has not been described in detail to this date it will be outlined briefly in the following section with the consent of Dr. Lemmon.

This global optimization algorithm uses a deterministic search strategy, but has also stochastic elements, since initial values are generated for the search area of the

optimization algorithm using randomized parameters. Additionally, the coefficients of the Helmholtz function (the binary specific departure function in case a mixture is fitted) can be randomized at the beginning of the optimization process by the user. Thus, the chances of getting “unstuck” in a local minimum are increased.

The iterative minimization algorithm is divided into two parts that build a nested loop. The outer part (the procedure MINIM) runs through the user defined number of iterations and controls which model parameters are varied in each iteration step. In the inner part (the procedure QUADMIN) the actual parameter variation is performed at each iteration step, and an optimized set of parameters is passed back to the outer part.

MINIM

This procedure controls which parameters are varied and in which boundaries they are allowed to be varied and then calls QUADMIN for the optimization of the *SOS*. The initial boundaries for the parameter variation are based on the initial parameter values, calculated by multiplying each variable parameter with a random number, and saved in the diagonal elements of the matrix OFFSET. The optimization algorithm then performs the following steps:

- Step 1: Using the columns in the OFFSET matrix as a boundary vector BND, each parameter is varied successively while keeping all other parameters constant. The new parameters are saved in the vector MN. The parameter with the highest impact on the *SOS* is identified and its position in the MN vector saved.
- Step 2: After a complete loop through all parameters, the boundaries for the parameter variation are reset to the difference between the new parameter values at the end of the first optimization loop and the original parameters. Using the new boundaries, all parameters are once varied simultaneously.
- Step 3: Finally, the column of the OFFSET matrix containing the parameter variation with the highest impact on the *SOS* is discarded by moving all columns with higher indices one column to the left. The last column of the OFFSET matrix is replaced with the new boundaries set in step 2, and the new parameter vector MN is written onto the original parameter vector. Then the algorithm is repeated with step 1.

Several exit criteria end the iteration process. Either a user defined maximum iteration number is reached or the change in the *SOS* drops below a certain threshold or some internal error criteria are fulfilled.

QUADMIN

This procedure is called by MINIM and performs the actual parameter variation in order to minimize the objective function *SOS*. The parameter variation is executed along a dimensionless set of coordinates VT, using a step direction and step length parameter TNEW in order to adjust the step size.

Initially, the original parameter vector and the original *SOS* are stored and the parameter vector MN is varied by adding the boundary vector BND. Then, the iterative parameter variation begins.

- Step 1: The *SOS* is evaluated with the new parameter set. If the new *SOS* is larger than the original *SOS*, multiplied with a random factor, the step parameter TNEW is assumed to be too large and is reduced.
- Step 2: In the first iteration loop TNEW is set to a fixed value. For all further iteration loops the value for TNEW is evaluated depending on three preceding calculation steps that form a set of coordinates that is renormalized at each calculation step.
- Step 3: A new parameter vector is generated using the original parameter vector MINA, the boundary vector BND and the step direction factor TNEW, according to

$$MN(i) = MINA(i) + TNEW * BND(i), \quad i = 1 \dots N_p, \quad 4.4$$

where N_p is the number of variable parameters. The algorithm continues with Step 1. Since TNEW can exceed the bounds $-1 < TNEW < 1$, the parameter variation may well exceed the boundaries originally given in BND. If only one parameter is varied, the vector BND has only one nonzero entry. If more than one parameter is varied (more than one nonzero entry in BND), they are all varied using the same step direction factor TNEW.

4.3 Fitting Mixture Equations of State Using REFPROP

Before starting to fit a binary mixture, all available (and useable) experimental data must be collected, transformed to a specific set of molar SI units, and put into a machine readable fitter input file. This file also holds the thermodynamic constraints described in Section 4.1, which are added when needed during the fitting process. It is recommended to start the fitting process with only a few experimental gas phase (and liquid phase if available) density points and some VLE data at different temperatures and pressures, thus giving the fitter general information on the two-phase region and the gas phase properties. The data points are included in the fit by setting numerical values (positive, nonzero) as weights for each individual data point entry in the fitter input file. The initial weights are usually small since the influence of different properties on the equation only shows during the fitting process.

When starting a new fit for a binary mixture, initially only the reducing parameters given in Eqns. 2.31 and 2.32 are adjusted. For mixtures with very limited experimental data or quite ideal mixing behavior, fitting the temperature and density reducing parameters $\gamma_{T,ij}$ and $\gamma_{v,ij}$ may prove sufficient. The second reducing parameters for temperature and density, $\beta_{T,ij}$ and $\beta_{v,ij}$, are already much more powerful and can distort the equation if not fitted carefully. They are introduced if the mixture becomes more non-ideal and cannot be described with just one binary reducing parameter for temperature and density each. Fitting all four parameters (two parameters for inverse reduced temperature and two parameters for reduced density) requires an increased amount of experimental data, both for the VLE region and the homogeneous phase. Since the reducing parameters already have a strong influence on the shape of the phase boundaries, they have to be monitored carefully during the fitting process, especially the shape of the critical region.

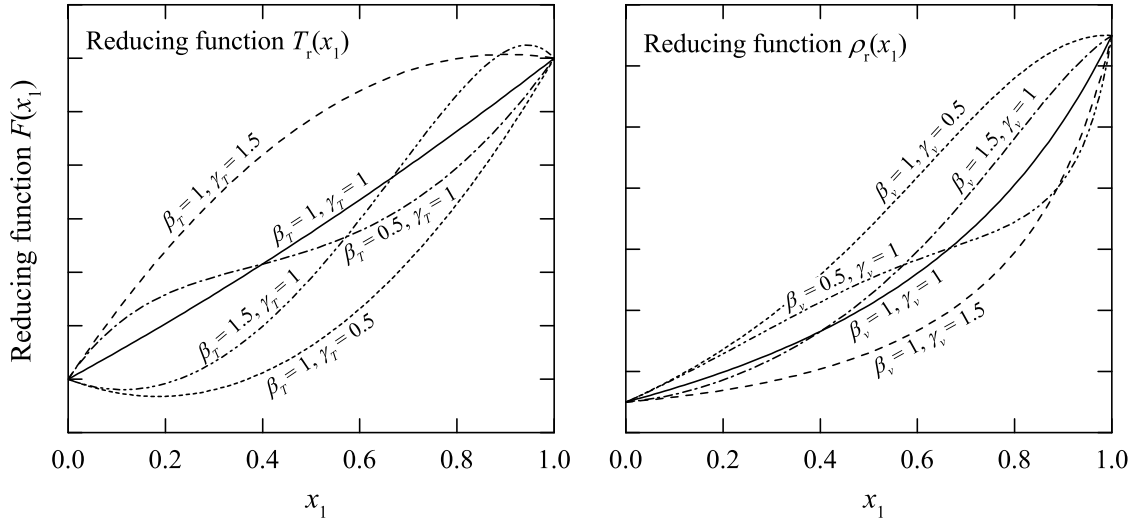


Figure 4.1: Influence of the binary parameters β and γ on the reducing functions $T_r(x_1)$ and $\rho_r(x_1)$ for an arbitrary binary mixture.

Fitting the parameters of the reducing functions affects at which reduced variables the pure fluid equations in the mixture model are evaluated for a given set of temperature, density, and composition. By changing the values for $\gamma_{T,ij}$ and $\gamma_{v,ij}$, the temperatures and densities where $\tau = 1$ and $\delta = 1$ (which indicate the critical isotherm and isochore for pure fluids but do not have the same meaning for the mixture) are moved to higher or lower temperatures or densities, respectively. The parameters $\beta_{T,ij}$ and $\beta_{v,ij}$ influence the curvature of $T_r(x_1)$ and $\rho_r(x_1)$ over composition and result in a more asymmetric mixing behavior when set to non-unity values. As shown in Figure 4.1, the reducing function $\rho_r(x_1)$ has already nonlinear characteristics for reducing parameters γ_v and β_v equal to one, resulting from the combination rule used for the critical parameters of the pure fluids (see Eqn. 2.31), while the reducing function $T_r(x_1)$ is almost linear when the reducing parameters $\gamma_{T,ij}$ and $\beta_{T,ij}$ are set to unity.

For a group of binary mixtures with very similar characteristics it may be advantageous to develop one general departure function and use only the weighing factor F_{ij} to adjust the departure function to each individual binary system of such a group. The general departure function is adjusted to the binary system with the best data set with a weighing factor of one. For all other binary systems the influence of the departure function on the mixture model is controlled only by fitting the weighing factor F_{ij} . Such a general departure function was developed in the GERG-2004 equation of state by Kunz *et al.* (2007) for the binary mixtures of Methane + n-Butane, Methane + Isobutane, Ethane + Propane, Ethane + n-Butane, Ethane + Isobutane, Propane + n-Butane, Propane + Isobutane, and n-Butane + Isobutane, where the binary system Methane + n-Butane was used for fitting the general departure function. In this work, the departure function developed for the system water + nitrogen was also used for water + oxygen and water + CO by adjusting the F_{ij} parameter.

A binary specific departure function (Eqn. 2.34) is only introduced when sufficient accurate experimental data are available and the mixture behaves strongly non-ideal (meaning that fitting only the reducing parameters proves to be insufficient to accurately describe reliable experimental data). The experimental data should cover the whole (measurable) VLE region, favorably $pTxy$ data on isotherms with data points up to the maximum pressure (or up to very high pressures in case the mixture does not have a maximum pressure in the VLE region at this temperature). Additionally, the density data should cover not only the gas but also the supercritical, and if possible the liquid region up to high pressures. Experimental data for speed of sound (especially at high densities), isochoric heat capacity or excess enthalpy should also be included in the fit if available.

Since the optimization problem becomes very complex when simultaneously fitting the reducing parameters and the parameters of a departure function, there is no general strategy that can be applied. However, the goal is to find the optimal set of experimental data points and constraints, together with their individual weights, to force the equation in the desired shape. Several different approaches have been tested and used in combination to fit the departure functions developed in this work.

Departure Function Fitting

The binary departure function α_{ij}^r introduced in Section 2.3 can be used to adjust the mixture model to experimental data of a binary system and to describe residual mixing behavior that cannot be predicted by the extended corresponding states approach with adjusted reducing parameters only. The general functional form used in the EOS-CG mixture model includes three different types of terms with polynomial and exponential functions of the reduced density δ and the inverse reduced temperature τ . It reads

$$\begin{aligned}
\alpha_{ij}^r(\delta, \tau) = & \sum_{k=1}^{K_{\text{pol},ij}} n_{ij,k} \delta^{d_{ij,k}} \tau^{t_{ij,k}} + \sum_{k=K_{\text{pol},ij}+1}^{K_{\text{pol},ij}+K_{\text{exp},ij}} n_{ij,k} \delta^{d_{ij,k}} \tau^{t_{ij,k}} \exp(-\delta^{l_{ij,k}}) \\
& + \sum_{k=K_{\text{pol},ij}+K_{\text{exp},ij}+1}^{K_{\text{pol},ij}+K_{\text{exp},ij}+K_{\text{spec},ij}} n_{ij,k} \delta^{d_{ij,k}} \tau^{t_{ij,k}} \exp\left[-\eta_{ij,k}(\delta - \varepsilon_{ij,k})^2 - \beta_{ij,k}(\delta - \gamma_{ij,k})\right].
\end{aligned} \tag{4.5}$$

Fitting a departure function usually starts with only one polynomial or exponential term. Initial values for the coefficient n_{ij} , the temperature exponent t_{ij} , the density exponent d_{ij} , and the density exponent in the exponential function, l_{ij} have to be set. It has proven useful to set all exponents to unity and give the coefficient a small value, e.g. 10^{-2} . In order to use a purely polynomial term the exponent l_{ij} is simply set to zero. Initially only the coefficient and the temperature exponent should be fitted (together with the four binary reducing parameters that are usually adjusted together with the departure function). Once the *SOS* reaches a stable value, meaning that under the current conditions the fitting algorithm does not find a better solution anymore, the resulting mixture model is analyzed with respect to the representation of all of the experimental data and the qualitative propagation of several thermodynamic properties along different isolines. Now an iterative process begins that involves the following steps (not necessarily in this order, and not necessarily all of them)

- Change weights of data points, add new data points, take out data points,
- Introduce a new constraint, change / remove an existing constraint,
- Make changes to the departure function,
- Analyze the fitting results.

Once the *SOS* does not improve anymore using the current combination of terms, and the result is not yet satisfactory, the parameter set has to be tested to check if the fit is only “stuck” in a local minimum and there exists a better solution with the current number of adjustable parameters, or if the *SOS* can only be reduced further by introducing an additional term to the departure function. Since this question cannot be answered directly, several methods can be applied in order to get “unstuck” from a local minimum and to try and find a better solution with the current set of adjustable parameters.

The initial randomization of the coefficients often helps the algorithm to leave a local minimum and find a different, better solution. Especially when the departure function holds higher temperature exponents ($t_{ij,k} > 3.0$) it may also be helpful to drastically change some or all of the temperature exponents in order to find a new solution. This can either be done manually or with a fitter command that introduces a new set of temperature exponents by creating random values in the range $0.5 < t_{ij,k} < 2.5$. Alternatively, a single temperature exponent can also be forced to slowly adopt a new value by using a constraint that only allows the exponent to be varied within a given limit.

In case the density exponents $d_{ij,k}$ and $l_{ij,k}$ are not adjusted by the fitter, these values can also be manipulated manually in order to find a different solution for the fit. Fitting the

density exponents together with the temperature exponents and the coefficients of the departure function may initially prove more efficient than changing them manually. However, as discussed by Span (2000) all density exponents in a Helmholtz equation of state need to be integer values in order to ensure physically correct extrapolation behavior of the model towards zero density. Thus, if the density exponents are included in the fit, they need to be rounded manually afterwards to become integer values. This process itself can drastically change the equation and make an originally good departure function with non-integer values for the exponents to become inferior due to the rounding process.

Once the number of terms in the departure function increases it becomes more likely that two terms intercorrelate or that a term has an insignificant or even negative influence on the equation. Intercorrelation can be avoided by a fitter command that forces the terms of the departure function to have significantly different temperature and density exponents. The significance of the individual terms in the departure function is not easily determined. Checking the increase in the *SOS* while taking out each term successively – and more importantly, the speed and magnitude of the following decrease while the fitter tries to optimize the *SOS* with the changed departure function – gives a good feeling for the significance of a term in the equation.

All the steps in the development of a departure function described above are part of an iterative trial-and-error process. Since for a new binary system the optimum number, combination and type of terms is unknown the best part of the fitting work includes finding the best combination and number of terms. In the fitting method used in the development of the GERG-2008 and other previous equations of state for pure substances developed by the Wagner group this process is automated by using a bank of terms and optimization formulations based on the Setzmann-Wagner algorithm by Setzmann and Wagner (1989). Such a bank of terms may include thousands of terms (different combinations of temperature and density exponents) from which the algorithm chooses the optimum combination to form the equation with the lowest *SOS*. However, although such an approach produces faster and more reproducible results than the fitting process employed here it has its limits.

The enormous flexibility of the nonlinear fitter used in this work concerning the simultaneous adjustment of the reducing parameters as well as all coefficients and exponents of the departure function allows for a more efficient use of adjustable parameters in the model since e.g. the temperature exponents are not limited to values preset in a bank of terms. This often results in a smaller number of terms in a Helmholtz model with similar accuracy than one developed with a bank of terms. Although the Setzmann-Wagner optimization method also allows the use of constraints to a certain degree, the potential is vastly increased with the nonlinear algorithm by Lemmon. Beside

the possibility of controlling the shape of almost any thermodynamic property the Helmholtz function itself can be directly manipulated during the fit.

One main reason for the lengthy fitting procedure of departure functions is that not only the optimum set of terms is unknown, but also the optimum set of data points and constraints and, even more important, the optimum combination of weights. Although some general rules can be applied for the use of weights (see below), especially the weights for VLE data have to be adjusted carefully by examining their effect on the equation, rather than only by the accuracy of the experimental data.

Weighing of Experimental Data Points

Assigning weights to data points included in the fit has a strong influence on the outcome of the fitting process. Since the weight of a data point reflects its influence on the fit it should reflect the quality of the measurement. Span (2000) suggested a method to calculate the weight for each individual data point from the estimated experimental uncertainty given by the author of the experimental data. The estimated experimental uncertainty is calculated by the well-known law of error propagation given by

$$\sigma_{p,m}^2 = \left(\left(\frac{\partial \zeta_p}{\partial y} \right)_{\bar{x}} \sigma_y \right)^2 + \sum_{k=1}^K \left(\left(\frac{\partial \zeta_p}{\partial x_k} \right)_{y, x_i \neq k} \sigma_k \right)^2, \quad 4.6$$

where $\sigma_{p,m}$ is the estimated expanded experimental uncertainty of the property y , x_k are independent variables of the property, and σ_y and σ_k are the individual experimental uncertainties of each variable. In order to calculate the experimental uncertainty for the development of an equation of state, the function $\zeta_p(y, \bar{x})$ has to be known that describes the relation between the property y and its independent variables x_k . The best approximation of this function is actually the equation of state, which is yet unknown at this point. It can be approximated by an auxiliary equation, which is a correlation equation sometimes given by the experimentalist or a preliminary or previous equation of state. The weight $W_{p,i}$ is related to the expanded uncertainty by

$$W_{p,i} = \frac{1}{\sigma_{p,m}}. \quad 4.7$$

This way, the experimental data point is represented by the equation of state within its experimental uncertainty if its contribution to the *SOS* is ≤ 1.0 .

However, this method has some practical limitations, especially when it comes to experimental data of mixtures. As pointed out by Span (2000), the first problem occurs when calculating the experimental uncertainty of the property. Estimates for each individual uncertainty in the measurement (e.g. for density measurements: uncertainty in temperature measurement, in pressure measurement, in density measurement, and in the determination of the composition) are often not given by the author or incomplete. Even if

uncertainties are given they often prove overly optimistic, especially for older data sets. In the case of mixtures, the uncertainty of the mixture composition is often neglected, whereas in fact this influence may well be stronger than the one of the temperature or pressure uncertainty. Also for properties and regions with a strongly nonlinear behavior (e.g. the isochoric heat capacity or the phase boundaries in the critical region), the approximation given in Eqn. 4.6 based on a linear Taylor series may not be valid anymore.

The largest problem in the determination of weights occurs with VLE data for mixtures. Since for a full $pTxy$ data set the differences of the fugacities at the vapor and liquid phase composition build the contribution of the *SOS* (see Table 4.1), the fugacity is the function needed to evaluate Eqn. 4.6 according to $\zeta_p = f(T, p, \bar{x})$. This function is usually strongly nonlinear in the composition range, and a good estimate from a preliminary equation does not exist. Mainly from experience the weights of data points have to be carefully adjusted and readjusted during the fitting process. At the critical point of a binary mixture the fugacity at constant T and p has a saddle point when plotted over composition, resulting in very small slopes in the extended critical region. This behavior leads to very small contributions of VLE points in the extended critical region and has to be considered by setting higher weights to these points.

Analyzing the Fitting Results

The first indicator on the progress of the fitting process is the decrease of the *SOS*. However, since this value includes contributions of a number of different property types (plus thermodynamic and non-thermodynamic constraints) it only gives a very rough indication on the actual quality of the equation. A better overview on the contribution of each property and constraint included in the fit gives a look at the individual deviations (with and without their weight) that make up the *SOS*. That way two questions can be addressed: Are the data points represented within acceptable deviations (e.g. within their experimental uncertainty)? How strong is the influence of the weighed data points on the *SOS*?

A more thorough and generally the best and fastest way to analyze the representation of all experimental data (not only the data included in the fit) in the homogeneous region by the equation of state is through viewing the deviation plots. Such plots can be generated quickly using the EOSPLOT tool that is part of the fitting software used in this work. This tool uses files of all available experimental data for each property type as input, recalculates the data points and returns the deviations between the current equation and the data. The deviations are generally plotted over temperature and pressure in order to identify systematic offsets and deviations. Additionally, for mixtures it is important to look at the deviations progressing over the composition in order to identify shortcomings in the composition-dependence of the mixture model.

Deviation plots are helpful for the analysis of the representation of e.g. density, heat capacity or speed of sound data in the gas or liquid phase. In the critical region the uncertainties of these data and also of the equation usually increase due to the steep slope of these properties along a near-critical isotherm. Since the critical line of a binary mixture is usually not known exactly, and since it progresses over temperature, pressure and composition, the identification of properties and their deviations in the critical region from (two-dimensional) deviation plots becomes difficult. Also the evaluation of VLE data is often not meaningful using deviation plots only. Deviations in saturation pressure, temperature or composition are only meaningful in certain regions, depending on the shape of the phase boundary line. If e.g. the phase boundary line in a p - x plot is very steep (which is the case for binary mixtures of water with gases at elevated pressures), the slightest offset between predicted and experimental phase compositions results in a huge difference in vapor pressure. A more meaningful way of evaluating the representation of experimental VLE data is to view at absolute plots, e.g. p - x plots at various isotherms, or p - T plots at fixed compositions. For mixtures with very small phase compositions – in this work mainly mixtures involving water – the solubility in a x - p diagram and at the saturated water content in a y - p diagram with double logarithmic scaling up to very high pressures reveals both the qualitative and quantitative behavior of the equation. Also excess properties (h^E , v^E) are best reviewed in absolute plots, since only here a qualitatively wrong shape of the calculated excess part of a property becomes obvious.

Beside the evaluation of the representation of experimental data by the equation, the qualitative behavior, especially in the two-phase region and outside the range of experimental data, has to be analyzed. This is also best done graphically using REFPROP. The plots used for analyzing equations of state are basically consistent to the thermodynamic constraints used for fitting (see Table 4.3). The most important plots for the evaluation of the equation in the two-phase region are the p - ρ plot and the PIP - ρ plot at constant composition. More information on the use of constraints and their evaluation in plots is given below.

Using Constraints

When fitting the departure function, the application of constraints is an important method to ensure the reasonable qualitative behavior of the equation, especially in the two-phase region. Since the terms of such a function are very powerful, they can easily change the characteristics of the equation, which may lead to unreasonable behavior outside the area where data are available for fitting. For example, when fitting binary mixtures of gases with water using departure functions, the equation tended to fit the available data quite well but showed unsatisfactory behavior in the two-phase region.

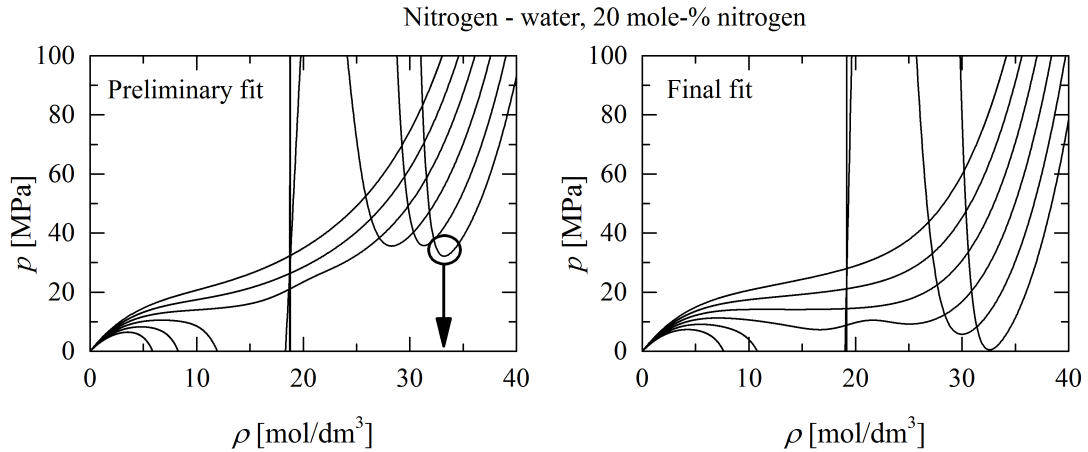


Figure 4.2: p - ρ plot of a preliminary and the final fit for the mixture nitrogen-water with isotherms at 450 K, 470 K, 490 K, 510 K, 530 K, and 550 K. The isotherms were reshaped using a constraint.

At the compositions, pressures and temperatures where this behavior was observed the system is unstable and thus the equation cannot return physically meaningful results. However, it still has to show characteristics that are in principle thermodynamically correct and numerically stable. In the example, the pressure-density plot showed for certain isotherms pressure regions where no thermodynamically correct density root exists, which may lead to a failure of the density solver when a flash calculation is performed at these pressures and temperatures. This effect could be corrected by applying a constraint that forces the pressure minimum at the highest density to be at low or negative pressures (see Figure 4.2 and Section 3.7 for more details).

The phase identification parameter (PIP) is an artificial thermodynamic property introduced by Venkatarathnam and Oellrich (2011) to identify the phase of a fluid at given state variables. It is a combination of partial derivatives of the pressure with respect to temperature and density and is given by the expression

$$\Pi = 2 - \rho \left(\frac{(\partial^2 p / \partial \rho \partial T)_{\bar{x}}}{(\partial p / \partial T)_{\rho, \bar{x}}} - \frac{(\partial^2 p / \partial \rho^2)_{T, \bar{x}}}{(\partial p / \partial \rho)_{T, \bar{x}}} \right). \quad 4.8$$

This parameter can be used to identify if a pure fluid or a fluid mixture is in a liquid or liquid-like state ($\Pi > 1$) or in a vapor state ($\Pi \leq 1$). Since this parameter includes higher order derivatives it can also be used during the fitting process to ensure qualitative behavior of the equation. In the two-phase region near the inflection point of the pressure over density at constant temperature and composition the PIP should progress smoothly over density without any “bumps”, having only one minimum and one maximum.

The fugacity is commonly used for the determination of the phase equilibrium. In multi-component phase equilibria the following condition is fulfilled for each component: the fugacities of any component i in the mixture are equal in all phases in equilibrium,

$$f'_i = f''_i = f'''_i = \dots = f_i, \quad i = 1 \dots N. \quad 4.9$$

For a binary mixture in a two-phase equilibrium at given T and p this general expression becomes

$$f'_i(T, p, x'_i) = f''_i(T, p, x''_i), \quad \text{with } i = 1, 2, \text{ and } x_2 = 1 - x_1. \quad 4.10$$

With the temperature and pressure kept constant the fugacity of a binary mixture is merely a function of the composition x_1 of component 1. In phase equilibrium this function must have at least one stationary point between the equilibrium compositions of x_1 in order to fulfill the condition of Eqn. 4.10. This consideration leads to the conclusion that at states for a given T and p where the mixture is homogeneous at all possible compositions, the fugacity is continuously ascending or descending with composition.¹⁴

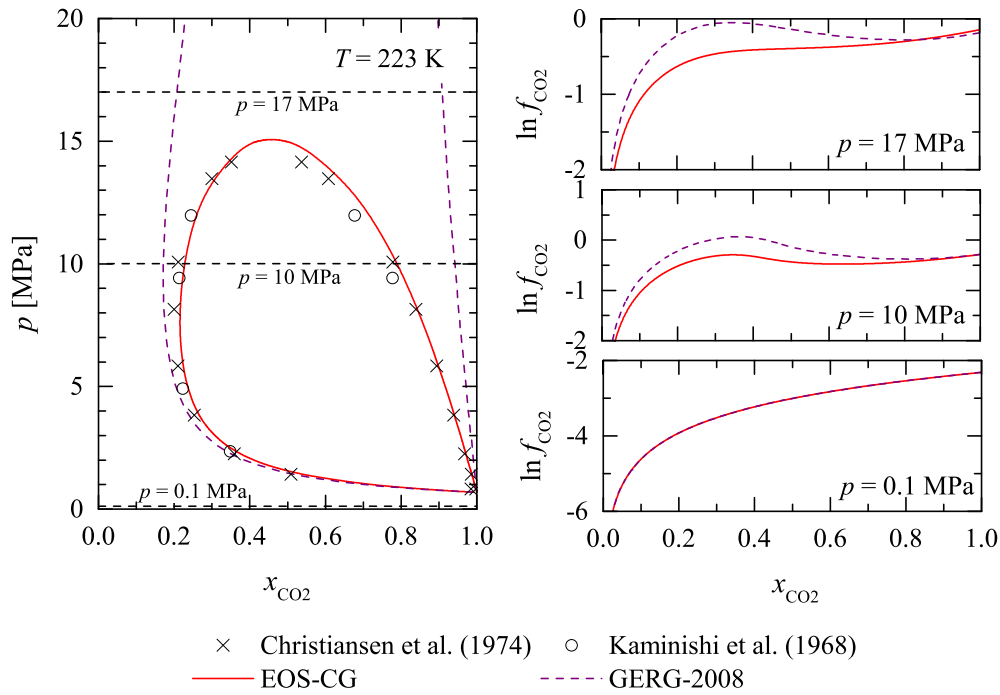


Figure 4.3: Phase boundaries (left) and the fugacity (right) over composition for the system carbon dioxide + carbon monoxide. Experimental values and calculated values from the GERG-2008 (no adjusted mixture parameters) and the EOS-CG model.

This assumption was used in the development of the new mixture model to constrain the VLE region. For mixtures and temperatures where one of the components is supercritical, the phase boundaries at fixed temperature may show a pressure maximum, which corresponds to the critical pressure at that temperature (see Figure 4.3, left for the system carbon dioxide + carbon monoxide at 223 K). When fitting the model parameters to

¹⁴ This conclusion is based on observation for a number of different binary mixtures and pT states and has proven useful for the development of the new mixture model. However, mixtures or states may exist where the fugacity as a function of composition at constant T and p has stationary points also in the homogeneous region.

experimental VLE data the description of the near-critical region proved insufficient, even by increasing the weights of the data in this region. The pressure maximum was generally predicted higher than the experimental data suggested. The introduction of a fugacity constraint helped improve the model predictions. For pressures above the maximum pressure the fugacity of one of the components increases continuously over the composition, resulting in a positive slope over the whole composition range, whereas this function shows a maximum and a minimum when the model predicts the mixture to be in phase equilibrium (see right side of Figure 4.3). Forcing the fugacity to have no change in slope for pressures slightly above the maximum pressure at a given temperature lead to an improved description of the pressure maximum and the whole VLE region.

5 COMPARISON OF THE NEW MIXTURE MODEL WITH EXPERIMENTAL DATA AND OTHER MODELS

In this chapter, the quality of the new Helmholtz-energy mixture model for humid gases and CCS mixtures (referred to as EOS-CG) is discussed based on comparisons with the available experimental data and other selected mixture models. The model mainly used for comparison is the GERG-2004 or GERG-2008 equation of state by Kunz *et al.* (2007) and Kunz and Wagner (2012), with the GERG-2008 being an expansion of the GERG-2004 including three additional components not considered in this mixture model. The reason for the extensive comparison to the GERG-2004 is that the new mixture model is based on the same mathematical structure with newly developed mixture parameters. Since the GERG-2008 already includes all six components considered in this work, comparisons for all binary mixtures are possible. Other models frequently used for comparison are the Predictive Soave-Redlich-Kwong (PSRK) cubic equation of state by Holderbaum and Gmehling (1991) and the Lee-Kesler-Plöcker corresponding states model formulated in the virial expansion of the compressibility factor Z by Plöcker *et al.* (1978). Both models were briefly introduced in Chapter 2. For the calculation of thermodynamic properties or phase compositions with the PSRK and the LKP, the software *Aspen Properties* 7.1 by Aspen Technology, Inc. (2008) was used with the respective binary mixture parameters preset in the software. For the calculation of thermodynamic properties from the GERG-2008 equation, either the GERG-2008 software by Wagner (2006) or the TREND 1.0 software by Span *et al.* (2012), a thermodynamic property calculation tool developed at the chair of Thermodynamics at the Ruhr-University Bochum, was used. This software was also employed to calculate properties from the new mixture model EOS-CG.

Whenever relative deviations are plotted or given as numerical values in the following sections, they are calculated in the fashion

$$\Delta z_{\text{rel},m} = \left[\left(\frac{z_{\text{exp}} - z_{\text{calc}}}{z_{\text{calc}}} \right) \cdot 100 \right]_m, \quad 5.1$$

where z_{exp} is the experimental value of the point m , and z_{calc} the respective value calculated from the mixture model. When relative deviations are shown in plots, the zero line represents the new EOS-CG mixture model (unless otherwise explicitly stated in the caption) and deviations to experimental data points are given as symbols. In some cases it is more meaningful to give the total deviations between experimental and calculated data points directly in the units of the property according to

$$\Delta z_{\text{tot},m} = [z_{\text{exp}} - z_{\text{calc}}]_m \quad 5.2$$

rather than in the relative, reduced form. Especially for properties that show a zero crossing like the second (cross) virial coefficient or the Joule-Thomson coefficient this notation is

preferred. But dew and bubble point temperature deviations are also given in total values. When the representation of a whole experimental data set by the model is discussed, this can be done in two ways. Either a deviation limit is given that includes all or most of the data points in the data set (or a group of data sets) or the *absolute average deviation* (AAD) of a data set is discussed. The AAD is calculated from the (relative or total) deviations of all data points in a data set (except for obvious outliers) according to

$$\text{AAD} = \frac{1}{M} \sum_{m=1}^M |\Delta z_m|, \quad 5.3$$

where M is the number of points in the data set. Due to the large number of data points the following discussion only covers a selected subset of data points that were chosen to give a characteristic impression of the quality of the mixture model and the data situation for a certain system. A comprehensive graphical comparison, together with a detailed statistical analysis including the AADs for each data set for binary and multi-component systems is given in appendix A1 and A2. In the following discussion of the representation of experimental data by the new mixture model, values of deviations between the model and experimental data are generally written with a preceding $\pm$ sign, since the deviations are mainly scattered within the given limit. When the experimental uncertainty of experimental data is referred to, this value is given without the preceding $\pm$ sign.

Statistical comparisons only provide limited information on the quality of an equation of state (usually the average deviation for one data set). They do not reveal systematic deviations of the model or a certain data set. Therefore, the following model evaluation is mainly based on graphical comparisons between the model and experimental data and other models along isotherms, isobars, or isopleths. These comparisons are often given in the form of deviation plots, especially for properties in the homogeneous region. However, for certain types of data, especially $pTxy$ data, plotting the absolute values often proved to be more meaningful than deviation plots.

For two reasons the comparison mainly focuses on binary mixtures. First, the available data for ternary or higher order mixtures is very limited and therefore a comparison only has limited significance. Second, the model was fitted to binary mixture data; therefore the comparison to the same data directly shows the success or limits of the fitting results.

5.1 Experimental Data Used for the Development of the New Mixture Model

The development of the new mixture model presented in this work is based on experimental data of several thermodynamic properties of all binary combinations of the considered components. Thus as a first step in this work a comprehensive database of experimental thermodynamic properties of all 15 binary systems that can be built from the six components carbon dioxide, water, nitrogen, oxygen, argon, and carbon monoxide was

established. Additionally, experimental data of several multi-component mixtures was collected for the evaluation of the mixture model.

The data collection is comprised mainly of density data ($p\rho T$ data) and measurements of the phase equilibrium compositions (VLE data). Other property types included in the data base are speed of sound, isobaric heat capacity, Joule-Thomson coefficient, second cross virial coefficient B_{12} , and excess enthalpy. The excess part z^E of a thermodynamic mixture property z is defined as

$$z^E(T, p, \bar{x}) = \begin{cases} z(T, p, \bar{x}) - \sum_{i=1}^N x_i z_{0,i}(T, p) + R \sum_{i=1}^N x_i \ln x_i & \text{for } z = s \\ z(T, p, \bar{x}) - \sum_{i=1}^N x_i z_{0,i}(T, p) - RT \sum_{i=1}^N x_i \ln x_i & \text{for } z = a, g \\ z(T, p, \bar{x}) - \sum_{i=1}^N x_i z_{0,i}(T, p) & \text{for all other properties,} \end{cases} \quad 5.4$$

where $z_{0,i}$ and x_i are the property and the mole fraction of the component i in the mixture, respectively. Additionally, isochoric heat capacity data and data of the second mixture virial coefficient were found for multi-component mixtures. A summary of all data collected for binary and multi-component mixtures is given in Table 5.1.

Table 5.1: Summary of experimental data for binary and multi-component mixtures collected during this work.

Property type	Number of data points		
	Binary mixtures	Multi-component mixtures	Total
$p\rho T$ data	12534	3167	15701
VLE data	5784	490	6274
Excess enthalpy	1879	—	1879
Speed of sound	124	470	594
Isobaric heat capacity	2200	88	2288
Isochoric heat capacity	—	300	300
Joule-Thomson coefficient	84	—	84
B_{12} and B data	293	115	408
Total	22898	4630	27528

About one third of the data collected in the database was taken from the GERG-2004 database, which was kindly provided by O. Kunz. References for these data can also be found in Kunz *et al.* (2007). Most of the data on the binary mixtures of the air components nitrogen, oxygen and argon, as well as most of the data on dry air and humid air was adopted from the database of the AA-CAES project (see Herrmann *et al.* (2009) or

Herrmann *et al.* (2010) for more information on this project), which was kindly provided by S. Herrmann. The remaining part, more than half of the data in this database, was procured in a literature search for original research articles, monographs, reports or other types of publication on experimental data. Great care was taken to not only collect the data points from the other databases but to also get copies of the original publications (where possible) from which the data were taken. This way, additional information e.g. on the experimental method and the uncertainty stated by the authors could be used to evaluate the quality of the data.

In order to use the data for the development of the mixture model and the computation of comparisons with the model, all data points were digitalized, converted to a common set of SI-based units and brought to a fixed machine-readable format. Additionally, temperature values published before 1990 were converted to the ITS-90 temperature scale with the algorithms proposed by Goldberg and Weir (1992). Temperature values published before 1948 were left unconverted. In order to find outliers or errors in the data digitalization and conversion process, all data points were recalculated using the GERG-2004 equation of state. As a result the database holds data files for each data set of each author (if a publication holds more than one data set, e.g. density data and VLE measurements, separate data files for each data set and each property type were produced), grouped into the respective binary and multi-component systems. Each data set and each data point have a unique identification number and can thus be identified and related to the respective publication. In order to use the experimental data together with the fitting software for the development of the mixture model, all data points of each binary system were compiled into one single fitter input file using a fixed line format and molar-based SI units. Once the new mixture model was finalized, these files were also used for the evaluation calculations.

More than 50 % of the experimental data for binary mixtures describe the $p\rho T$ relation in the homogeneous gas or liquid phase or at the phase boundaries. About 25 % of the binary mixture data describe the phase compositions at given temperature and pressure in vapor-liquid or liquid-liquid equilibrium. Excess enthalpy data contribute about 8 % to the binary mixture database, with the main contributions by the group around C. J. Wormald from the School of Chemistry at the University of Bristol, U.K. (e.g. Wormald *et al.* (1997) or Wormald and Lancaster (1988)), who measured excess enthalpies for several binary mixtures with water. Very little data are available for other caloric properties like the isobaric or isochoric heat capacity or the speed of sound. The relatively large number of isobaric heat capacity data results mainly from one large data set for the nitrogen + oxygen mixture by Perkins and Cieszkiewicz (1991), which however is of poor quality. This lack of caloric data for a large number of systems poses a problem for the development of Helmholtz-energy mixture models. As mentioned at the beginning of Chapter 4, the empirical model explicit in the reduced Helmholtz free energy α is fitted to experimental

data via its partial derivatives, through which it is linked to the different thermal and caloric properties (see Table 2.6). In Table 5.2 these relations are again summarized for the thermodynamic properties for which experimental data of binary mixtures is available. Although in principle VLE data and density data cover all first and second order partial derivatives of the residual part of the Helmholtz free energy (only this part is fitted to mixture data), accurate speed of sound or heat capacity data in the homogeneous gas and liquid region are crucial for the development of accurate mixture models that cover the whole fluid region since these properties incorporate most of the partial derivatives of the reduced Helmholtz free energy.

Table 5.2: Thermodynamic properties available as experimental data and their relation to partial derivatives of the reduced Helmholtz free energy α .

Thermodynamic property	Related derivatives of $\alpha(\delta, \tau, \bar{x})$
$p\rho T$ relation: $p(\rho, T, \bar{x})$, B_{12} , B	α_δ^r
Fugacity $f_i(p, T, \bar{x})$ (for VLE/LLE calculation)	α_δ^r , $\alpha_{\delta\delta}^r$, $\alpha_{\delta\tau}^r$, α_τ^r , $\alpha_{\tau\tau}^r$, α_x^r , α_{xx}^r
Speed of sound $w(p, T, \bar{x})$	α_δ^r , $\alpha_{\delta\delta}^r$, $\alpha_{\delta\tau}^r$, $\alpha_{\tau\tau}^r$, $\alpha_{\tau\tau}^0$
Joule-Thomson coefficient $\mu_{JT}(p, T, \bar{x})$	α_δ^r , $\alpha_{\delta\delta}^r$, $\alpha_{\delta\tau}^r$, $\alpha_{\tau\tau}^r$, $\alpha_{\tau\tau}^0$
Isobaric heat capacity $c_p(p, T, \bar{x})$	α_δ^r , $\alpha_{\delta\delta}^r$, $\alpha_{\delta\tau}^r$, $\alpha_{\tau\tau}^r$, $\alpha_{\tau\tau}^0$
Isochoric heat capacity $c_v(\rho, T, \bar{x})$	$\alpha_{\tau\tau}^r$, $\alpha_{\tau\tau}^0$
Enthalpy, excess enthalpy $h(p, T, \bar{x})$, $h^E(p, T, \bar{x})$	α_δ^r , α_τ^r , α_τ^0

Only very limited data on multi-component mixtures of the components considered in this work were found in the literature. Most of these data are comprised of the well-measured ternary mixture of nitrogen, oxygen and argon (*dry air*) plus data on the mixture of dry air with water (*humid air*).

Beside the property type and the absolute number of available data points the quality and covered temperature, pressure and composition range of the data plays a major role for the development of mixture models. Depending on the binary system the data situation diverges considerably. However, some similarities can be observed for certain groups of mixtures. The data situation for the 15 binary systems considered in this work is summarized in Table 5.3. An overview on the data collected for multi-component mixtures is given in Table 5.4. A detailed discussion of the available data sets and the covered range is given in Sections 5.2 and 5.3. Additionally, a detailed overview of all data points and publications used for the development of this mixture model is given in appendix A2 in Table A2.1.

Table 5.3: Summary of the available experimental data used for the development of binary model parameters for the 15 binary mixtures of the new mixture model.

Binary mixture	Number of data points		Covered range		
	total ^a	used ^b	Temperature [K]	Pressure [MPa]	Composition x_1^c
CO₂-H₂O					
$p\rho T$ data	3168	177	278 – 1023	0.0 – 600.0	0.00 – 0.99
VLE data	1488	88	251 – 623	0.1 – 350.0	0.08 – 1.00
Excess enthalpy	880	37	323 – 698	0.0 – 25.5	0.00 – 0.95
Isobaric heat capacity	25	24	298 – 703	0.1 – 28.0	0.00
B_{12} data	9	0	298 – 473		
Total	5570	326	251 – 1023	0.0 – 600.0	0.00 – 1.00
CO₂-N₂^d					
$p\rho T$ data	4958	0	208 – 673	0.0 – 273.7	0.10 – 0.98
VLE data	435	0	208 – 303	0.7 – 21.4	0.15 – 0.99
Excess enthalpy	666	0	283 – 353	1.0 – 12.1	0.10 – 0.90
Speed of sound	104	0	249 – 422	0.5 – 400.0	0.39 – 0.95
Isobaric heat capacity	203	0	313 – 363	0.1 – 16.5	0.68 – 0.93
B_{12} data	13	0	289 – 363		
Total	6379	0	208 – 673	0.0 – 400.0	0.10 – 0.99
CO₂-O₂					
$p\rho T$ data	235	65	273 – 383	0.0 – 20.0	0.49 – 0.96
VLE data	133	70	218 – 298	0.9 – 13.5	0.19 – 0.93
Speed of sound	20	20	268 – 301	10.4 – 40.9	0.93
B_{12} data	6	0	289 – 363		
Total	394	155	218 – 383	0.0 – 40.9	0.19 – 0.96
CO₂-Ar					
$p\rho T$ data	1161	219	288 – 573	0.3 – 101.3	0.12 – 0.96
VLE data	93	61	233 – 299	1.5 – 14.0	0.25 – 0.99
Joule-Thomson coeff.	84	67	233 – 383	0.0 – 20.2	0.46 – 0.75
B_{12} data	14	6	289 – 573		
Total	1352	353	233 – 573	0.0 – 101.3	0.12 – 0.99
CO₂-CO					
$p\rho T$ data	281	63	308 – 423	0.1 – 47.0	0.29 – 0.95
VLE data	56	22	223 – 283	0.8 – 14.2	0.20 – 0.98
B_{12} data	8	5	223 – 423		
Total	345	90	223 – 423	0.1 – 47.0	0.20 – 0.98

Table 5.3 continued...

Binary mixture	Number of data points		Covered range		
	total ^a	used ^b	Temperature [K]	Pressure [MPa]	Composition x_1^c
H₂O-N₂					
$p\rho T$ data	429	179	428 – 706	1.1 – 286.1	0.06 – 0.95
VLE data	851	84	233 – 657	0.1 – 270.5	0.01 – 1.00
Excess enthalpy	255	30	373 – 698	0.1 – 12.5	0.24 – 0.79
B_{12} data	57	0	223 – 663		
Total	1592	293	223 – 706	0.1 – 286.1	0.01 – 1.00
H₂O-O₂					
$p\rho T$ data	146	34	471 – 672	19.5 – 324.0	0.06 – 0.90
VLE data	172	37	281 – 656	0.1 – 279.8	0.00 – 0.99
B_{12} data	23	0	100 – 2000		
Total	341	71	100 – 2000	0.1 – 324.0	0.00 – 0.99
H₂O-Ar					
$p\rho T$ data	236	78	322 – 716	10.4 – 337.2	0.20 – 0.99
VLE data	386	37	258 – 662	0.1 – 337.2	0.00 – 0.76
Isobaric heat capacity	50	16	305 – 720	16.6 – 32.3	0.99
Excess enthalpy	52	8	373 – 698	0.1 – 13.3	0.50
B_{12} data	27	0	233 – 373		
Total	751	139	233 – 720	0.1 – 337.2	0.00 – 0.99
H₂O-CO					
VLE data	18	16	310 – 588	0.3 – 13.8	0.00 – 0.55
Excess enthalpy	26	11	363 – 698	0.0 – 12.1	0.50
B_{12} data	14	0	200 – 2000		
Total	58	27	200 – 2000	0.0 – 13.8	0.00 – 0.55
N₂-O₂^d					
$p\rho T$ data	237	0	66 – 333	0.1 – 15.6	0.10 – 0.79
VLE data	650	0	62 – 136	0.0 – 3.0	0.10 – 1.00
Isobaric heat capacity	1922	0	64 – 304	0.2 – 70.4	0.24 – 0.50
B_{12} data	48	0	72 – 480		
Total	2857	0	62 – 480	0.0 – 70.4	0.10 – 1.00
N₂-Ar					
$p\rho T$ data	1023	58	73 – 423	0.1 – 800.0	0.16 – 0.80
VLE data	537	35	77 – 133	0.1 – 2.7	0.05 – 1.00
B_{12} data	58	0	72 – 474		

Table 5.3 *continued...*

Binary mixture	Number of data points		Covered range		
	total ^a	used ^b	Temperature [K]	Pressure [MPa]	Composition x_1^c
N₂-Ar <i>continued</i>					
Total	1618	93	72 – 474	0.1 – 800.0	0.16 – 1.00
N₂-CO					
<i>pρT</i> data	558	267	273 – 353	0.3 – 30.1	0.85 – 0.96
VLE data	292	35	68 – 122	0.0 – 2.8	0.11 – 1.00
<i>B</i> ₁₂ data	8	0	303 – 348		
Total	858	302	68 – 353	0.0 – 30.1	0.11 – 1.00
O₂-Ar					
<i>pρT</i> data	93	8	70 – 298	0.0 – 12.6	0.00 – 0.99
VLE data	646	43	82 – 138	0.0 – 2.6	0.03 – 1.00
<i>B</i> ₁₂ data	8	0	289 – 463		
Total	747	51	70 – 463	0.0 – 12.6	0.00 – 1.00
O₂-CO					
<i>No experimental data available</i>					
Ar-CO ^d					
<i>pρT</i> data	7	0	83	0.01	0.28 – 0.76
VLE data	27	0	83 – 137	0.1 – 3.5	0.05 – 0.90
Total	34	0	83 – 137	0.0 – 3.5	0.05 – 0.90

^a Number of all available data points.^b Number of data points used for the development of the mixture model.^c Mole fraction of the first component in the mixture. For VLE data this range corresponds to the saturated vapor phase composition. Mole fractions of 0.0 or 1.0 correspond to mixtures with very small amounts of one of the components.^d No data were used for fitting since the original mixing rules of the GERG-2004 equation of state were used.**Table 5.4:** Multi-component mixture data used for comparison with the new mixture model.

Multi-component mixture	Number of data points	Covered range		
		Temperature [K]	Pressure [MPa]	Composition x_1 ^a
CO₂-N₂-O₂				
Saturated density	23	273	5.2 – 10.6	0.60 – 0.78
VLE data	76	218 – 273	5.2 – 13.1	0.60 – 0.92
Total	99	218 – 273	5.2 – 13.1	0.60 – 0.92

Table 5.4 *continued...*

Multi-component mixture	Number of data points		Covered range	
N₂-O₂-Ar-H₂O (<i>humid air</i>)				
<i>ppT</i> data	708	300 – 672	0.1 – 279.5	0.15 – 0.78
VLE data	267	288 – 413	0.1 – 25.0	0.41 – 0.78
Speed of sound	23	450	0.1 – 1.2	0.63
Total	998	288 – 672	0.1 – 279.5	0.15 – 0.78
N₂-O₂-Ar (<i>dry air</i>)				
<i>ppT</i> data	2436	60 – 1273	0.0 – 303.9	0.78
VLE data	147	81 – 132	0.1 – 3.8	0.08 – 0.94
Speed of sound	447	90 – 1572	0.0 – 13.8	0.78
Isobaric heat capacity	88	271 – 2499	0.0 – 29.4	0.78
Isochoric heat capacity	300	66 – 298	2.0 – 32.9 ^b	0.78
<i>B</i> data	115	49 – 1501		0.78
Total	3533	49 – 2499	0.0 – 303.9	0.08 – 0.94

^a Mole fraction of the first component in the mixture. For VLE data this range corresponds to the saturated vapor phase composition. Mole fractions of 0.0 or 1.0 correspond to mixtures with very small amounts of one of the components.

^b Density range given in [mol/dm³] instead of pressure range.

5.2 Representation of Thermodynamic Properties of Binary Mixtures

In the following paragraphs the new mixture model is evaluated for its performance regarding binary mixtures by detailed comparisons with experimental data and other mixture models. The evaluation is divided in three parts, each holding groups of binary mixtures with similar characteristics with regard to their phase boundaries. The first group, discussed in Section 5.2.1, includes mixtures of carbon dioxide with lighter gases. Mixtures of water with all other components considered in the new mixture model are evaluated in Section 5.2.2; and an overview of all remaining binary systems is given in Section 5.2.3. Finally, the calculation of virial and cross virial coefficients from the mixture model is discussed in Section 5.2.4.

5.2.1 Binary Mixtures with Carbon Dioxide

The mixtures of CO₂ with nitrogen, oxygen, argon, and CO generally have a similar behavior concerning the shape and range of the two-phase region. With regard to the temperature range, this region is limited by the critical temperature of CO₂ (ca. 304 K) as the upper boundary and the freezing point of CO₂ (sublimation line or melting line, depending on the pressure, ca. 216 K) as the lower boundary. The pressure range of the

VLE region extends from the CO₂ triple point pressure (ca. 0.6 MPa) to about 20 MPa, depending on the binary system and on the composition. For CO₂ contents below ca. 5 mole-% the mixtures do not split into two fluid phases, but CO₂ is dissolved completely in the other component. However, it will form a solid phase in equilibrium with a vapor phase below its sublimation or freezing temperature.

Carbon Dioxide + Nitrogen

As mentioned earlier, the mixing parameters for this system were adopted from the GERG-2008 equation of state by Kunz and Wagner (2012) without alteration, since an accurate mixture model including a binary departure function, is already available in the GERG-2008 model. Still, this mixture will be discussed here to give a full overview on all binary systems included in the new mixture model.

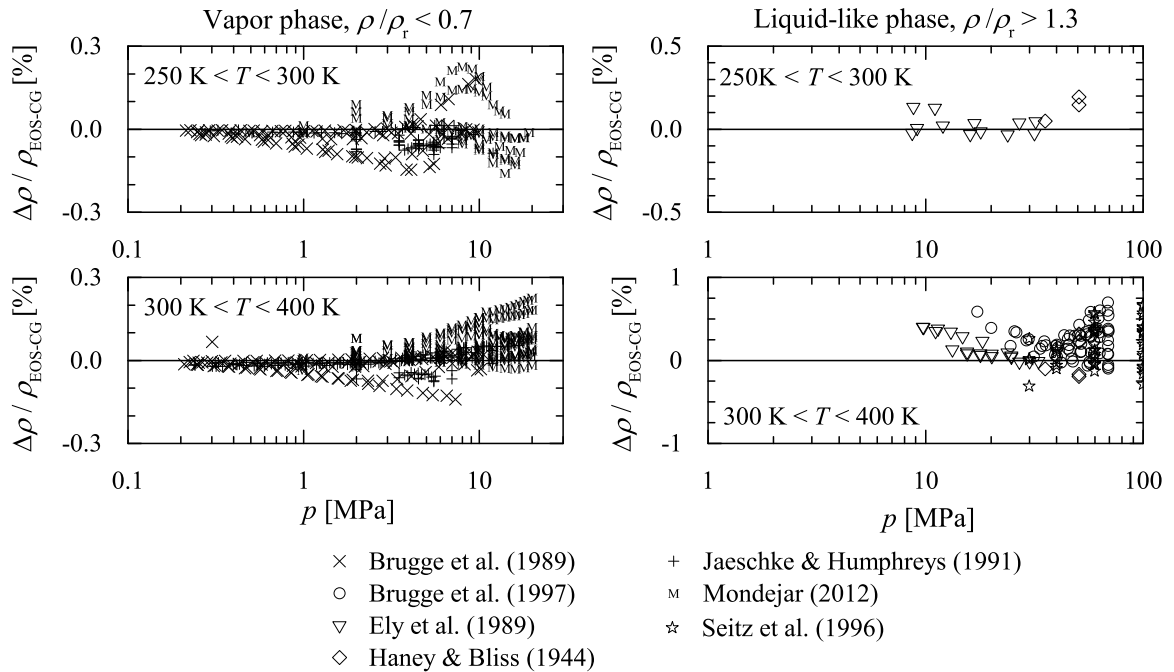


Figure 5.1: Deviations between selected $p\rho T$ data and the new mixture model for the system carbon dioxide + nitrogen.

A large number of experimental density data (25 data sets with almost 5000 $p\rho T$ data points) are available for this system, covering a wide density range, the major part of the composition range (leaving only a gap for $x_{\text{CO}_2} < 0.1$) and temperatures from 200 K to 700 K. In the vapor phase, the most accurate data sets are the ones published by Jaeschke and Humphreys (1991), Brugge *et al.* (1989), Ely *et al.* (1989), Haney and Bliss (1944), and two recent data sets by Mondéjar *et al.* (2011a) and Mondéjar *et al.* (2012), which were not available for the development of the GERG-2008 model. While the older data sets were measured using the isochoric Burnett method or optical techniques, a high-accuracy single sinker densimeter was used for the measurements in the new data sets. The data by Jaeschke and Humphreys (1991) show the best agreement with the model, with an

absolute average deviation (AAD) of 0.025 % and a maximum deviation of about ± 0.1 %. They cover pressures up to 26 MPa and temperatures between 275 K and 350 K, but only CO₂ contents up to 32 mole-%. The deviations between the data by Mondéjar and the model increase with pressure and CO₂ content, but are still represented within ± 0.3 %, which is also believed to be a conservative estimate of the accuracy of the model in the vapor phase. In the supercritical region and at temperatures above 400 K the deviations increase to ± 1 %; however, mainly less accurate experimental data e.g. by Brugge *et al.* (1997), Bailey *et al.* (1989) or Seitz *et al.* (1996) are available in this region. In the liquid-like phase the uncertainty of the model is estimated to be ± 0.5 %. A selection of deviation plots is given in Figure 5.1; Figure A1.1 in the appendix A1 holds a detailed overview of density deviations between the model and the most accurate experimental data.

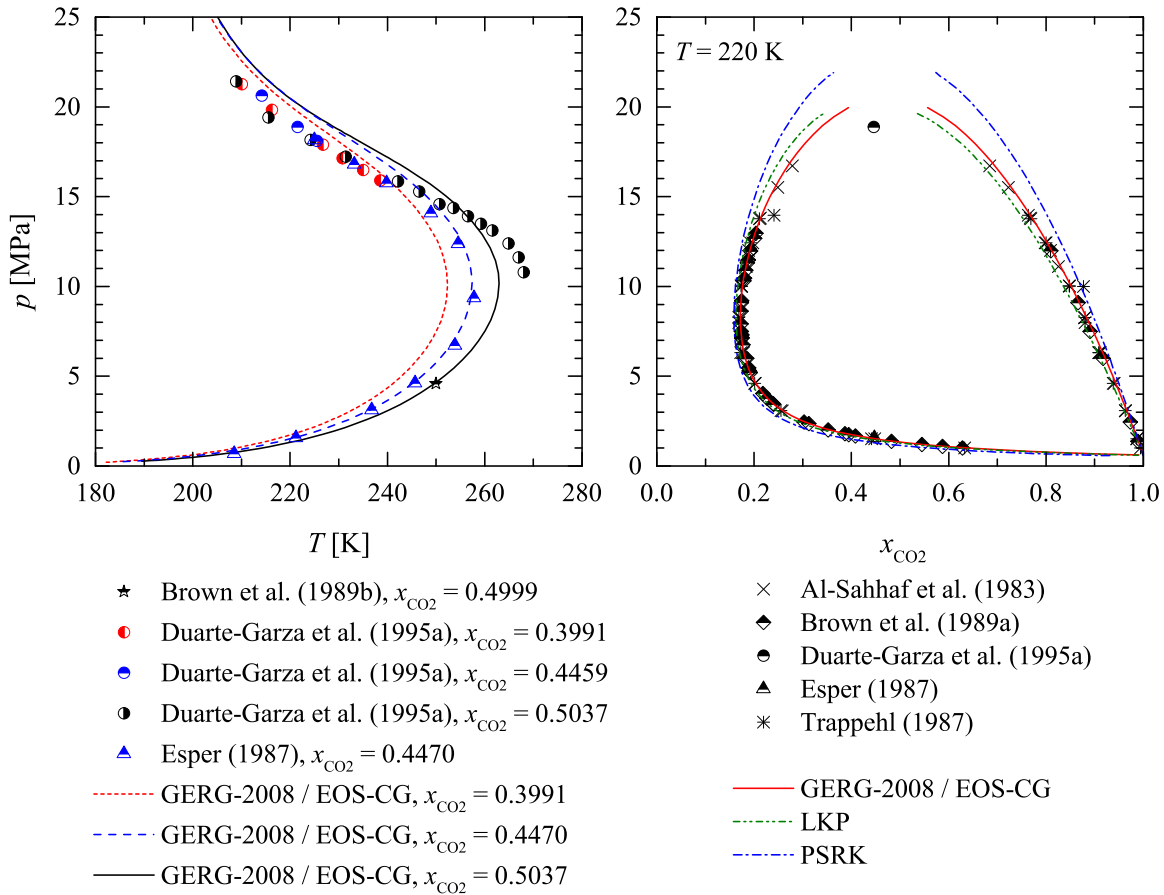


Figure 5.2: Left: Phase envelope for the system carbon dioxide + nitrogen for approximately equimolar mixtures: experimental data and values calculated from the new mixture model. Right: Phase boundaries at 220 K, experimental and calculated values.

The phase boundaries of this system have been measured by 21 authors, among them e.g. the accurate data sets by Brown *et al.* (1989b), Weber *et al.* (1984), and Xu *et al.* (1992). The data sets cover the two-phase region over the whole temperature range, but leave gaps at pressures close to the critical pressures in the low temperature region. As a result the model predicts the phase boundary well until about $0.8 p_c$, but at higher pressures and low

temperatures the few available data suggest that the model overestimates the bubble pressure line by up to 1 MPa (see Figure 5.2). The LKP and PSRK models show significantly larger deviations from the experimental data, especially in the high-pressure region close to the critical point. The bubble point data by Duarte-Garza *et al.* (1995a) were measured along the equimolar isopleth and show systematic deviations at higher temperatures where the phase envelope reaches its maximum temperature. However, the data by Esper (1987), which were measured at a 5 % lower CO₂ content, agree well with the model in the same temperature region (left side of Figure 5.2). More plots of the phase boundaries at different isotherms, as well as deviation plots of dew and bubble temperatures for all experimental data are given in appendix A1 in Figure A1.2.

For pressures up to 10 MPa the experimental dew and bubble point temperatures are reproduced by the model within ± 1 K at a given pressure and composition. When temperature and pressure are given and the experimental phase compositions are recalculated, the deviations between the model and the best experimental data lie within ± 0.5 mole-% and ± 0.8 mole-% in the saturated liquid and gas phase, respectively.

Three data sets with experimental speed of sound data and one data set with isobaric heat capacities are available for this system. The speed of sound data by Younglove *et al.* (1993) for pressures up to 10 MPa are reproduced mainly within ± 1.0 %, while the deviations increase for the high-pressure data set by Kachanov *et al.* (1983) and the data by Alsiyabi *et al.* (2012), which had to be extracted from plots (see Figure A1.3). The heat capacity data by Bishnoi *et al.* (1972) were measured close to the critical point where c_p shows a steep increase. Still, the predictions by the model are within ± 2.0 % from the main part of the data and within ± 10.0 % near the critical point (see Figure A1.4).

Carbon Dioxide + Argon

Although the data situation for the mixture of carbon dioxide with argon is already much more limited than for the mixture with nitrogen, the amount and quality of the data was considered sufficient for the development of a binary specific departure function for this system. Since the two systems show quite similar characteristics, the term structure of the binary departure function for the system carbon dioxide + nitrogen was used as a starting point for the fit. While the density exponents and the special exponential terms were kept at the original values of the carbon dioxide + nitrogen departure function, the temperature exponents and coefficients were fitted together with the reducing parameters to experimental VLE, $p\rho T$, and Joule-Thomson coefficient data of the system carbon dioxide + argon. In the final fit, one β_{ij} parameter of one of the special exponential terms with the functional form $n_{ij}\delta^{d_{ij}}\tau^{t_{ij}}\exp[-\eta_{ij}(\delta-\varepsilon_{ij})^2-\beta_{ij}(\delta-\gamma_{ij})]$ introduced in the GERG-2008 model was adjusted as well.

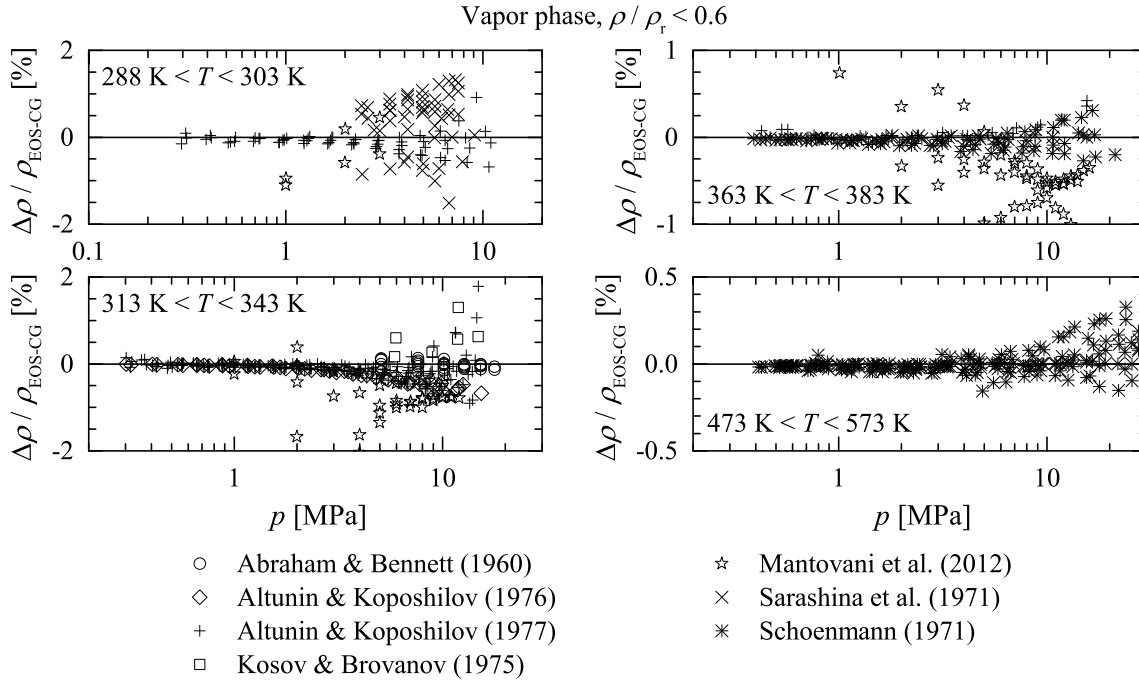


Figure 5.3: Deviations between selected $p\rho T$ data in the gas phase and the new mixture model for the system carbon dioxide + argon.

For the description of the $p\rho T$ relation seven data sets are available that cover the vapor, liquid-like, and supercritical regions for temperatures from 288 K to 573 K and pressures up to 100 MPa. However, these data sets cannot be considered as accurate as the best data sets for the mixture with nitrogen. While the model reproduces the data sets of Altunin and Koposhilov (1976), Altunin and Koposhilov (1977), and Schönmann (1971) within acceptable deviations of $\pm 0.5\%$ in the gas region at elevated temperatures or low pressures, and $\pm 1\%$ in the vicinity of the phase boundary, the data by Kosov and Brovanov (1975) and Mantovani *et al.* (2012) show considerable deviations already at low pressures. Therefore, these data sets were considered not reliable enough to be used for fitting the mixture model. Deviations between experimental gas phase densities and the new mixture model are given in Figure 5.3. Deviation plots for all available experimental data are given in the appendix A1 in Figure A1.5. Sarashina *et al.* (1971b) measured densities close to the phase boundaries, as well as dew and bubble points at 288 K. Although their saturated densities are reproduced qualitatively correct, the saturated liquid densities seem to extrapolate to a saturated liquid density of pure CO_2 that is much higher than the value calculated from the high-accuracy reference equation of state by Span and Wagner (1996), leading to large deviations from the model at higher CO_2 contents (see Figure A1.6). At high densities and temperatures above the cricondentherm (about 300 K) the major part of the experimental density data are reproduced within $\pm 1\%$. Since for pressures above the bubble line and temperatures below the cricondentherm only the data sets of Kosov and Brovanov (1975) and Mantovani *et al.* (2012) are available the uncertainty of the model is assumed to be higher in this region.

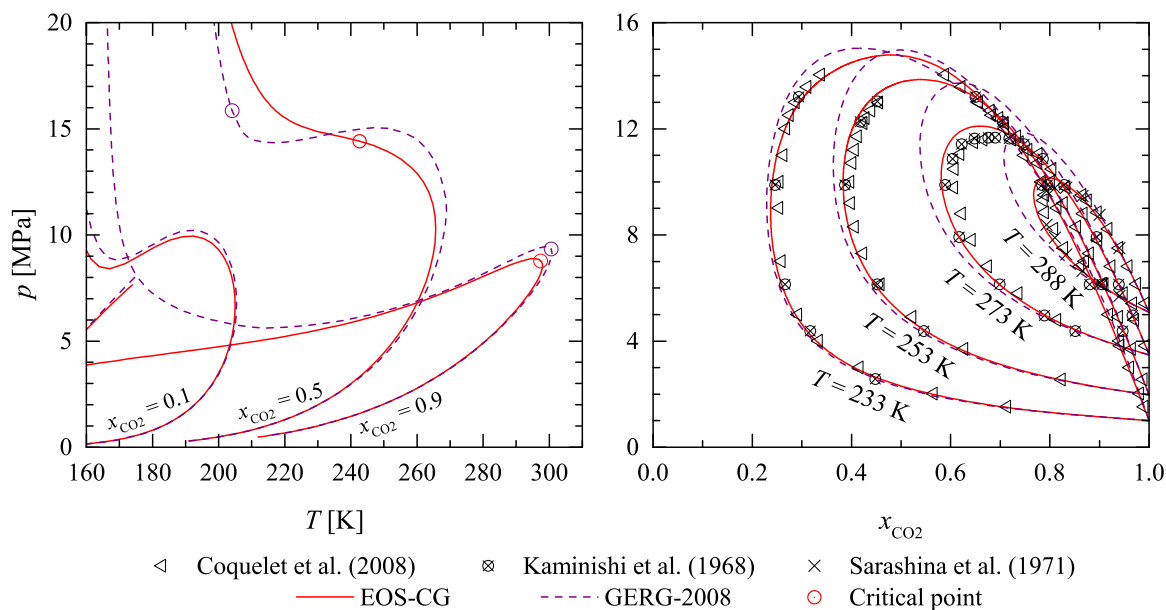


Figure 5.4: Description of the phase boundaries of the system carbon dioxide + argon by the GERG-2008 and the EOS-CG model. Left: Phase envelopes at selected compositions. Right: Measured and calculated phase compositions at four different isotherms.

For the description of the phase boundaries three $pTxy$ data sets are available for temperatures above 230 K, with the one by Coquelet *et al.* (2008) being the most recent and accurate one. Fitting the model to these data considerably improved the description of the phase compositions and phase boundaries compared to the GERG-2008 (see Figure 5.4), especially in the high-temperature region for temperatures above 250 K and pressures above 5 MPa. However, even with the new mixture model the critical pressures are still overestimated by up to 0.4 MPa for temperatures above 270 K (see Figure A1.6 in appendix A1). The phase compositions are reproduced with deviations within ± 1.0 mole-% for most points, except close to the critical pressures. The phase boundary plots in the appendix also show values calculated from the LKP and PSRK models. With the mixing parameters given in the *Aspen Properties 7.1* software the predicted phase boundaries deviate considerably from the experimental data.

In the left diagram in Figure 5.4, three phase envelopes are plotted for the system carbon dioxide + argon for 10 %, 50 %, and 90 % CO₂ (molar), calculated with the new EOS-CG mixture model and the GERG-2008. While the models show good agreement along the dew line at moderate pressures, the location of the maximum and critical pressures, as well as the shape and location of the bubble line, diverge strongly. However, although the phase boundary lines are plotted in a temperature range between 160 K and 305 K, the system will form a solid phase (dry ice) below temperatures around 216 K (depending on the composition). Fluid phase boundaries calculated at lower temperatures are therefore only model extrapolations, since the models do not include solid phases.

The only data set with Joule-Thomson coefficients (JTC) by Strakey *et al.* (1974) was also included in the fit. Since the JTC varies between 4 and 20 K/MPa in the gas phase to values very close to zero in the liquid phase, and the contribution to the SOS is calculated from the relative deviation between model and data, the weights had to be adjusted carefully in order to avoid overfitting of the liquid phase JTC data. In the gas phase, the experimental data are reproduced mainly within the experimental uncertainty of 2.5 % given by the authors. The experimental uncertainty of 1 % in the liquid phase cannot be met by the model, but is believed to be unrealistic since, as mentioned before, the values of JTC become very close to zero at high pressures (see Figure 5.5).

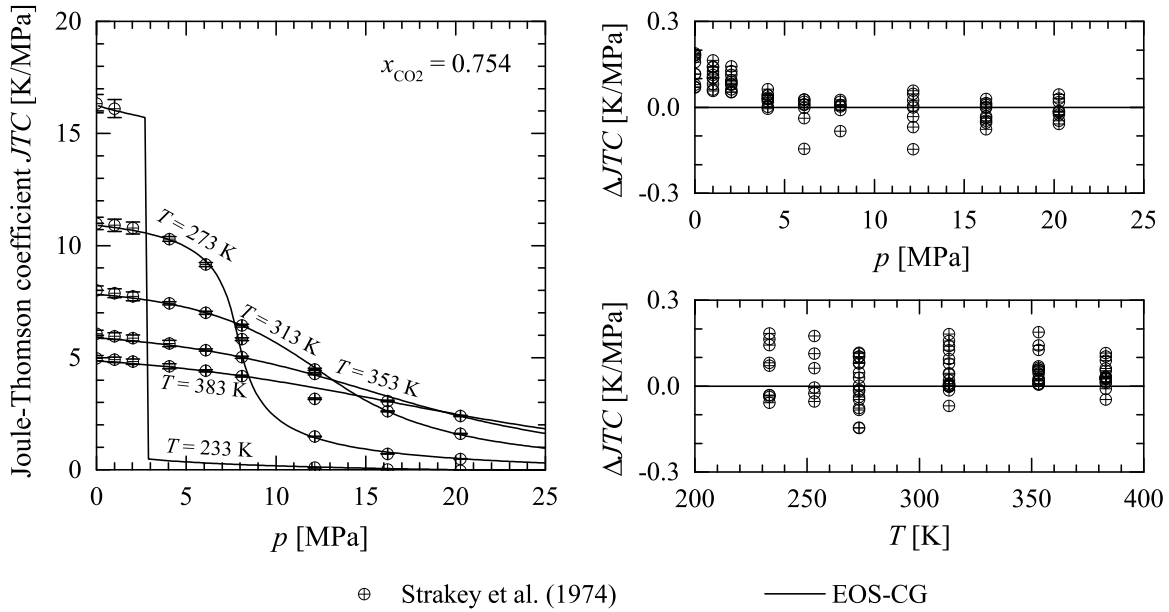


Figure 5.5: Left: Experimental Joule-Thomson coefficients and values calculated from the new mixture model at different isotherms for the system carbon dioxide + argon. Right: Total deviations between experimental JTC values and the new mixture model.

Carbon Dioxide + Oxygen and Carbon Dioxide + Carbon Monoxide

Due to little experimental information on $p\rho T$ and other data in the homogeneous phases of the mixtures of oxygen and carbon monoxide with carbon dioxide no departure functions were developed for these systems. For the mixture with oxygen the only existing $p\rho T$ data set in the homogeneous high-pressure region by Mantovani *et al.* (2012) deviates considerably from the model. However, these data could not be considered reliable, and were therefore not used with high weights in the fitting of the model parameters, since data from the same publication for the system carbon dioxide + argon also showed large deviations from the model and from other experimental data. One data set with densities on the phase boundary for the 273 K isotherm is available by Muirbrook (1964). While values at lower pressures agree well with the model the deviations become larger closer to the

critical pressure since the model overestimates the two-phase area in this region (see Figure A1.7 and Figure A1.8 for more details).

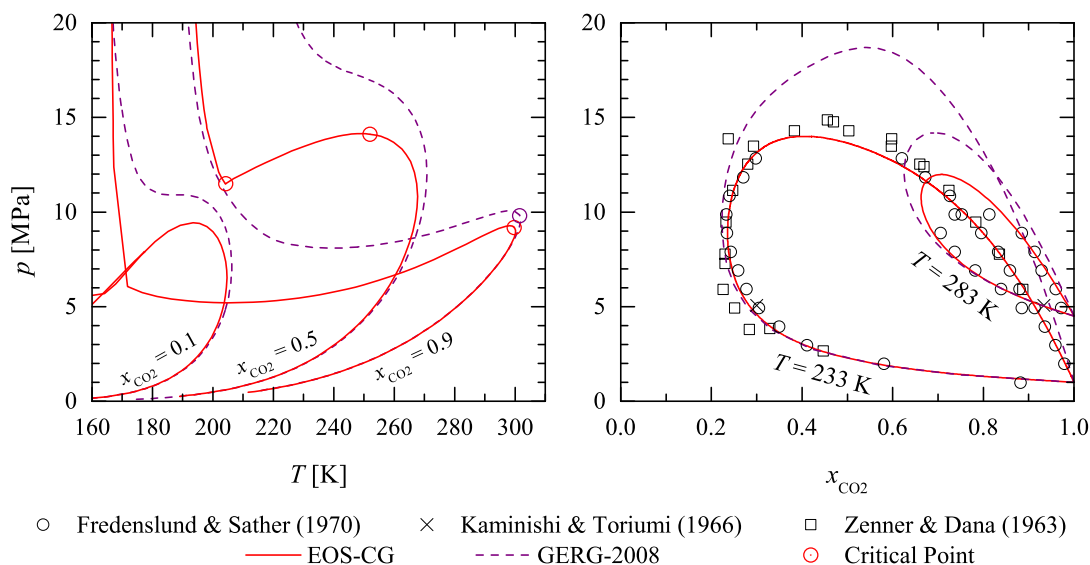


Figure 5.6: Description of the phase boundaries of the system carbon dioxide + oxygen by the GERG-2008 and the EOS-CG models. Left: Phase envelopes at selected compositions. Right: Measured and calculated phase compositions at two different isotherms.

The available experimental VLE data scatter strongly, especially the data by Zenner and Dana (1963). But also the more accurate data set by Fredenslund and Sather (1970) does not extrapolate well towards the vapor pressure of pure CO₂ at high temperatures. The experimental data at the 283 K isotherm in Figure A1.7 indicate a CO₂ vapor pressure of about 4 MPa, while the highly accurate reference EOS by Span *et al.* (2000) – which is part of the EOS-CG model – predicts a vapor pressure of about 4.5 MPa. Still, as shown in Figure 5.6, the prediction of the phase boundaries is significantly improved compared to the GERG-2008, especially the bubble line for higher oxygen contents and lower temperatures. Due to the inferior data situation only the γ_T and γ_V parameters of the reducing functions were adjusted for this system, while the β_T and β_V parameters, which control the asymmetry of the reducing function, were kept at unity. Fitting the β parameters lead to unwanted “bumps” in the shape of the phase boundaries, which could not be counteracted without more experimental $p\rho T$ data in the homogeneous region.

The system carbon dioxide + carbon monoxide is represented by three $p\rho T$ and two VLE data sets. All four reducing parameters were fitted to the data, leading to considerable improvements in the description of the phase boundaries, comparable to the carbon dioxide + oxygen system. Since the $p\rho T$ data only cover a limited area of the gas and liquid phase region the uncertainty of the model can only be a rough guess, based on the representation of the experimental data. In the gas phase the uncertainty is estimated to be within $\pm 1\%$, while it may well increase to $\pm 2\text{--}3\%$ in the liquid region at high pressures. Based on the

$pTxy$ data set by Kaminishi *et al.* (1968), which shows considerable deviations in the bubble line compositions from the data by Christiansen *et al.* (1974), the phase compositions are reproduced within ± 1 mole-%, except close to the critical pressure. The graphical evaluation for this system is given in the appendix in Figure A1.9 and Figure A1.10.

5.2.2 Binary Mixtures with Water

Mixtures of water with CO_2 , nitrogen, oxygen, argon or CO are characterized by the low solubility of these gases in water and by small water contents in the saturated gases. In combination with the large differences in critical temperatures and pressures between the respective gases and water this results in a large $pTxy$ region where the system splits into two phases – a water-rich liquid phase and either a gas-rich vapor phase or a second liquid phase, depending on the pressure in the system. Over a large temperature range, the VLE/LLE region is not limited by a maximum pressure, but increases to “infinite” pressures. The temperature range of the two-phase region is roughly defined by the critical temperature of water on the upper end and the formation temperature of ice or hydrate on the lower end. Phase equilibrium data for mixtures of gases with water often only hold information on one phase, e.g. solubility data.

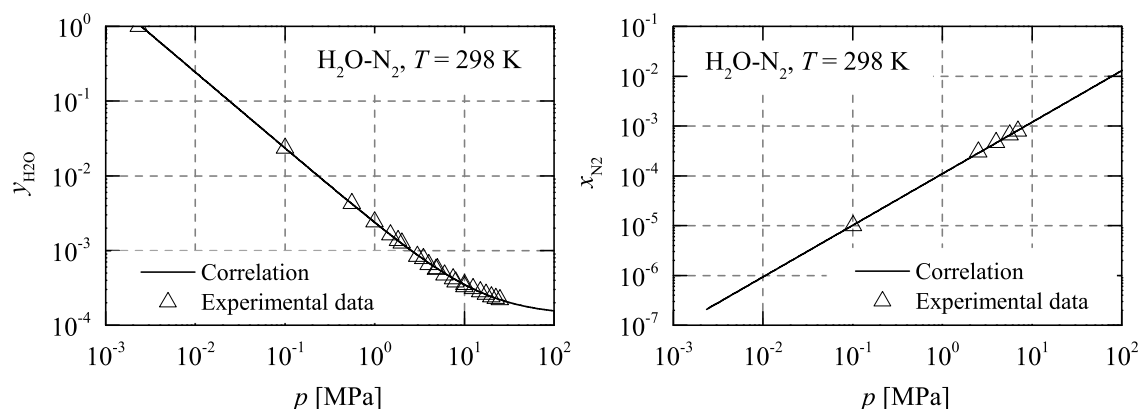


Figure 5.7: Correlation of saturation water content and solubility for the system water + nitrogen at 298 K.

As mentioned before, only a complete $pTxy$ data set can efficiently be used in the fitting programs for the development of mixture models when applying the methods described here. If no reliable $pTxy$ data sets are available for a mixture but good data on the solubility (pTx data) and data on the saturation water content in the gas phase (pTy data) are available on the same isotherm and over an extended pressure range, the missing phase information can be calculated using the correlation

$$y_{\text{H}_2\text{O}} = A''p^{B''} + C'', \quad \text{and} \quad x_{\text{Gas}} = A'p^{B'} + C' \quad 5.5$$

which provides a good general estimate of the pressure dependence of the saturation compositions along an isotherm (see Figure 5.7 for an example showing the system water

+ nitrogen). The parameters A'' , B'' , and C'' are fitted to experimental pTy data, and the parameters A' , B' , and C' are fitted to experimental pTx data at the same temperature. The vapor pressure of water, calculated from the reference equation by Wagner and Pruß (1999) was included in the fits, providing additional data points for $y_{H_2O} = 1$ and $x_{Gas} = 0$. Using the correlation equations given in Eqn. 5.5 the pTy and pTx data sets were completed using the correlated values for x_{Gas} and y_{H_2O} , respectively, for the missing phase compositions. Once a good preliminary mixture model was available the correlated phase compositions were replaced by values calculated from this model.

In water-gas mixtures the water content in the saturated pressurized gas is often expressed by the *vapor pressure enhancement factor* f_w . This dimensionless factor represents the deviation of the real, measured saturation pressure from the concept of partial pressures where $p_i = py_i$, combined with Raoult's law $p_i = x_i p_{sat,i}$. The combination of these two models, together with the assumption that due to the low gas solubility in water the mole fraction of gas in the liquid is negligible, leads to the following relationship between the phase compositions in phase equilibrium

$$p_{sat,H_2O} = py_{H_2O}, \quad \text{or} \quad p = \frac{p_{sat,H_2O}}{y_{H_2O}}. \quad 5.6$$

The enhancement factor f_w is introduced to correct the expression given in Eqn. 5.6 and reads

$$f_w = \left[p \frac{y_{H_2O}}{p_{sat,H_2O}} \right]_T. \quad 5.7$$

It is close to unity at low pressures and increases almost linearly with pressure at constant temperature. With the help of f_w isothermal pTy data sets by different authors can be compared graphically over a wide pressure range with a useful scale.

Water + Carbon Dioxide

This binary system shows unique characteristics among the systems considered in this work. Out of the five gases considered in this work that form mixtures with water, CO_2 is the only one with its critical temperature above the freezing temperature of water. When the system is in phase equilibrium a water-rich phase and a CO_2 -rich phase coexist over a wide range of compositions (Two water- or CO_2 -rich phases can be in equilibrium as well when the other component is present in very small amounts). Due to low miscibility the CO_2 -rich phase almost behaves like a pure fluid and undergoes a phase change from vapor to liquid at a pressure close to the vapor pressure of pure CO_2 . This means that for temperatures below the critical temperature of CO_2 (about 304 K) and above the freezing point of water the system may either form a vapor-liquid equilibrium at pressures below the vapor pressure of CO_2 , or a liquid-liquid equilibrium for higher pressures. The two

regions are separated by a three-phase line where all three fluid phases (a water-rich liquid, a CO₂-rich liquid and a CO₂-rich vapor) are in equilibrium. This line is almost identical to the vapor pressure line of pure CO₂. For higher temperatures the CO₂-rich phase behaves like a supercritical fluid and does not undergo a phase change but shows a continuous increase in density with pressure. Although still very limited, the CO₂-solubility in water is much higher than the solubility of other gases like nitrogen or oxygen (by a factor of 10 to 100). This increased solubility is caused by a chemical reaction, the formation of carbonic acid.

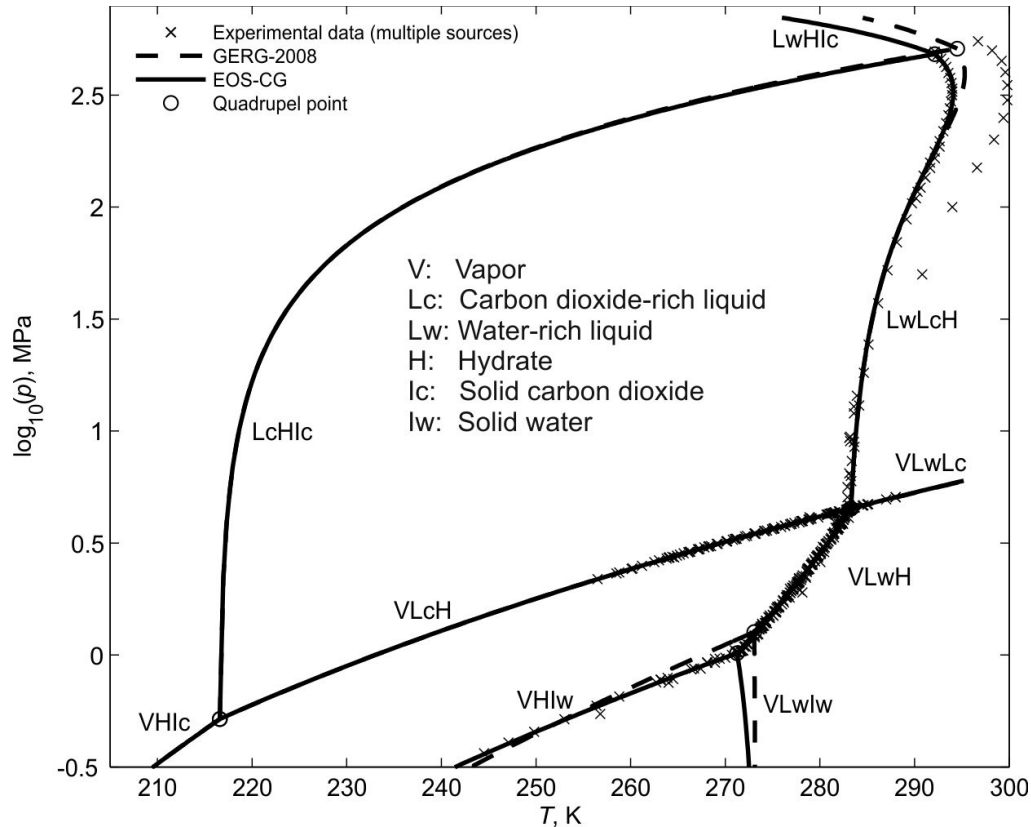


Figure 5.8: Phase diagram with three-phase lines for the system water + carbon dioxide in the hydrate and ice regions. Source: Jäger *et al.* (2013).

Below temperatures of about 283 K (depending on the pressure) carbon dioxide forms a hydrate phase in water. This solid phase has a (almost) fixed composition based on the lattice structure formed by the water and CO₂ molecules. In combination with the formation of dry ice (solid CO₂) and water ice and several different fluid phases the phase diagram becomes highly complex: The different two-phase regions are separated by three-phase lines which are connected by quadruple points (see Figure 5.8). Several models have been developed for the description of these solid-fluid phase equilibria, the most recent one by Jäger *et al.* (2013) who use the EOS-CG mixture model for the description of the fluid phases. The model presented in this work however was developed solely for the fluid region; values calculated in the region where equilibria with solid phases occur are therefore purely model-specific extrapolations.

The mixture model for the system carbon dioxide + water presented here is a compromise between several controversial criteria that had to be considered. It was found that independent on the chosen form or number of terms for the binary departure function the two-phase region could not be described accurately over the whole pressure and temperature range covered by experimental data. If the model was forced to follow the high-temperature, high-pressure data (especially for temperatures above 500 K) the phase compositions at lower temperatures were not represented well, and vice versa. A similar compromise had to be found for the representation of experimental $p\rho T$ data. One issue common to all binary mixture models with water as one of the components was the behavior of the equation in the two-phase region that resulted in pressure regions where the density solver would not find a meaningful density value (see also the discussion of constraints in Section 4.3). This behavior was successfully counteracted with a constraint, but with the result of an inferior description of high-pressure VLE and $p\rho T$ data.

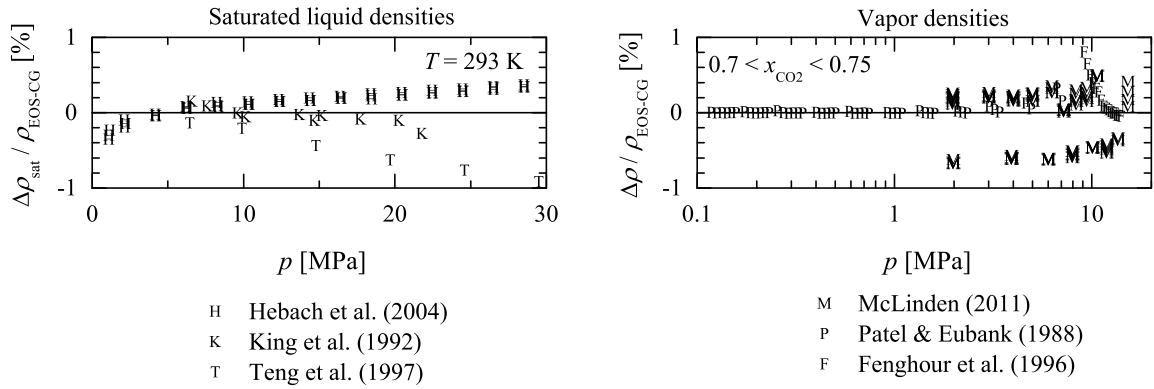


Figure 5.9: Selected density deviations between experimental data and the new mixture model in the saturated liquid and vapor phase.

Almost 3000 $p\rho T$ data points cover temperatures up to 1032 K and pressures up to 600 MPa. The most reliable data sets are the gas-phase data by Patel and Eubank (1988) and McLinden (2011), which cover temperatures between 323 K and 619 K and pressures up to 16.4 MPa. Several data sets for densities of the liquid water-rich phase are available, covering temperatures between 278 K and 332 K and pressures up to 30 MPa. The different data sets diverge up to 1.5 % with the largest differences between the data sets by Hebach *et al.* (2004) and Teng *et al.* (1997). The gas phase density data by Patel and Eubank (1988), which cover a temperature range between 323 K and 500 K with pressures up to 10 MPa and CO_2 contents $> 50 \%$, are reproduced within $\pm 0.2 \%$ with an AAD of 0.02 %. The data by Fenghour and Wakeham (1996) and the unpublished data by McLinden (2011), which cover higher temperatures up to 700 K and pressures up to 35 MPa, already show much higher deviations up to $\pm 2 \%$ (see Figure 5.9). However, both data sets possibly have some systematic errors. While the Fenghour data show the same systematic deviations for the system water + nitrogen, the data by McLinden do not extrapolate well towards low pressures, especially the measurements at $x_{\text{CO}_2} = 0.3647$ and

620 K which also show the largest deviation from the model. Data in the supercritical high-density region start at temperatures above 650 K and cover pressures from 30 to 600 MPa. Large discrepancies between the different data sets, e.g. by Seitz and Blencoe (1999), Abdulagatov *et al.* (1994), Zakirov (1984), and Gehrig (1980), made an accurate fit in this region impossible since no data set could be identified as significantly more accurate than the others (see Figure A1.11, bottom). Still, the data by Seitz and Blencoe (1999) agree best with the model with deviations mainly within $\pm 2\%$. As mentioned before, the different data sets with liquid densities diverge considerably. In this region the data set by Hebach *et al.* (2004) was considered the most reliable one. However, it does not hold information on the phase composition of the saturated liquid phase. In order to use this data set for fitting, the phase compositions had to be calculated from an intermediate model. The data by Hebach agree best with the data set by King *et al.* (1992); both data sets are reproduced by the model within $\pm 0.5\%$ over the whole pressure and temperature range and within $\pm 0.2\%$ up to 10 MPa. Exemplary deviation plots for gas phase, liquid phase and supercritical densities are given in appendix A1 in Figure A1.11.

A huge number of experimental data is available in the literature on CO₂ solubility and saturation water content, with almost 1500 data points from 41 different data sets. However, only 17 of these data sets contain the full $pTxy$ information, the rest contain only information on one of the phases in equilibrium. The data cover the whole temperature range and pressures up to 350 MPa. The major part of the data cover pressures up to 30 MPa, only the two $pTxy$ data sets by Takenouchi and Kennedy (1964) and Tödheide and Franck (1963) cover large temperature and pressure ranges in the high-temperature, high-pressure VLE region. However, these data sets show large differences in the phase compositions and critical pressures (see Figure A1.12). At low temperatures, accurate solubility measurements (VLE region), e.g. by Anderson (2002), Chapoy (2004) and Dalmolin *et al.* (2006), are reproduced within maximum deviations of 0.2 mole-%. However, although all other models used for comparison show much larger deviations, the new model still shows a pressure-dependent offset from the data (see Figure 5.10), tending to overestimate the solubility at elevated temperatures.

Data by several authors (e.g. Gillespie and Wilson (1982), Teng *et al.* (1997), King *et al.* (1992), and a yet unpublished data set by Trusler (2012)) describe LLE phase equilibria at pressures up to 40 MPa. While the data by Trusler show distinct deviations from the other data at 298 K, the EOS-CG model follows the data by King and Teng with small deviations up to ± 0.3 mole-%. At supercritical temperatures (above 304 K) and pressures above 20 MPa the available data sets deviate strongly from each other, especially the gas phase compositions. Here the data by Bamberger *et al.* (2000), Müller and Maurer (1982), and Trusler (2012) were considered most reliable and used for fitting the model. For

temperatures above 500 K and pressures above 20 MPa the model starts to deviate strongly from the experimental VLE data.

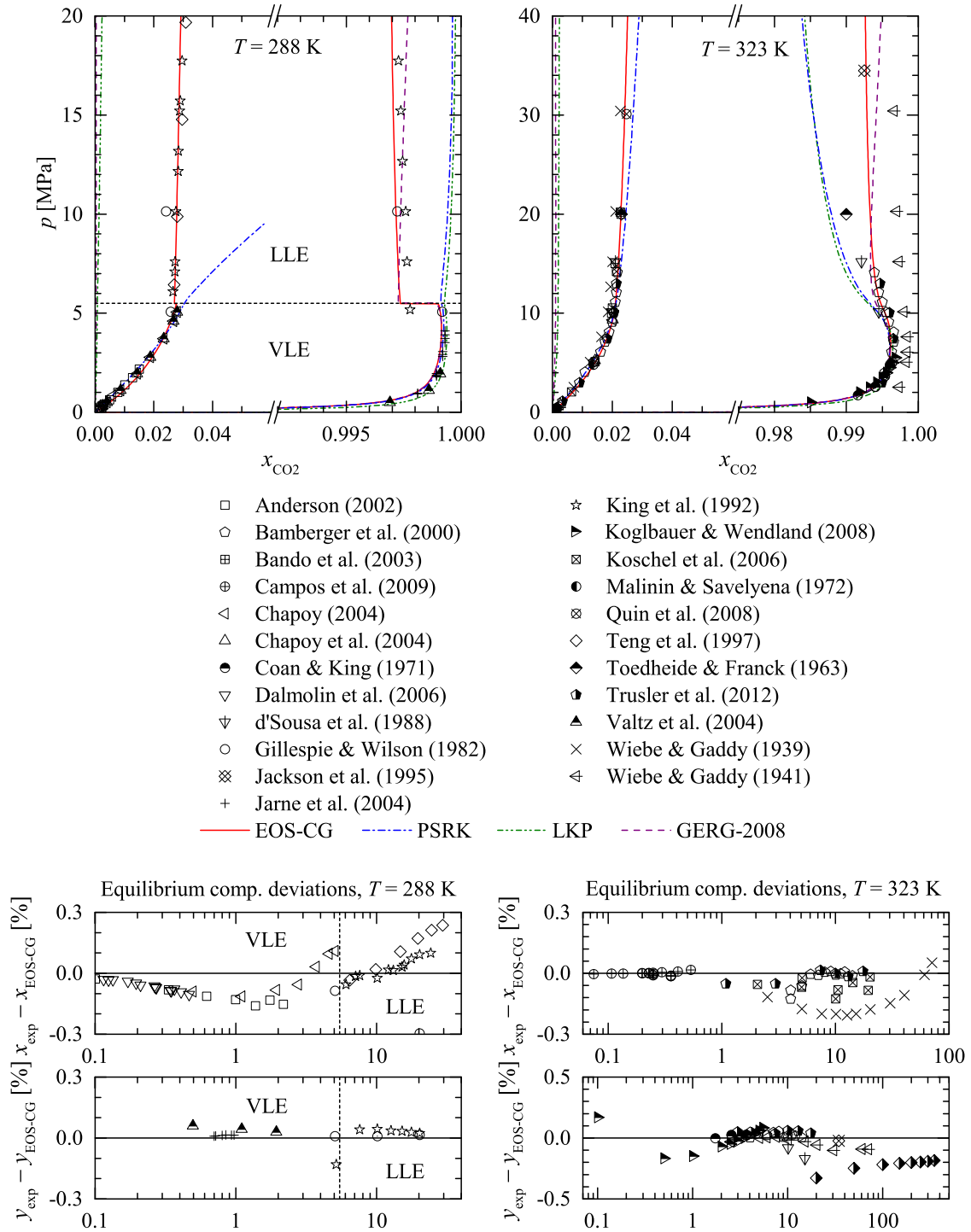


Figure 5.10: Measured and calculated phase compositions for the system water + carbon dioxide at two different isotherms.

While the data sets by Takenouchi and Kennedy (1964) and Tödheide and Franck (1963) suggest a “closed” VLE region above 540 K with critical pressures below 140 MPa the model predicts an “open” VLE region (no critical pressures) up to 600 K (see Figure 5.11 and Figure A1.12). While all other models used for comparison fall short behind the new

model in the accurate prediction of low-pressure phase equilibria, the PSRK and LKP models perform qualitatively better at high temperatures and pressures than the new EOS-CG model.

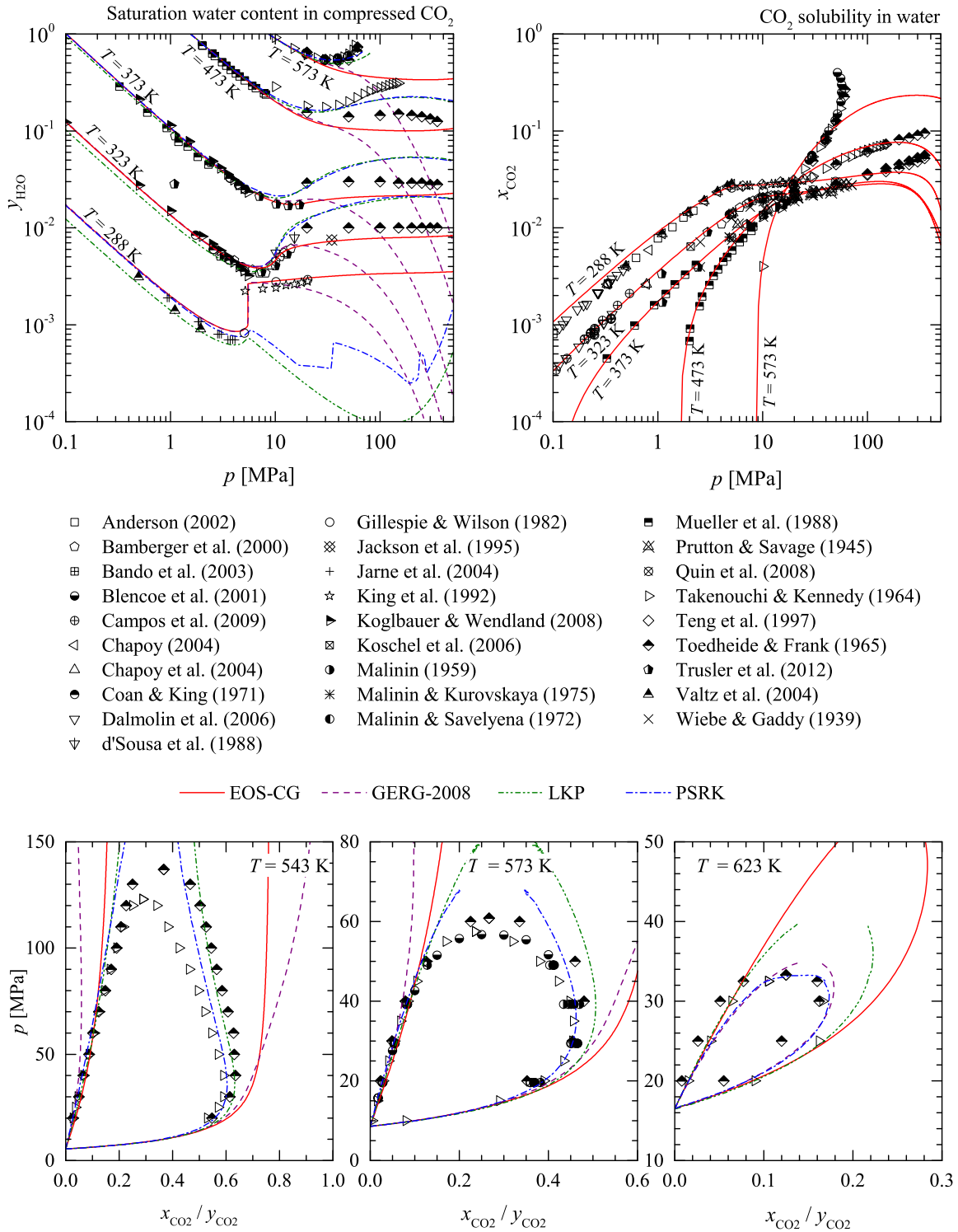


Figure 5.11: Top: Experimental and calculated solubility and saturation water content values at different isotherms. Bottom: Experimental and calculated phase compositions at high temperatures for the system water + carbon dioxide

Although only a few VLE data are available at constant concentration, phase envelope plots (phase boundaries at fixed composition) reveal some additional interesting characteristics of the system water + carbon dioxide (Figure 5.12).

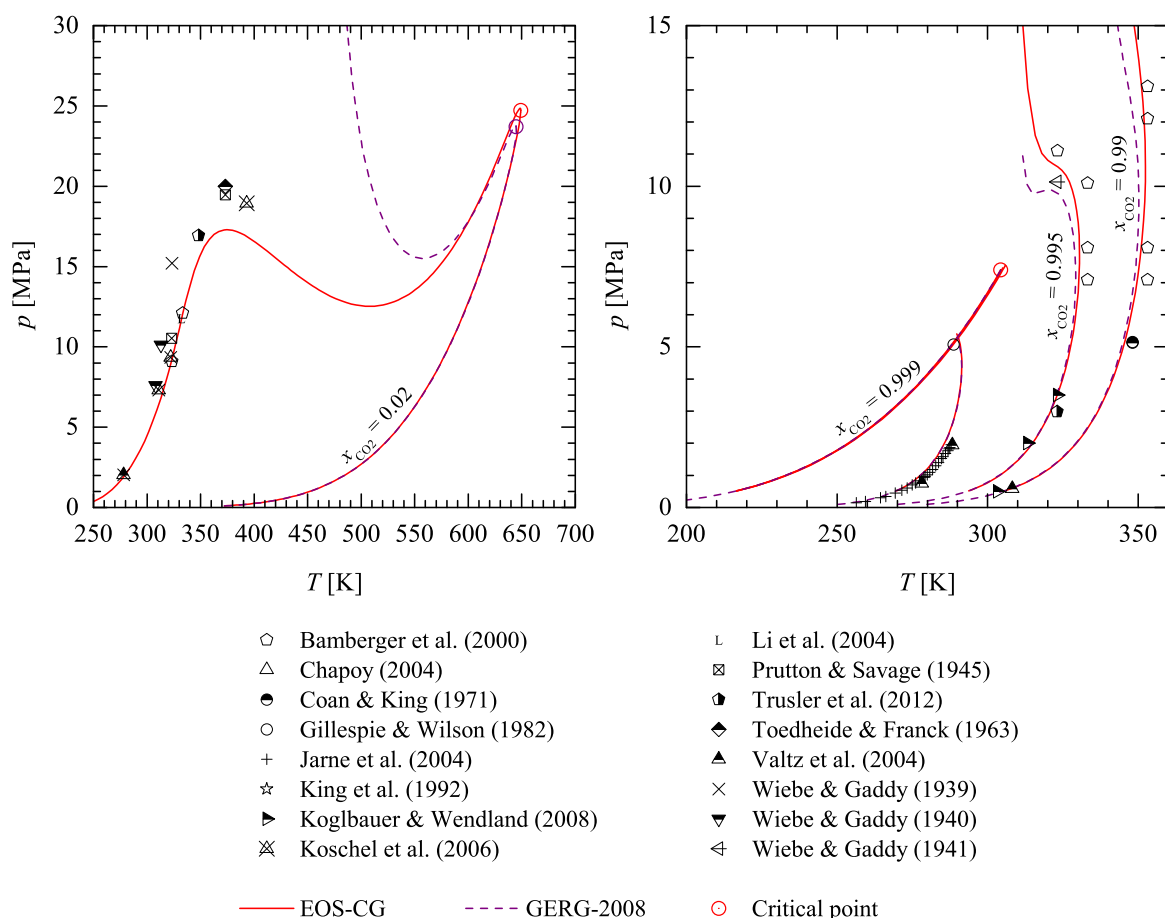


Figure 5.12: Experimental data and calculated values of phase boundaries at different CO_2 concentrations for the system water + carbon dioxide.

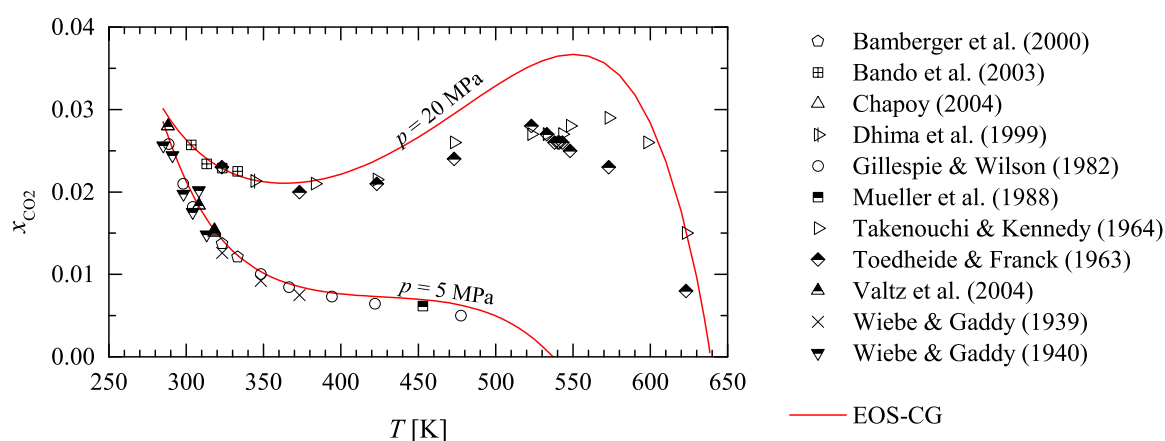


Figure 5.13: Experimental and calculated solubility values over temperature at isobars of 5 and 20 MPa for the system carbon dioxide + water.

At small CO_2 concentrations the bubble line calculated with the EOS-CG model shows two pressure maxima. In addition to the pressure maximum at the end of the dew line the bubble line has a maximum at about 350 K. The few available data support this

characteristic, although they suggest the first pressure maximum at a higher temperature and a lower pressure. The reason for this pressure maximum is a solubility minimum at the respective temperature for pressures above ca. 12 MPa. At high pressures the solubility of CO₂ in water first decreases with rising temperatures up to ca. 350 K. Above this temperature the solubility increases again until it reaches a maximum value before it drops again to zero at the saturation temperature of water. Although this behavior is overestimated by the model it can be proven by experimental data. At lower pressures this solubility maximum is not present (see Figure 5.13).

At very high CO₂ concentrations the phase boundary shows another peculiar characteristic. For CO₂ contents above ca. 99.7 mole-% the dew line – with a water-rich liquid as the incipient phase – ends at the vapor pressure line of pure CO₂. Once the vapor pressure line is reached, the CO₂-rich vapor turns into a liquid. Since the water solubility in the CO₂-rich liquid is higher than in the vapor, the water can now be completely dissolved in the CO₂, which means that as soon as the CO₂ turns liquid no second water-rich phase is formed. Additionally, inside the two-phase region below the CO₂ vapor pressure line the water-rich phase is assumed to form a hydrate phase once the temperature falls below the hydrate formation temperature. (The hydrate formation line is not given in Figure 5.12.)

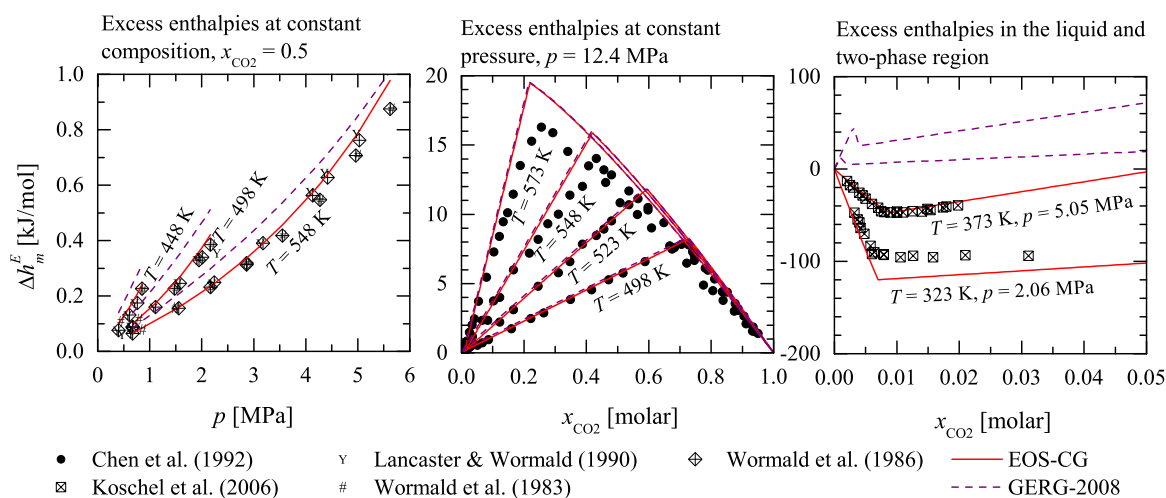


Figure 5.14: Experimental and calculated excess enthalpy values at constant composition (left) and constant pressure (middle, right) for the system water + carbon dioxide.

Experimental excess enthalpy data for the system water + carbon dioxide cover temperatures from 323 K up to about 700 K and pressures up to 25.5 MPa. Most of these data were measured and published by the group around Wormald and extend from the gas phase into the two-phase region at high temperatures and pressures. The only data set covering the whole composition range and thus giving complete information on the shape of the excess function was published by Chen *et al.* (1992). The measurements lie in a temperature and pressure range where within a certain composition range the system is in phase equilibrium; the location of the phase boundary is characterized by a sharp bend of

the excess enthalpy at constant temperature and pressure (see Figure 5.14, middle and right plots). These data are overestimated by both the GERG-2008 and EOS-CG models by up to +15 % at high temperatures, an improvement could not be achieved by including the data in the fit. The PSRK and LKP models deviate even stronger from the data. At lower pressures the representation of data at or around equimolar composition e.g. by Lancaster and Wormald (1990), Wormald *et al.* (1983) and Wormald *et al.* (1986) have been improved with the new model in comparison to the GERG-2008 (see Figure 5.14, left). At low CO₂ contents in the (un)saturated liquid water-rich phase the model predicts negative excess enthalpy values with a minimum at the saturation composition before the function increases to positive values at higher CO₂ contents in the two-phase region. This minimum in the excess enthalpy function is confirmed by the data by Koschel *et al.* (2006) although the model shows a systematic offset, while the GERG-2008 model predicts a qualitatively wrong, positive progression (see Figure 5.14, right).

Two data sets by Barbero *et al.* (1983) and Hnedkovsky and Wood (1997) for the isobaric heat capacity of the water-rich phase cover a limited temperature and pressure range. Outside the vicinity of the critical point these data are reproduced within ± 1 %, the deviations increase to ± 3 % close the critical temperature (see Figure A1.14).

Water + Nitrogen

Next to the system water + carbon dioxide the mixture of water with nitrogen is the system with the best coverage by experimental data among the water mixtures. Therefore a departure function with five polynomial and exponential terms was developed for this binary mixture in order to fit the model to the available experimental VLE, $p\rho T$ and h^E data over a wide temperature, pressure and composition range. In some regards the system shows similar characteristics to the water + carbon dioxide system concerning the phase boundaries. However, the gas solubility is even lower, and since nitrogen is in a supercritical state over the whole fluid region of the mixture it shows no regular LLE area.

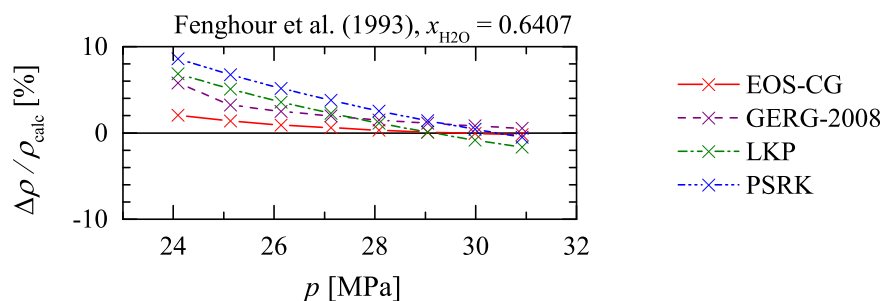


Figure 5.15: Density deviations between the experimental data by Fenghour *et al.* (1993) and different mixture models for the isochore and composition with the largest deviations in the data set.

The available $p\rho T$ data by five different authors (where, however, the data by Fenghour *et al.* (1993) and Gallagher *et al.* (1993b) are identical) for the system water + nitrogen

comprise 328 data points that cover the gas and supercritical phase. No data are available for liquid densities or in the gas phase at temperatures below 323 K. The data by Fenghour *et al.* (1993) show similar deviations from the new mixture model as their data on the system water + carbon dioxide. Their deviations from the GERG-2008, LKP and PSRK models show the same characteristics as from the new EOS-CG model (only with larger absolute values, see Figure 5.15), which suggests a systematic error in their data (possibly in the volume correction calculation of the isochoric apparatus). Their data are represented mainly within ± 1 % with a maximum deviation of ± 2 % and an AAD of 0.3 %.

The yet unpublished data by McLinden (2011) cover a similar region in the gas phase ($T = 500$ K to 620 K, $p < 25$ MPa) but were measured with a single-sinker densimeter along isotherms and isopleths. They are considered generally more reliable than the Fenghour data and show better extrapolation behavior towards low pressures than the McLinden measurements for the system water + carbon dioxide. Deviations between these data and the EOS-CG model are mainly within ± 0.5 % with a maximum of ± 1 % and an AAD of 0.2 %. The data by Abdulagatov *et al.* (1993) and Japas and Franck (1985a) cover the same temperature range as the McLinden data but include measurements up to 70 MPa and 286 MPa, respectively. They are considered less accurate, with estimated experimental uncertainties up to 2.3 % for the data by Japas and Franck (1985a). Deviation plots for all available experimental data are given in the appendix in Figure A1.15.

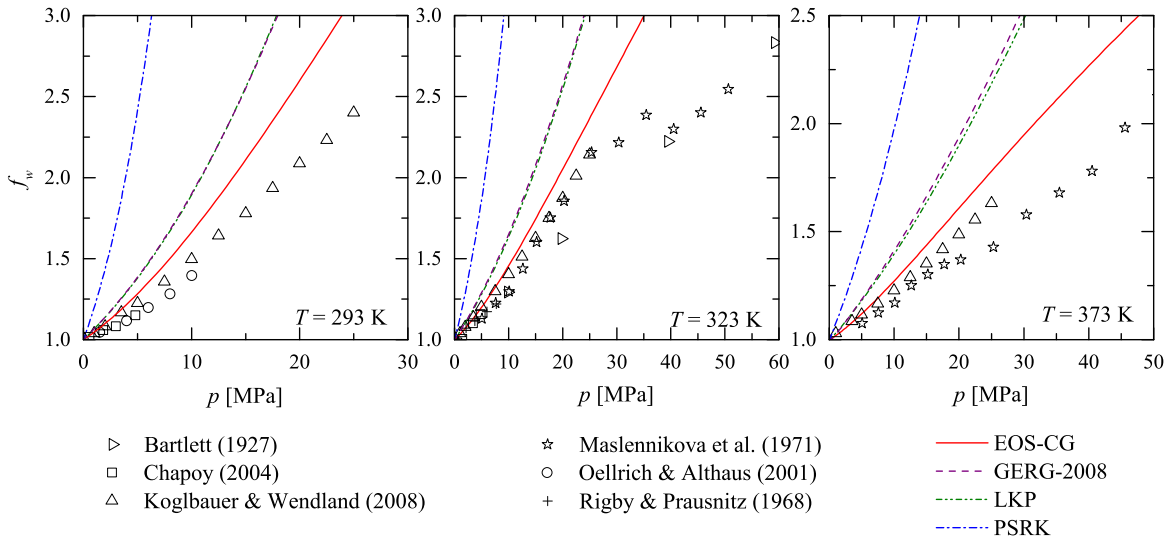


Figure 5.16: Experimental and calculated values of the vapor pressure enhancement factor f_w at different isotherms for the system water + nitrogen.

30 pTx or pTy data sets have been collected for the system water + nitrogen, but only one $pTxy$ data set of moderate quality by Gillespie and Wilson (1980) is available, making the correlations of the mixing phase compositions mentioned above necessary. With only a few data points by Alvarez *et al.* (1988) and Gillespie and Wilson (1980) the solubility data above 400 K are very limited, thus the description of the pressure dependence of the

nitrogen solubility at high temperatures by the new mixture model is basically predicted. The available pTy data at high temperatures by Maslennikova *et al.* (1971) show considerable inconsistencies when compared to other data sets in intersecting pT regions, resulting in large uncertainties in the description of the high-temperature, high-pressure VLE region of this system.

When plotting the saturation water content in the compressed nitrogen in terms of the vapor pressure enhancement factor f_w (as introduced in Eqn. 5.7) the inconsistencies between the different pTy data sets become apparent (see Figure 5.16). While the data by Oellrich and Althaus (2001) and Chapoy (2004) agree well, the measurements by Koglbauer and Wendland (2008) tend towards higher f_w values at the same temperature and pressure. The inconsistencies of the data by Maslennikova *et al.* (1971) mentioned above become visible by the sharp bend in the progression of the f_w value over pressure along any isotherm. Although the EOS-CG overestimates the experimental f_w , it still shows considerable improvements when compared to the other models. Also, up to ca. 500 K the extrapolation behavior of the predicted phase compositions towards high pressures is reasonable while the other models, especially the PSRK, should not be used for pressures above 10 MPa (see Figure 5.17).

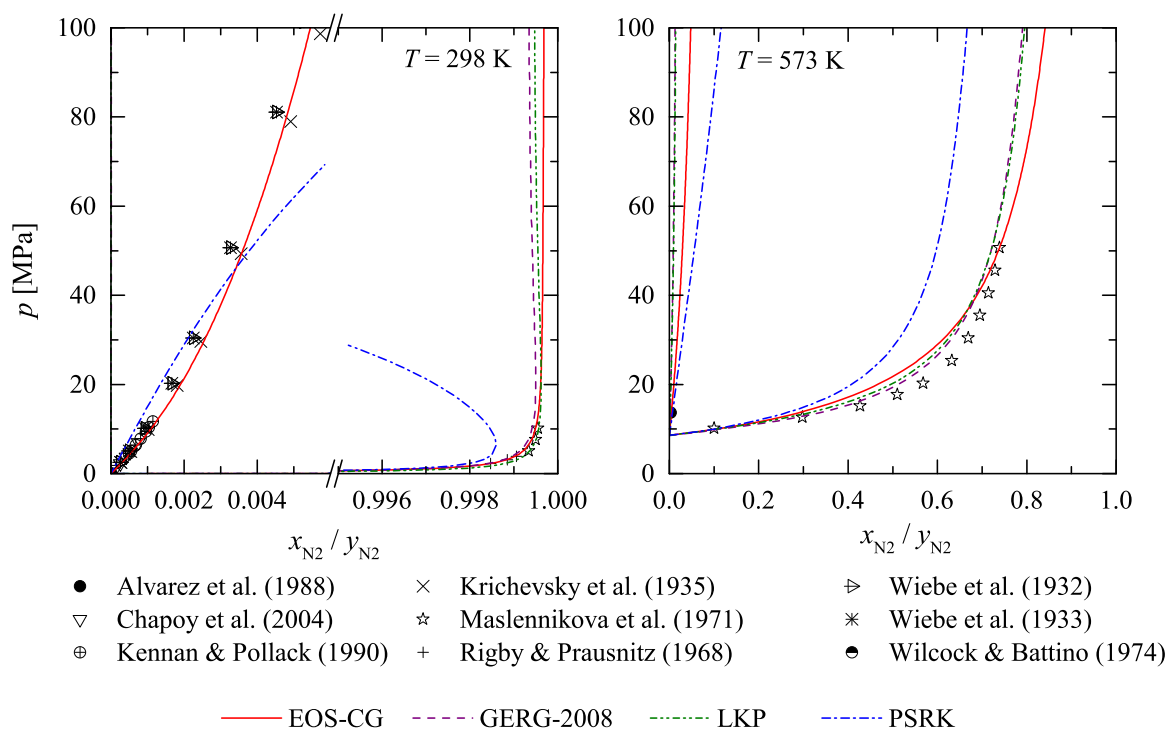


Figure 5.17: Experimental and calculated phase compositions at two isotherms for the system water + nitrogen.

As for all water mixtures, the solubility of nitrogen in water is drastically underestimated both by the GERG-2008 and LKP model. The new mixture model gives a qualitatively correct description of the temperature and pressure dependence of the solubility up to

573 K and up to 100 MPa (with reasonable extrapolation behavior up to 500 MPa). Accurate solubility measurements by Chapoy *et al.* (2004b), Smith *et al.* (1962) or Kennan and Pollack (1990) are reproduced with AAD values below 0.007 mole-% and maximum deviations up to about ± 0.013 mole-% nitrogen. Generally the model slightly overestimates the solubility at elevated pressures (up to +0.12 mole-% at 100 MPa and 373 K compared to the data by Krichevsky and Kasarnovsky (1935)). A selection of isothermal p - x diagrams as well as solubility and saturation water content plots for this system is given in the appendix in Figure A1.17.

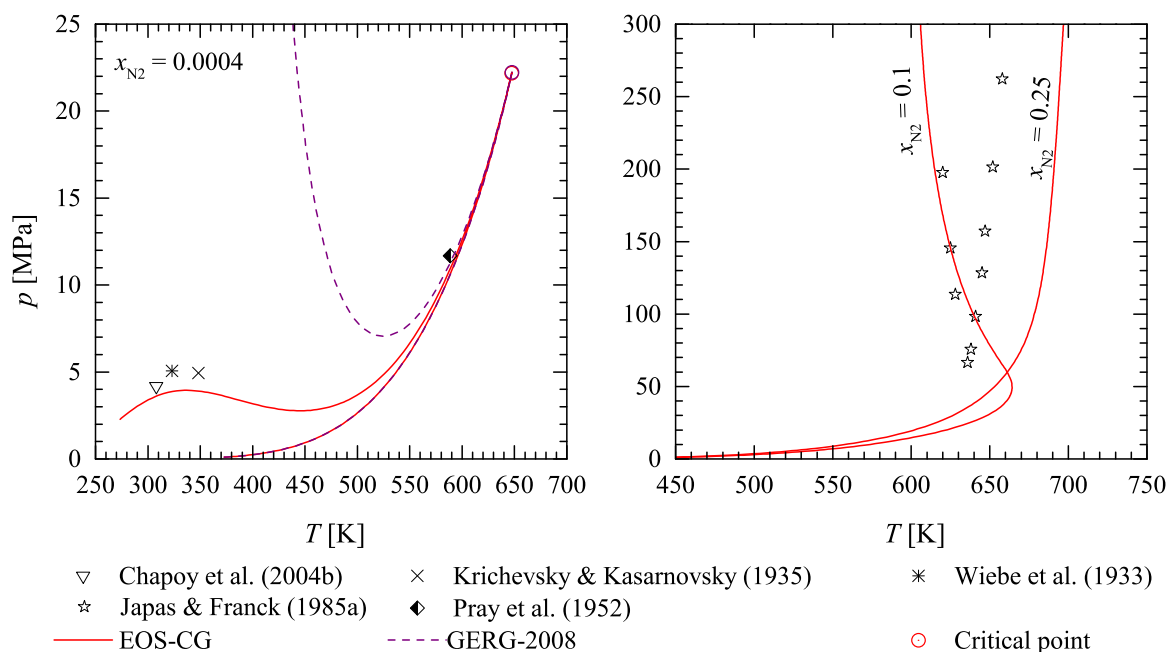


Figure 5.18: Experimental and calculated values of the phase boundaries at different nitrogen concentrations for the system water + nitrogen.

At low nitrogen concentrations – below the maximum solubility at moderate temperatures – the phase envelope resembles that of the water + carbon dioxide system, showing a second pressure maximum at low reduced temperatures beside the cricondenbar near the critical point (see Figure 5.18). Again this characteristic is not predicted by the GERG-2008 model. The relatively large offset of the bubble line calculated from the EOS-CG model from the data corresponds to the (relatively small) overestimation of the nitrogen solubility at these pressures and temperatures. As with the mixture with carbon dioxide the high-pressure, high-temperature VLE region, more precisely the supercritical dew line for higher nitrogen concentrations ($T > 550$ K, $p > 30$ MPa, $x_{N_2} > 0.01$), is not predicted correctly by the new model. Although very little data are available in this region (only the dew point measurements by Japas and Franck (1985a)), the model shows a large overestimation of the dew point temperatures and a qualitatively wrong progression of the critical line (see right side of Figure 5.18).

From the four available excess enthalpy data sets by the group around Wormald, the one by Wormald and Colling (1983) shows clear deviations at high pressures due to a reported calculation error. Corrected values were published later by Lancaster and Wormald (1990). At elevated temperatures the description of excess enthalpies were improved with the new mixture model compared to the other models, while at low temperatures the excess enthalpy is generally overestimated by the EOS-CG model (see Figure A1.16). However, this overestimation by up to 50 % has a comparably small influence on the uncertainty of the total enthalpy since the excess enthalpy at 1 MPa is by a factor of ten smaller than the excess enthalpy at 10 MPa.

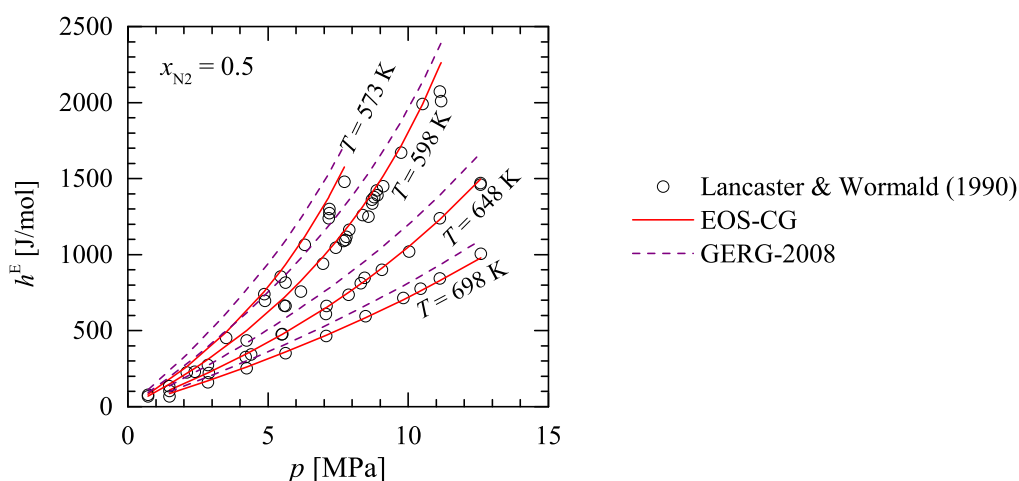


Figure 5.19: Experimental and calculated excess enthalpy data over pressure at several isotherms and $x_{\text{N}_2} = 0.5$.

The temperature and pressure dependence of the excess enthalpy at equimolar composition measured by Lancaster and Wormald (1990) is reproduced by the new mixture model within the scatter of the experimental data while the GERG-2008 model shows a systematic offset (see Figure 5.19).

Water + Oxygen and Water + Argon

The data situation for the mixtures of water with argon and oxygen is very similar, therefore these two mixtures are discussed together. For both systems one data set with high-pressure VLE and $p\rho T$ data (by Japas and Franck (1985b) for water + oxygen and Wu *et al.* (1990) for water + argon) is available for pressures up to around 300 MPa, with high uncertainties that go along with such high-pressure measurement methods (ca. 5 % in density). Additionally, for the system water + argon densities of the water-rich phase ($x_{\text{Ar}} < 0.002$) were measured by Biggerstaff and Wood (1988a).

A few pTx and pTy data sets are available but there is no complete $pTxy$ information. The coverage of the VLE region shows large gaps, especially the solubility at elevated temperatures and pressures. For water + argon only one data set at 298 K by Kennan and Pollack (1990) is available for the description of the pressure dependence of the solubility

up to 9 MPa, while for water + oxygen the data by Pray *et al.* (1952) cover temperatures between 435 K and 616 K with pressures up to 17.4 MPa. The saturation water content in the compressed gas is described by the data of Oellrich and Althaus (2001), Koglbauer and Wendland (2008) and Rigby and Prausnitz (1968) for argon, and Wylie and Fisher (1996a) for oxygen. The phase boundaries at supercritical pressures and temperatures were determined by Wu *et al.* (1990) and Japas and Franck (1985b) for the mixtures with argon and oxygen, respectively.

For both mixtures no departure function was developed in the EOS-CG mixture model due to the limited amount of data, especially the lack of accurate gas phase $p\rho T$ data. However, for the system water + oxygen the departure function of the system water + nitrogen was used as a generalized departure function together with an adjusted weight parameter F_{ij} (see Section 2.3 for more details). For the system water + argon such a generalized departure function did not improve the description of the experimental data and was not applied – here only the four reducing parameters were adjusted.

While gas phase densities at low pressures and temperatures are generally predicted accurately by the new mixture model even without fitting the reducing parameters, simply by the use of accurate pure-fluid EOS, most of the few available $p\rho T$ data for the two systems lie in the high-pressure, high-temperature region outside of the range of validity of the new mixture model, especially regarding the prediction of the phase boundaries. Consequently, the deviations between the experimental $p\rho T$ data and the model in the homogeneous phase increase up to $\pm 5\%$. Since the phase boundary compositions at given values of T and p are off by 10 mole-% or more in this region, the saturated densities calculated with these wrong saturation compositions may deviate up to $\pm 50\%$ (see Figure A1.19 and Figure A1.21). The measurements in the water-rich phase by Biggerstaff and Wood (1988a) are reproduced within $\pm 0.06\%$ for typical liquid states and within $\pm 3\%$ in the near-critical region.

Compared to the GERG-2008 the description of the phase boundaries was improved in the new mixture model for pressures up to 25 MPa and temperatures up to 550 K. The solubility data are mainly reproduced within ± 0.001 to ± 0.05 mole-%, and the model gives, as far as the sparse experimental data suggest, a qualitatively correct description of the temperature and pressure dependence of the solubility up to 500 K and 100 MPa. The dew points of the system water + argon were measured by Oellrich and Althaus (2001), Koglbauer and Wendland (2008) and Rigby and Prausnitz (1968). The low temperature data by Oellrich and Althaus (2001) (up to 288 K) are reproduced accurately by the new model within ± 0.002 mole-%. As shown in Figure 5.20 (here given as the vapor pressure enhancement factor f_w), the two latter data sets show a slight disagreement in the pressure dependence, especially at lower pressures and temperatures, where the data by Koglbauer

and Wendland (2008) show a different progression over pressure. The prediction of the new mixture model lies somewhere in between these two data sets. At higher temperatures ($T > 350$ K) the model follows the data by Koglbauer and Wendland (2008). Both data sets are reproduced mainly within ± 0.05 mole-%, with the highest deviations ($< \pm 0.5$ mole-%) being also at the highest water content (up to 70 mole-% at low pressures). For the system water + oxygen the few dew point data by Wylie and Fisher (1996a) are reproduced within ± 0.02 mole-%. A graphical overview on the VLE data for the two systems is given in the appendix in Figure A1.18 and Figure A1.22.

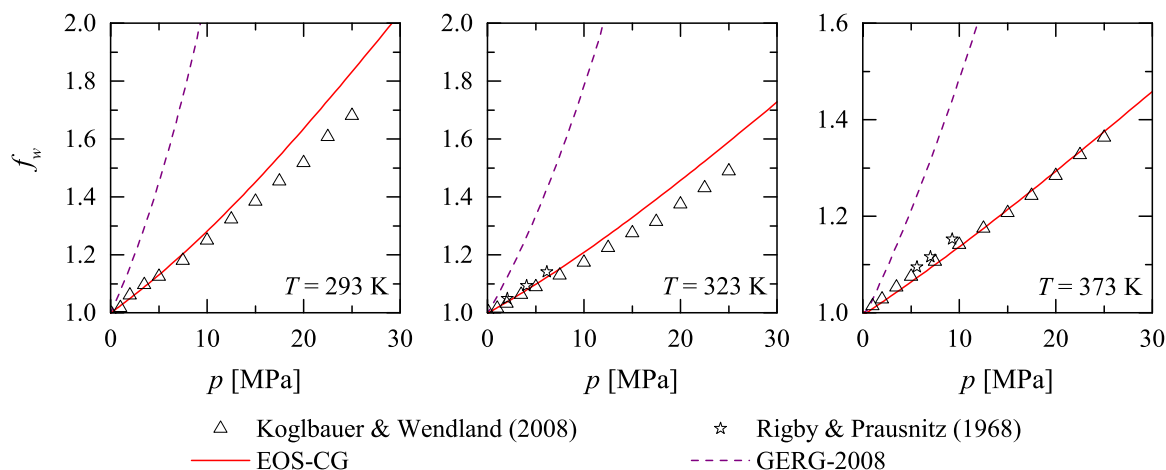


Figure 5.20: Experimental and calculated values of the vapor pressure enhancement factor f_w at different isotherms for the system water + argon.

For the system water + argon two sets of excess enthalpy data were measured by Wormald and Lancaster (1988) and Wormald and Colling (1993) at equimolar composition, pressures up to 13.3 MPa and temperatures between 373 K and 698 K. Although a part of these data was included in the fit they are reproduced with a distinctive offset by the new mixture model (see left side of Figure A1.20). When forced to reproduce these data more accurately in the fitting process, the model showed larger deviations from the accurate VLE data.

Two data sets of isobaric heat capacities in the liquid and near-critical region of the water-rich fluid were published by Biggerstaff *et al.* (1985) and Biggerstaff and Wood (1988b). These data are reproduced mainly within deviations of ± 0.5 %, and ± 2 % near the critical point (see Figure A1.20, right).

Water + Carbon Monoxide

For the system water + carbon monoxide no $p\rho T$ data were available in the literature. Only one data set with $pTxy$ data by Gillespie and Wilson (1980), covering temperatures between 310 K and 588 K and pressures up to 14 MPa, plus two excess enthalpy data sets by Lancaster and Wormald (1990) and Wormald and Lancaster (1988) at equimolar composition and temperatures between 363 K and 698 K and pressures up to 12 MPa, are

available in the data base. Due to the limited data situation the binary interaction parameters had to be adjusted carefully in order to avoid overfitting with distorted prediction of properties not covered by data. Only three of the four binary reducing parameters were adjusted, the asymmetric parameter of the density reducing function, $\beta_{v,ij}$, was kept at unity. However, as with the system water + oxygen, the departure function developed for the system water + nitrogen was also used as a generalized departure function by adjusting the weight parameter F_{ij} , this way improving the phase boundary and excess enthalpy description as well as the extrapolation behavior towards higher pressures.

As shown in Figure A1.23 in the appendix, the VLE data by Gillespie and Wilson (1980) are reproduced by the new mixture model with maximum deviations and AADs of ± 0.03 mole-% and 0.011 mole-%, respectively, in the liquid phase and ± 2 mole-% and 0.372 mole-%, respectively, in the gas phase. The phase boundaries extrapolate qualitatively correctly to pressures above 100 MPa. The excess enthalpy data are reproduced qualitatively correctly. However, deviations increase at lower temperatures, where the model overestimates the excess enthalpy contribution at elevated temperatures (see Figure A1.24).

5.2.3 Other Binary Mixtures

The remaining binary mixtures to be discussed here are all binary combinations of the main components of air, namely nitrogen, oxygen, and argon, plus carbon monoxide. All these fluids have rather similar characteristics with regard to their vapor pressure curves and critical properties. Consequently the two-phase region is comparably small since it is placed mainly between the respective vapor pressure curves. Additionally, none of these components shows strong polarity or chemical reactions with any of the mixing partners. Therefore the description of the mixing behavior is simple compared to the systems including water or carbon dioxide described above. The accuracy of the new mixture model for these mixtures is mainly related to the accuracy of the equations of state for the pure components (which are generally of reference quality with the exception of the EOS for carbon monoxide, which is a short fundamental equation developed by Lemmon and Span (2006)). None of these binary mixtures required the use of a departure function in order to accurately represent the available experimental data. This is partly due to the comparably ideal mixing behavior described above and partly due to the limited data situation. For the binary mixtures of the air components the major part of the available experimental data was measured before the 1970s, and while the phase boundaries were measured thoroughly due to the industrial interest with regard to air separation, the available experimental data on other properties in the homogeneous region are rather limited. For mixtures including carbon monoxide the data situation is generally very limited.

As mentioned above all binary mixtures of the four remaining components show a small two-phase region with regard to temperature and pressure. While for mixtures including carbon dioxide or water the comparison of experimental and calculated VLE data was mainly done by looking at the phase compositions at a given pressure and temperature, such an approach alone does not lead to meaningful results, since already very small changes in temperature or pressure lead to large changes in the phase boundary compositions. Thus it is more suitable to compare calculated dew and bubble point pressures or temperatures at a given composition. In the following discussions as well as in the overview in Table A2.1 in the appendix, the temperature is chosen as the property used for comparison.

Nitrogen + Oxygen

For this system the adjusted reducing parameters of the GERG-2008 model were adopted without any new fitting, since these parameters already represent the optimal fit to the available data (and no new data are available since the development of the GERG-2008). The fact that all adjusted reducing parameters are very close to unity (see Table 2.9) shows that for this mixture the residual mixing behavior due to molecular interactions of unlike molecules is small. Although no new fitting was necessary for this mixture the representation of the experimental data by the new model will be described in the following.

Five data sets describing the $p\rho T$ relation in the homogeneous gas, supercritical, and liquid phase are available for this system. Only three of these data sets cover pressures above atmospheric pressure, namely the data by Kuenen *et al.* (1922) and the two unpublished data sets by Wöll (2003) and Schilling (2003) from the thermodynamics group at the Ruhr-University Bochum. While the two latter sets cover the supercritical gas region, Kuenen also measured close to the critical point and in the supercritical liquid-like region, but with considerably larger uncertainties than the more than 80 years younger data sets. In the gas phase, the deviations between the EOS-CG model and the data are within $\pm 0.1\%$, and within $\pm 0.025\%$ for pressures below 7 MPa. Near the critical point the data by Kuenen are reproduced mainly within deviations of $\pm 1\%$ in pressure, while for the few liquid-like densities the scatter of the data increases up to deviations of $\pm 2\%$ in density. Deviation plots for all available experimental $p\rho T$ data for this mixture are given in the appendix in Figure A1.25.

For the description of the phase boundaries 13 data sets are in the data base, mostly describing the full $pTxy$ relation. Again, most of the data are older than 40 years; the most recent data sets are the measurements by Hiza *et al.* (1990) and Baba-Ahmed *et al.* (1999). As mentioned before the two-phase region is relatively small and is located somewhere between the vapor pressure curves of the pure components for all compositions (see Figure

5.21, right). The experimental data are generally reproduced within their scatter; no systematic offset between the model and data is recognizable (see the left side of Figure 5.21). Deviations between experimental and calculated dew and bubble point temperatures are mainly below ± 0.5 K; the AAD values for the most accurate data sets by Hiza *et al.* (1990) and Baba-Ahmed *et al.* (1999) are below 0.01 K. A graphical overview on the representation of the experimental VLE data is given in the appendix in Figure A1.27.

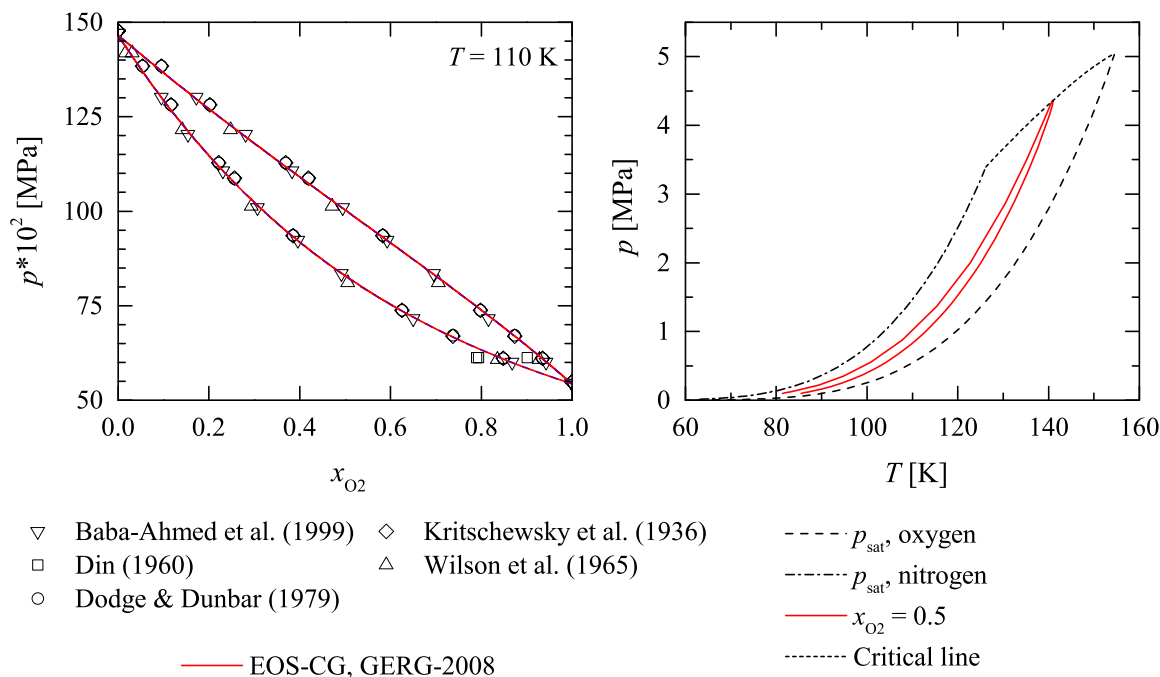


Figure 5.21: Left: Experimental and calculated phase compositions at 110 K for the system nitrogen + oxygen. Right: Phase boundaries of the pure components and the equimolar mixture and the critical line of the system nitrogen + oxygen.

Several authors have published experimental or pseudo-experimental B_{12} data for this system. In spite of the general limits of the new mixture model in the prediction of B_{ij} data (see Section 5.3 for more details) it follows the data qualitatively correctly, and the deviations are mainly within ± 1 cm³/mol (see Figure A1.26).¹⁵

Nitrogen + Argon

For the system nitrogen + argon the reducing parameters of the GERG-2008 model were slightly readjusted to account for the different pure fluid equations used in the EOS-CG mixture model. Still, the two models show basically identical predictions both for the $p\rho T$ relation and the phase boundaries.

At first glance the coverage for this system with $p\rho T$ data seems much better than for the system nitrogen + oxygen. More than 1000 data points from nine different publications

¹⁵ Since the second virial coefficient B as well as the B_{ij} values as a function of temperature have a zero crossing, a comparison based on relative deviations is not suitable.

cover temperatures between 70 K and 423 K and pressures up to 800 MPa. However, all data sets except the one by Ricardo *et al.* (1992) were published before 1980, and none of the available data sets can be considered very accurate; even the liquid-density data by Ricardo show a systematic offset towards the other experimental data in the same temperature, pressure and composition range. In the gas phase the deviations of the model from the experimental data lie mainly within ± 0.5 %, with the highest deviations for temperatures close to the critical temperature. For densities close to the critical density the deviations increase as expected. However, except for the strongly scattering data by Crain and Sonntag (1966) deviations are still within ± 1 % in density in the extended critical region. Most of the liquid-like density data is also reproduced within ± 0.5 % by the model, even most of the high-pressure data by Maslennikova *et al.* (1979) ($100 \text{ MPa} < p < 800 \text{ MPa}$). Deviation plots including all experimental data are given in the appendix in Figure A1.28.

For the description of the phase boundaries 12 data sets with a total of over 500 data points cover nearly the whole two-phase region. Beside a slight overestimation of the dew point temperatures (ca. $+0.1 \text{ K}$) the model represents the data within the experimental scatter (ca. $\pm 0.5 \text{ K}$, see Figure A1.29).

The available B_{12} data are predicted qualitatively correctly but with a small offset (ca. 1.5 %) towards the data by Wilson *et al.* (1965) and Zandbergen and Beenakker (1967), which are considered most reliable among the available data. The measurements by Dymond and Smith (1980) show a distinctively different temperature function of the B_{12} value compared to the other data (see Figure A1.28).

Oxygen + Argon

The third binary system of the dry air components, the mixture oxygen + argon, is not as well represented by accurate experimental data as the other two binaries. Only three data sets from before the 1960s are available for the $p\rho T$ relation, one by Masson and Dolley (1923) for the equimolar gaseous mixture at 298 K, and two data sets with liquid density data at low pressures by Blagoi and Rudenko (1958) and Saji and Okuda (1965). While the data by Masson and Dolley (1923) can only be reproduced within ± 2 %, with an offset of about -1.3 %, the deviations between the liquid densities and the model are mainly within ± 0.5 %. Deviation plots for all available data are given in Figure A1.31.

The phase boundaries were measured by 12 different authors, with the more accurate data sets by Burn and Din (1962), Clark *et al.* (1954), Narinskii (1957) and Pool *et al.* (1962). As can be seen in Figure A1.30, the isothermal bubble and dew lines in a p - x diagram show a clearly non-linear progression over composition, as opposed to the two other air binaries that show a much more linear characteristic. Although the vapor pressures

calculated by the new mixture model as well as the GERG-2008 are slightly above the experimental values, the deviations between experimental and calculated bubble and dew point temperatures are mainly within ± 0.05 K for the authors mentioned above.

The few data points on the second cross virial coefficient B_{12} are represented within their estimated experimental uncertainty. However, at temperatures below 100 K (well outside the region covered by data) the new mixture model deviates from the GERG-2008, the B_{12} values increasing again sharply after passing through a minimum at about 62 K (see Figure A1.31, bottom). This behavior is not intended or physically founded, but could not be avoided since the pure-fluid equation of state for oxygen by Schmidt and Wagner (1985) used in this mixture model shows this characteristic, while the pure-fluid equation used in the GERG-2008 mixture model behaves physically more reasonable in this region (see also Section 5.2.4 for a more thorough discussion on the calculation of virial coefficients from the new mixture model).

Nitrogen + Carbon Monoxide

For the mixture of nitrogen with carbon monoxide two highly accurate data sets describing the $p\rho T$ relation in the supercritical gas phase are available. One data set was published by Jaeschke and Humphreys (1991) and is part of the GERG databank. These measurements were performed by the former E.ON Ruhrgas company, which was a member of the GERG group. Two different series of measurements were performed, one with a Burnett apparatus and the second one with an optical interferometry method, with estimated experimental uncertainties of 0.07 % and 0.08 %, respectively. Only one mixture with a high nitrogen fraction ($x_{N_2} = 0.9699$) was measured in a temperature range from 273 K to 353 K and for pressures up to 30 MPa. The second data set by Mondéjar *et al.* (2011b) covers a wider temperature range (250 K to 400 K) and includes two compositions ($x_{N_2} = 0.85$ and 0.95). The estimated experimental uncertainty of these data is 0.10 %. Both data sets are reproduced by the new mixture model with deviations below ± 0.05 % (see Figure A1.32). However, no experimental data are available for liquid-like densities or mixtures with CO contents above 15 %, leaving a large gap in the $p\rho T x$ region where the model cannot be evaluated.

Eight data sets are available for the description of the phase boundaries. While the data by Torotscheschnikow (1937) and Yushkevich and Torocheshnikov (1936) cover a wide pTx region, they both show a large scatter, and isothermal phase compositions extrapolate to incorrect vapor pressures of the pure components (see Figure A1.33). The data by Duncan and Staveley (1966), Gill and Morrison (1966), Pool *et al.* (1962), and Sprow and Prausnitz (1966) are more accurate; except for the data by Sprow they only include information on one phase composition. The predictions of the phase boundaries by the GERG-2008 and the new mixture model are almost identical, and both models follow the

accurate data by Gill and Morrison (1966), Pool *et al.* (1962), and Sprow and Prausnitz (1966) with dew and bubble point temperature deviations below ± 0.05 K.

Oxygen + Carbon Monoxide and Argon + Carbon monoxide

For the last two binary systems to be discussed little to no experimental information is available on the data base established in this work. While for the system argon + carbon monoxide two data sets by Duncan and Staveley (1966) and Christiansen *et al.* (1973) are available describing the phase boundaries at three different isotherms and one data set by Pool *et al.* (1962) on the excess volume at the triple point conditions of pure argon, no data at all was found on the system oxygen + carbon monoxide.

Due to the poor data situation the adjusted parameters of the GERG-2008 model for the system argon + carbon monoxide (only the γ_{ij} parameters for temperature and density were adjusted) were adopted for the new mixture model without new fitting. With these parameters the phase boundary data is reproduced qualitatively correctly (although the data by Duncan and Staveley (1966) show a qualitatively wrong progression towards high argon fractions) and the density data is represented within 0.2 % uncertainty (see Figure A1.34).

5.2.4 Representation of Virial Coefficients

The concept of virial coefficients is based on the development of a Taylor series for the compression factor Z that describes the relation between the thermal properties

$$Z = \frac{p}{\rho RT} = 1 + B\rho + C\rho^2 + \dots \quad 5.8$$

Depending on the aspired accuracy of the model the expansion is cut off after the second virial coefficient B (only valid for the description of the gas phase at low densities) or extended to the third (C) or higher virial coefficients. The virial coefficients are functions of the temperature only and are usually fitted to experimental $p\rho T$ data at very low pressures. However, it may also be useful for some applications to create a simple virial equation of state using virial coefficients that are fitted to values calculated from a highly accurate Helmholtz energy model. The second virial coefficient B can be derived from the relation

$$\lim_{\rho \rightarrow 0} \left(\frac{Z-1}{\rho} \right) = B, \quad 5.9$$

since all terms with higher virial coefficients become negligible at very small densities. It is related to the Helmholtz energy model by

$$B = \lim_{\rho \rightarrow 0} \left(\frac{1}{\rho} \delta \alpha_{\delta}^r \right), \quad 5.10$$

and thus describes the extrapolation behavior of the residual part of the Helmholtz energy to zero density. It can also be determined graphically by plotting the function $(Z-1)/\rho$ over the density at different isotherms and extrapolating the isotherms to the ordinate ($\rho=0$, see Figure 5.22). The virial concept can be extended to mixtures by applying mixing rules to the virial coefficients that are rigorously derived from statistical thermodynamics, see e.g. Hirschfelder *et al.* (1954). The second virial coefficient thus becomes a function of composition and temperature and is calculated from the pure fluid second virial coefficients B_i and the binary second cross virial coefficients B_{ij} by

$$B(T, \bar{x}) = \sum_{i=1}^N x_i^2 B_i(T) + 2 \sum_{i=1}^{N-1} \sum_{j=i+1}^N x_i x_j B_{ij}(T). \quad 5.11$$

Values for the second cross virial coefficient can be generated from experimental values of B that are extrapolated from low-pressure $p\rho T$ measurements, and solving Eqn. 5.11 for B_{ij} . More recently, molecular simulation has been employed for the generation of B_{ij} values e.g. by Hodges *et al.* (2002) or Tulegenov *et al.* (2007).

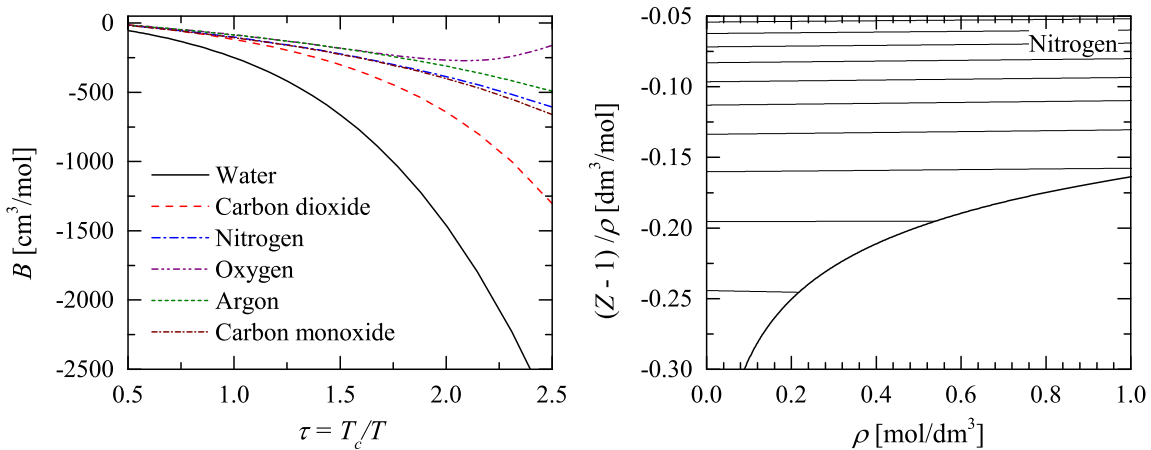


Figure 5.22: Left: Second virial coefficient for the fluids considered in the mixture model.¹⁶ Right: $(Z-1)/\rho$ - ρ diagram for nitrogen, calculated with the reference equation by Span *et al.* (2000). The thin lines are 10 K-spaced isotherms between 80 K and 170 K, the thick line is the dew curve. The values of the isotherms at $\rho=0$ correspond to the value of B at this temperature.

Beside other properties, experimental B_{ij} data were also used for the development of the new mixture model. Mostly the data were only used for comparison, but for some mixtures B_{ij} data points were also used for fitting (see Table A2.1). However, for binary mixtures including water, the model predictions of B_{ij} deviate strongly from all experimental data, especially at lower temperatures, where the B_{ij} increases to positive values instead of showing the typical drop to negative infinity. The reason for this behavior lies partly in the

¹⁶ Note that the second virial coefficient of oxygen increases at higher reduced temperatures instead of decreasing. This behavior is not physically based, but is believed to be a weakness of the equation of state.

model and partly in the specific characteristics of the second virial coefficient of water calculated from the EOS used in the mixture model.

When calculating B from the Helmholtz energy mixture model using the relation given in Eqn. 5.10, the mixture property is calculated from the pure fluid properties of the mixture components at a common reduced density δ and inverse reduced temperature τ . This approach is based on the assumption that all fluids show similar characteristics in relation to their critical point and is called the *corresponding states* approach (see also Chapter 2). This principle has been applied very successfully in most mixture models that are based on pure fluid equations of state, and generates accurate results for many different mixtures. However, the corresponding states mixing rules used in this mixture model reach their limits in the qualitative description of virial coefficients for mixtures with water. In Figure 5.22 the second virial coefficients of the pure components used in this mixture model is plotted over the inverse reduced temperature (the reducing parameter is the critical temperature). Following the corresponding states approach, one would expect a very similar progression of these plots, independent on the substance. Yet, the value calculated from the EOS for water by Wagner and Pruß (1999) shows a much steeper slope towards negative values at increasing values of τ than the other fluids. When calculating B of the mixture, the effect of a much lower B value for water than for the gas in mixture with water at the same reduced temperature is partly compensated by the mixing rules of the new mixture model (see Figure 5.23, right). However, when calculating B_{ij} from the model, the two pure-fluid virial coefficients are evaluated at the same temperature and then subtracted from the mixture virial coefficient. Due to the much higher critical temperature of water (in the mixture with nitrogen by a factor of four), the virial coefficient of water is evaluated at a much higher inverse reduced temperature than the one of the other fluid and mixture coefficient, resulting in a large negative value being subtracted, and in the erroneous description of B_{ij} shown in Figure 5.23, left.

Beside the erroneous temperature function of B_{ij} values of water mixtures also the mixture dependence of B does not reflect the simple quadratic characteristics given in Eqn. 5.11. In the right-hand diagram in Figure 5.23, the mixing behavior of the new mixture model for B is plotted together with the mixing rule given in Eqn. 5.11, using the correlation by Tulegenov *et al.* (2007) for B_{ij} of the water + nitrogen system, and a simple linear, ideal mixing rule. The composition function of B calculated from the new mixture model is clearly not quadratic, which is again a result of the corresponding states approach. The mixing rules for the pure-fluid contributions to the Helmholtz energy of the mixture are linear, but the pure fluids are not evaluated at the same temperature but at the same inverse reduced temperature. The mixing rules for the reducing parameters T_r and ρ_r are quadratic indeed, but together with the linear combination of the pure fluids contributions two effects

superpose. This way the mixing behavior of the second virial coefficient at constant temperature as given in Eqn. 5.11 is not correctly reproduced by the model.

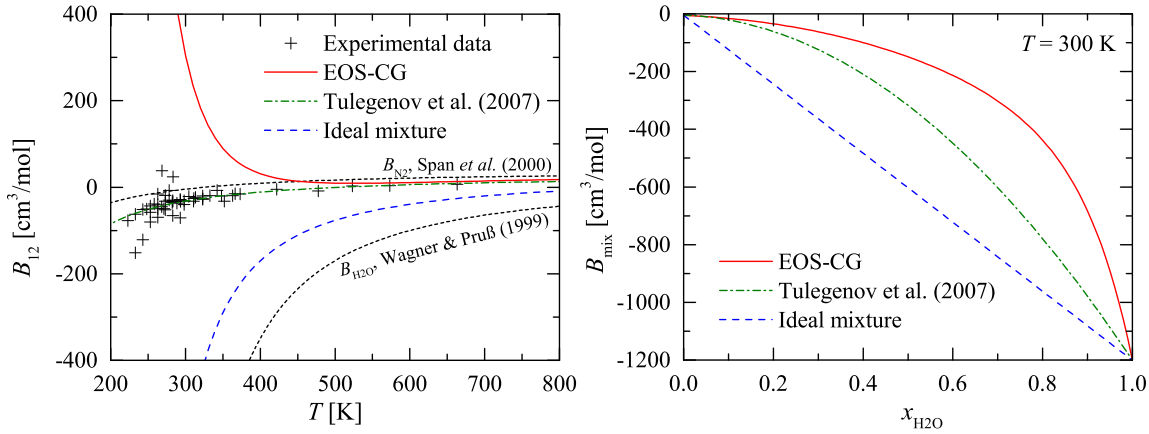


Figure 5.23: Left: The second cross virial coefficient B_{ij} for the system water + nitrogen: Experimental data and calculated values by the correlation of Tulegenov *et al.* (2007), an ideal mixture of real gases model, and the new mixture model. Right: Composition dependence of B_i predicted by different mixture models.

The two effects described above have only a small influence on mixtures of components with similar critical temperatures and temperature dependence of B , but cannot be neglected for non-ideal mixtures like the binary systems of water with light gases.

5.3 Representation of Multi-Component Mixtures

Like most other thermodynamic mixture models, the model presented in this work is only adjusted to experimental data of binary mixtures. Based on this approach the prediction of thermodynamic properties of multi-component mixtures is assumed to be valid since compared to the binary molecular interaction the ternary or higher interaction of molecules in a mixture is small (as long as no chemical reaction or association of molecules occurs). The practical application of this assumption has been shown many times, mostly for the prediction of thermodynamic properties of natural gas mixtures, mainly because such multi-component mixtures are comparably well measured due to the economical interest in the accurate knowledge of the properties of natural gas (see e.g. Kunz *et al.* (2007) for examples on the prediction of natural gas properties).

For the components under consideration in this work only a small amount of experimental data on multi-component mixtures could be retrieved. Especially data on typical CCS mixtures ($> 90\%$ CO_2 plus small amounts of N_2 , O_2 , Ar, and H_2O) would be interesting for the validation of the new mixture model but could not be found in the literature. The only data on ternary CO_2 mixtures are the VLE measurements by Muirbrook and Prausnitz (1965) and Zenner and Dana (1963) for the system carbon dioxide + nitrogen + oxygen. At lower temperatures the experimental data are reproduced accurately by the model but at higher temperatures and pressures the vapor composition line shows a qualitatively

different trend towards high oxygen contents than the experimental data (see Figure 5.24). The GERG-2008 model shows the same trend as the EOS-CG model, and additionally a distinctive offset in the prediction of the liquid phase compositions.

These results agree with the reproduction of the binary VLE data of the three components. While the two models agree well for compositions close to the binary mixture carbon dioxide + nitrogen (for which the same binary parameters are used both in the GERG-2008 and the EOS-CG models) they diverge clearly for compositions close to the binary mixture carbon dioxide + oxygen (with very little nitrogen content), where they also differ more from the experimental data. This offset results from the mixture model for carbon dioxide + oxygen, where a similar offset from the experimental data can be observed for VLE data and where the EOS-CG model shows much better but not perfect reproduction of the isothermal phase boundaries at higher temperatures than the GERG-2008 model (see Figure A1.7). The linear progression of the liquid and vapor composition lines in the ternary VLE diagram in Figure 5.24 also confirms that for this system the effect of ternary molecular interactions on the phase boundaries is negligible.

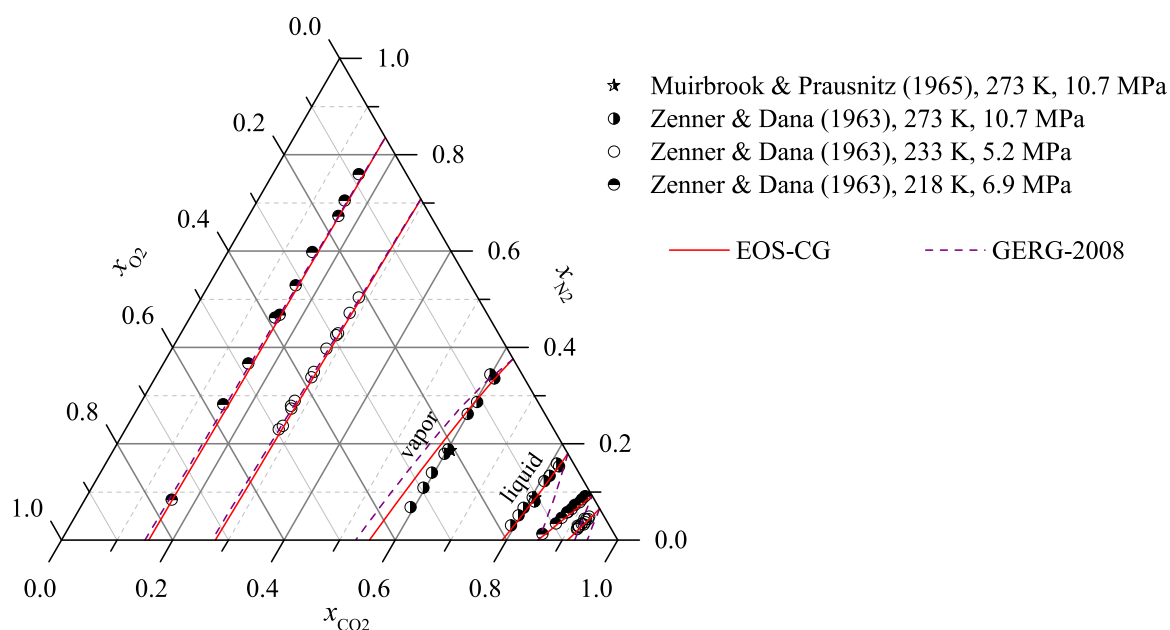


Figure 5.24: Experimental and calculated phase compositions for the system carbon dioxide + nitrogen + oxygen at different isotherm-isobar combinations.

A large number of measurements were carried out on the thermodynamic properties of air, which in this context is represented by the ternary system nitrogen + oxygen + argon. The available experimental data have been measured for a number of different compositions, however a standard composition of $x_{N_2} = 0.7812$, $x_{O_2} = 0.2096$, and $x_{Ar} = 0.0092$ is widely established in the literature. For this system Lemmon *et al.* (2000) developed a highly accurate multi-parameter reference equation of state explicit in the Helmholtz free energy, which is strictly speaking not a mixture model since air is treated as a pseudo pure fluid and the model is fitted directly to the mixture data at the fixed composition given above.

This model (calculated using REFPROP 9.0) is used together with the experimental data in the evaluation of the EOS-CG mixture model.

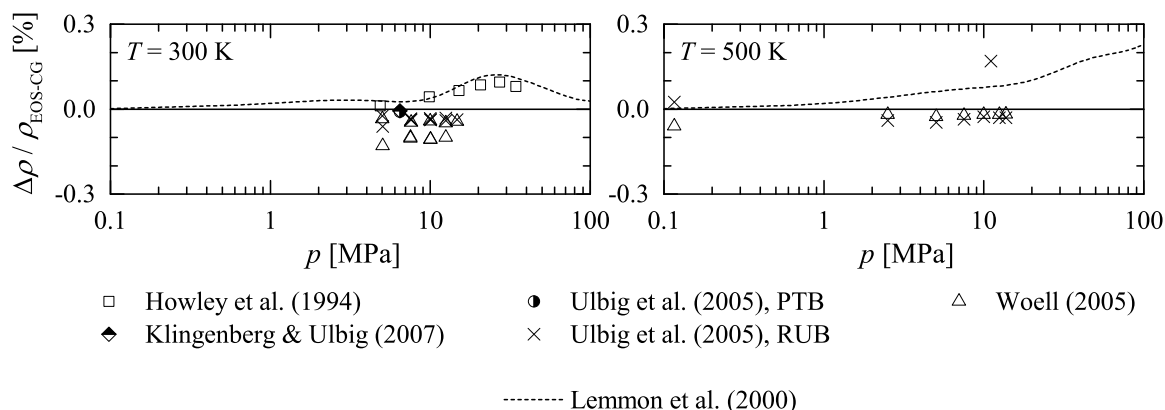


Figure 5.25: Deviations of selected experimental data and the model by Lemmon *et al.* (2000) from the new mixture model for the system nitrogen + oxygen + argon (air).

25 data sets on the description of the $p\rho T$ relation are available, with low-temperature data e.g. by Blanke (1977), Diller *et al.* (1991), Romberg (1971), and Vassermann *et al.* (1976) and supercritical gas densities by e.g. Kozlov (1968), Holborn and Schultze (1915), Klingenberg and Ulbig (2007), Ulbig *et al.* (2005), and Wöll (2005). Although some systematic deviations between the EOS-CG model and the experimental data are recognizable, the data are generally reproduced within $\pm 0.5 \%$. While the model by Lemmon *et al.* (2000) naturally reproduces all data published before 2000 more accurately than the EOS-CG model (since it was fitted directly to these data), it is noteworthy that the more recent data by Ulbig *et al.* (2005) and Wöll (2005) diverge from the data by Kozlov (1968) at elevated temperatures and pressures. While the Lemmon model follows the Kozlov data, the new data show much better agreement with the EOS-CG mixture model (see Figure 5.25 and Figure A1.35 in the appendix). This proves again the reliability of the prediction of multi-component properties from the new mixture model when the binary systems are fitted accurately.

Although several data sets on the isobaric and isochoric heat capacity of air are available, these data are generally quite inaccurate and show either large scatter or systematic deviations (e.g. the data by Pofertl *et al.* (1959), see Figure A1.37). Here the comparison to the reference equation is more suitable. As shown in Figure A1.37, the two models are in very good agreement; only for temperatures above 1000 K the new mixture model starts to diverge slightly from the reference equation. The deviations stay below 0.3 %, independent on the pressure.

The speed of sound of air was measured by 13 different authors, the most accurate data sets are by Ewing and Goodwin (1993), Younglove and Frederick (1992), and measurements done by the group around Martin Trusler at the Imperial College of Science, Technology and Medicine, London (ICSTM), published in Ulbig *et al.* (2005). While the

new mixture model shows distinctive deviations from the reference equation and the data at subcritical temperatures in the liquid phase (up to 1.0 %), it agrees better than the reference model with the data by Younglove and Frederick (1992) and Trusler at temperatures above 300 K, with deviations below 0.05 % (see Figure A1.38).

The gaseous mixture of nitrogen + oxygen + argon + water is usually referred to as *humid air* when the composition relations between the first three, “non-condensable” components are fixed and correspond to the mole fraction relations of air. The water content in this system is limited by the saturation content at a given temperature and pressure. Such a mixture relates more closely to the “real”, atmospheric air mixture and is often used as a synthetic fluid mixture for process simulations of processes with air as working fluid, where condensation may occur (e.g. in air conditioning or processes involving compression and expansion of air, such as CAES). Several attempts have been made to measure the $p\rho T$ relation of this system, e.g. as part of the AA-CAES project by the group around Trusler at ICSTM, and at PTB (see Ulbig *et al.* (2005)), and by Wöll (2005). Another data set from this project was later published by Klingenberg and Ulbig (2007). Additionally, a data set with molecular simulation data by Eckl *et al.* (2009) is available. While the simulation data by Eckl *et al.* (2009), which cover pressures up to 25 MPa, temperatures between 333 K and 524 K and water contents up to 5.3 mole-%, are reproduced by the new mixture model within ± 1 %, all of the experimental data show large scatter and systematic errors, and consequently do not suffice to evaluate the model for this system. The deviations from the data by Wöll increase up to ± 20 % at low pressures.

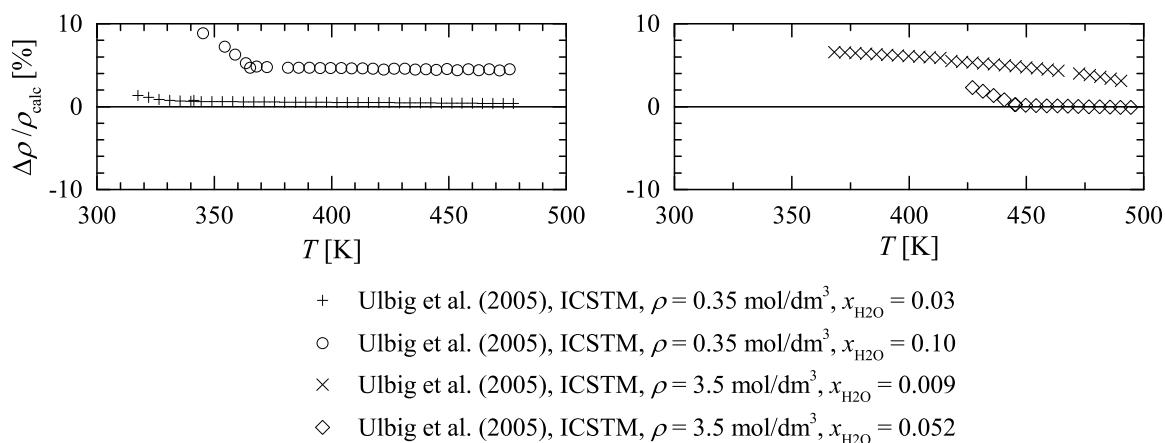


Figure 5.26: Deviations between the isochoric $p\rho T$ data for humid air measured at the ICSTM and the new mixture model at different isochores and water contents.

The data measured at ICSTM include mixtures with water contents up to 22 mole-%. These isochoric measurements reveal some interesting characteristics. As shown in Figure 5.26, the deviations from the new mixture model increase at low densities with increasing water content, while for higher densities the opposite trend can be observed. Additionally, the deviations for isochores of mixtures with higher water content show a kink when

plotted over temperature. This kink suggests that the system enters the two-phase region at this temperature and water starts to condensate.

All these observations suggest that the different challenges connected with measuring water- and oxygen-rich mixtures at elevated pressures and temperatures (corrosion of equipment, adsorption, condensation etc.) lead to unwanted effects that disturb the experimental results and render the data basically useless.

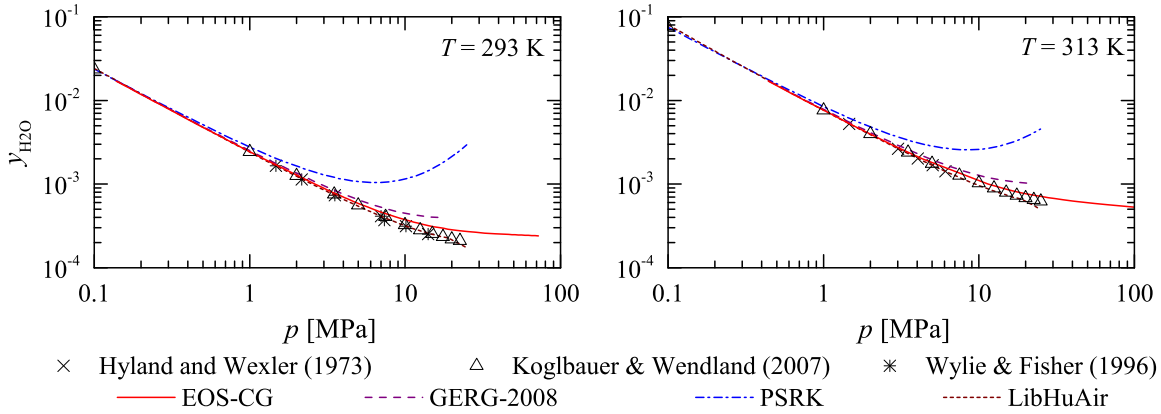


Figure 5.27: Experimental and calculated values of water saturation content for humid air at selected isotherms.

Seven data sets are available on the dew point of humid air for pressures up to 30 MPa and temperatures between 250 K and 420 K. While the data by Hyland and Wexler (1973), Wylie and Fisher (1996b), and Webster (1950) are in good agreement, the data by Koglbauer and Wendland (2008) show a systematic offset at higher pressures, similar to their dew point measurements for binary water mixtures. The reproduction of the experimental data by the new mixture model is compared to the GERG-2008, the PSRK, and the LibHuAir model by Herrmann *et al.* (2009). The latter one is a correlation for the dew point of humid air based on the Poynting method and the only model fitted directly to experimental data of humid air.

Except for the LibHuAir model the new mixture model shows the best reproduction of the saturation water content (see Figure 5.27 and Figure A1.41 in the appendix). However, the predictions still show systematic deviations from the experimental data at elevated pressures, since the model underestimated the saturation water content. This results in an underestimation of the dew point temperatures at given pressure and composition of up to -5 K at 25 MPa. For low pressures (< 1 MPa) the experimental dew point temperatures are still reproduced within ± 1 K. On the other hand the new mixture model gives the best extrapolation behavior of the experimental data towards high pressures, since even the correlation shows a systematically wrong progression of the water concentration at saturation at high pressures, even within the range covered by data.

6 CONCLUSIONS AND OUTLOOK

In this work a new mixture model explicit in the reduced Helmholtz free energy is proposed for mixtures of carbon dioxide, water, nitrogen, oxygen, argon, and carbon monoxide. This model aims to improve the prediction of thermodynamic properties for CO₂-rich fluids typical in the separation, compression and transport of carbon dioxide from fossil-fuelled power plants, of humid combustion gases, and of humid, compressed air. The mathematical structure of the new model is based on the approach suggested by Kunz *et al.* (2007) and Kunz and Wagner (2012), which resulted in the GERG-2004 and its extension, the GERG-2008 mixture models that represent the state of the art in the accurate description of natural gas mixtures. This class of mixture models includes accurate Helmholtz energy equations of state for the description of the contributions of the pure components to the mixture property, which are evaluated at common reduced variables. The reducing parameters are functions of the mixture composition and can be adjusted to experimental data of any thermodynamic property of binary mixtures by four binary parameters. Furthermore, the model allows for the use of an additional excess function, the so-called *departure function* that is also fitted to experimental data of binary mixtures with all its coefficients and exponents. Although all components considered in this work are already part of the GERG-2008 model, it only includes a small number of adjusted binary parameters, and these parameters were fitted with the focus mainly on the description of properties in the unsaturated gas phase.

The data base needed for fitting the mixture model was drastically increased compared to the database used for the development of the respective mixture parameters in the GERG-2008 model, providing more detailed information on the characteristics of the binary mixtures and thus allowing a more advanced fitting of the model parameters. However, this database still shows large gaps for temperature, pressure, and mixture regions where no or only few experimental information on thermodynamic properties is available. A new fitting technique, which was to this day mainly used for the development of equations of state for pure fluids, was applied in this work for the development of the EOS-CG mixture model. Different from the technique used in the development of the GERG-2008 model, it allows the direct nonlinear fitting of all adjustable model parameters, including the exponents in the departure function. Additionally, thermodynamic and non-thermodynamic constraints were developed and used in this work that ensure a physically meaningful and mathematically robust thermodynamic model over a wide temperature, pressure and composition range, even far beyond the available experimental data.

New model parameters are presented for 11 out of the 15 binary systems that result from all possible binary combinations of the six components considered in the model. For three out of the four remaining systems the model parameters were adopted from the GERG-

2008 model since no new experimental data were available for these systems and the GERG-2008 already represents the best possible fit. For the system oxygen + carbon monoxide no experimental data could be retrieved at all. For four binary systems departure functions increase the accuracy of the model, three of these functions were developed as part of this work. Two more systems use one of the binary departure functions developed in this work as a generalized departure function with adjusted weight parameters.

Based on the available experimental data and the comparison to other established models, the new mixture model was thoroughly evaluated concerning the accuracy of predicted or reproduced thermodynamic properties for binary and some selected multi-component mixtures, as well as the physically reasonable extrapolation behavior into regions where no experimental data are available. The major findings of this evaluation can be summarized for three groups of binary systems:

- For mixtures of carbon dioxide with any of the other components except water the phase boundaries are predicted accurately over a wide temperature and pressure range, but the critical pressures are slightly overestimated close to the critical point of CO₂. Density data are predicted with uncertainties of ± 1.0 % or better up to 20 MPa and between 220 K and 500 K, with increasing uncertainties in the supercritical liquid region.
- For systems with water as one of the constituents the reproduction of the phase boundaries is accurate and qualitatively correct for temperatures up to 600 K and pressures up to 20 MPa. For temperatures below 450 K the phase boundaries are predicted qualitatively correct up to 100 MPa. The extrapolation of the model beyond the desired range of validity for the description of the phase boundaries in the critical region ($p > 25$ MPa, $T > 600$ K) is not valid. Gas and liquid phase densities are predicted within uncertainties of ± 0.5 % or better for temperatures below 600 K and pressures up to 20 MPa. The uncertainties increase in the supercritical region and for higher temperatures.
- Mixtures of the air components and carbon monoxide are modeled very accurately and show simple mixing behavior. Accurate gas phase density data are reproduced within their experimental uncertainty (0.05 % to 1.0 %) up to 100 MPa and 500 K. Larger uncertainties have to be expected for sub-critical temperatures. Dew and bubble point temperatures are calculated with an estimated uncertainty below ± 0.5 K.

A detailed summary of the estimated uncertainties of the new mixture model based on the reproduction of experimental data and their experimental uncertainty is given in Table 6.1. For properties or regions where no estimates are given no (reliable) experimental data is available for the model evaluation. In these cases only rough estimates based on the

experience of the author can be made. For gas phase data at pressures below 5 MPa the expected uncertainties in density and speed of sound are $< 1\%$, and $< 2\%$ in isobaric heat capacity. For higher pressures and supercritical or liquid-like states the uncertainties cannot be estimated reasonably without an experimental basis. Generally the uncertainties of *gas phase properties* calculated from the mixture model decrease for mixtures with one component being the major constituent (> 99 mole-%). The mixing effects become negligible and the accuracy of the respective pure-fluid equation of state is predominant (which is generally much higher than the accuracy of the mixture model). This does not hold true for other regions, since even tiny impurities may have a large influence on the shape of the two-phase region and the thermodynamic properties in the liquid and supercritical phase.

Table 6.1: Estimated uncertainties of the new mixture model for the different binary mixtures and selected thermodynamic properties, based on the reproduction of the best available experimental data.

Binary system	VLE data		$p\rho T$ data ^a			w data ^a	c_p data ^a
	gas	liquid	gas ^d	crit. ^e	liquid ^f		
CO ₂ –H ₂ O	$<0.5\%^b$	$<0.3\%^b$	$<0.3\%$	$<2.0\%$	$<0.5\%$	–	$<1.0\%$
CO ₂ –N ₂	$<0.5\%^b$	$<0.8\%^b$	$<0.3\%$	$<1.0\%$	$<0.5\%$	$<0.5\%$	$<1.0\%$
CO ₂ –O ₂	$<2.0\%^b$	$<2.0\%^b$	$<1.0\%$	$<5.0\%$	$<4.0\%$	$<1.0\%$	–
CO ₂ –Ar	$<1.0\%^b$	$<1.0\%^b$	$<0.5\%$	$<1.0\%$	$<2.0\%$	–	–
CO ₂ –CO	$<2.0\%^b$	$<2.0\%^b$	$<1.0\%$	–	$<4.0\%$	–	–
H ₂ O–N ₂	$<0.1\%^b$	$<0.01\%^b$	$<0.5\%$	$<2.0\%$	–	–	–
H ₂ O–O ₂	$<0.2\%^b$	$<0.05\%^b$	–	$<3.0\%$	–	–	–
H ₂ O–Ar	$<0.5\%^b$	$<0.05\%^b$	–	$<3.0\%$	<0.1	–	$<0.5\%$
H ₂ O–CO	$<0.5\%^b$	$<0.03\%^b$	–	–	–	–	–
N ₂ –O ₂	$<0.5\text{ K}^c$	$<0.5\text{ K}^c$	$<0.1\%$	$<2.0\%$	$<2.0\%$	–	–
N ₂ –Ar	$<0.3\text{ K}^c$	$<0.3\text{ K}^c$	$<0.5\%$	$<1.0\%$	$<0.5\%$	–	–
N ₂ –CO	$<0.2\text{ K}^c$	$<0.2\text{ K}^c$	$<0.05\%$	–	–	–	–
O ₂ –Ar	$<0.2\text{ K}^c$	$<0.2\text{ K}^c$	$<1.0\%$	–	$<0.5\%$	–	–
O ₂ –CO	–	–	–	–	–	–	–
Ar–CO	$<0.5\text{ K}^c$	$<0.5\text{ K}^c$	$<0.5\%$	–	–	–	–

^a Estimated uncertainties are given as a percentage value of the respective property.

^b Estimated uncertainties are given as a percentage of the molar phase composition.

^c Estimated uncertainties are given as dew or bubble point temperature ranges.

^d gas: Low-density gas phase region: $\rho/\rho_c < 0.6$.

^e crit.: Supercritical region at densities close to the critical density: $0.6 < \rho/\rho_c < 1.4$.

^f liquid: Sub- and supercritical region at liquid-like densities: $\rho/\rho_c > 1.4$.

The new mixture model presents a significant improvement in the description of thermodynamic properties of humid gases and CCS mixtures. Especially the location of the phase boundaries is predicted much more accurately over a wide temperature and pressure range than with the models used for comparison. The GERG-2008, the only other mixture model based on highly accurate Helmholtz energy equations of state for the pure components available for these fluids, was clearly not designed for mixtures with high carbon dioxide fractions or water mixtures. However, its flexible and powerful mathematical structure that was adopted with some minor alterations for the new mixture model proved to be able to describe these mixtures much more accurately when carefully fitted to accurate experimental data. Since the model uses the most accurate reference equations of state for the description of the pure fluid contributions, it ensures highly accurate description of properties in states where the pure fluid contributions are predominant. Moreover consistency and the highest accuracy are guaranteed for the calculation of mixtures where one component is almost pure, and the model extrapolates towards a highly accurate description of pure fluid properties. The model finds its limits in the description of the “complete” phase boundaries of water mixtures at temperatures and pressures above the critical point of water. Although several data sets are available in this region it was not possible to adjust the model to these data without a loss in accuracy in other regions, even with the introduction of an extensive departure function.

The fitting technique used for the development of the EOS-CG mixture model has huge potential due to the flexible use of constraints and the possibility of manipulating all model parameters directly without prior data linearization or the use of a bank of terms. However, the lack of a “good initial estimate” for the number and type of terms of the departure function made the development of such functions a tedious and time-consuming work. Hundreds of preliminary models were developed and then rejected, dozens of different constraints and fitting strategies tried until the final model was found. Since the fitter gets quickly stuck in a local optimum without the manual change of weights, parameters, or constraints, this process requires constant user input and monitoring.

It is inherent to an empirical model that its quality is limited by the accuracy and availability of the experimental data that poses its basis. It was shown in this work that although a large amount of data has been collected there are still regions and whole binary systems where the amount of accurate data is insufficient for the development of an adequate mixture model. Several projects are on the way at the thermodynamics group at the Ruhr-University Bochum, as well as in other research groups, with the goal to close these gaps with accurate density, speed of sound, and saturation point measurements. Once new experimental data are available the mixture model needs to be reviewed and if necessary, refitted.

Finally, the components considered in this model are only the main constituents of typical combustion gases or CCS mixtures. Several other fluids, e.g. SO_2 , NO_x , H_2 , and H_2S , are possible minor impurities, depending on the application. For none of these fluids the mixing behavior is expected to be simple; chemical reactions and large differences in critical parameters have a major impact on the location of the phase boundaries and pose challenges for future work.

Consequently the model presented here has to be considered as a “next step” based on the previous developments, and the best possible fit to the current data base. New experimental data, new components, and further developments in the fitting technique and software leave room for improvement and future research.

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A1 GRAPHICAL REPRESENTATION OF EXPERIMENTAL DATA

In the following section a comprehensive graphical overview on the representation of experimental data by the new EOS-CG mixture model, the GERG-2008 and other selected mixture models is given, supplementary to the examples given in Chapter 5. For each binary and multi-component system discussed in Chapter 5 plots of the phase boundary compositions at a number of isotherms (p - x/y or x - p and y - p plots) are shown for evaluation of the VLE data. The isotherms chosen for the plots represent the temperature range covered by experimental data and are generally chosen so that the best available experimental data are represented. In addition the representation of experimental VLE data is complemented for several binary systems by plots showing deviations between experimental and calculated dew and bubble point temperatures T_{vap} and T_{liq} , where

$$T_{\text{vap}} = T(p, \bar{y})_{\text{sat.}}, \quad \text{and} \quad T_{\text{liq}} = T(p, \bar{x})_{\text{sat.}}. \quad \text{A1.1}$$

The evaluation of $p\rho T$, speed of sound (w), and heat capacity (c_p , c_v) data is mainly performed by use of deviation plots, where the new mixture model represents the base line if not explicitly stated otherwise. Where possible, the data used in these plots is sorted by temperature or composition intervals, while the deviations are usually plotted over pressure. For heat capacity data the deviations are plotted over temperature. Comparisons to other models than the GERG-2008 are usually not given, since cubic equations of state like the PSRK and even the much more complex the LKP model proved to be generally inferior in the description of $p\rho T$ data, and caloric properties cannot be calculated from such models without additional correlations for c_p° . The representation of excess enthalpy (h^E) data is evaluated using h^E - x or h^E - p plots rather than deviation plots. This way the qualitative behavior of the model can be directly observed.

The plots are given in the same order as the discussion of binary and multi-component systems in Chapter 5. However, in order to avoid a number of only half used pages (due to the size of the plots) the order of plots for one system does not always follow the discussion in the text.

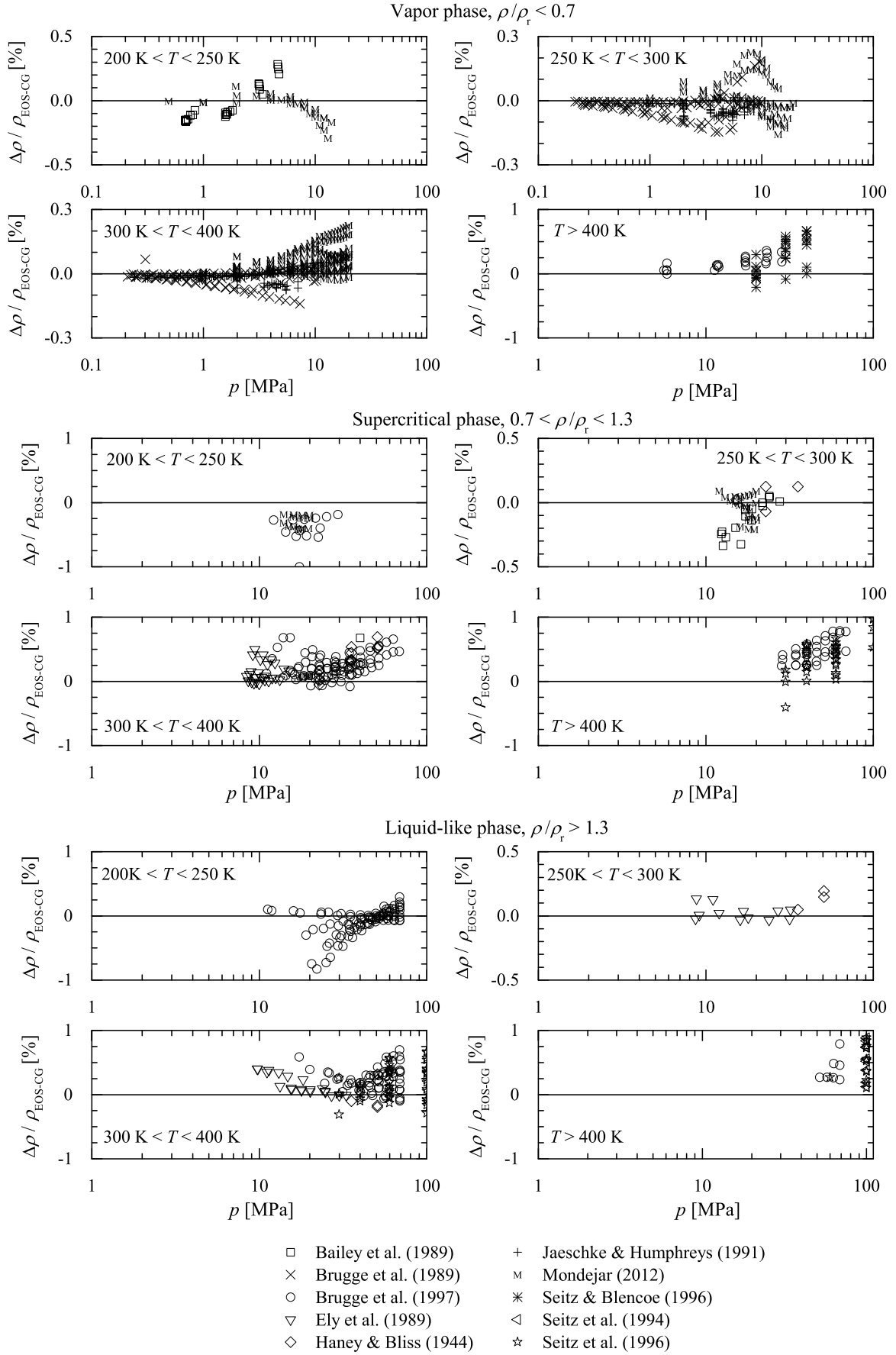


Figure A1.1: Deviations between selected experimental $p\rho T$ data and the new mixture model for the system carbon dioxide + nitrogen.

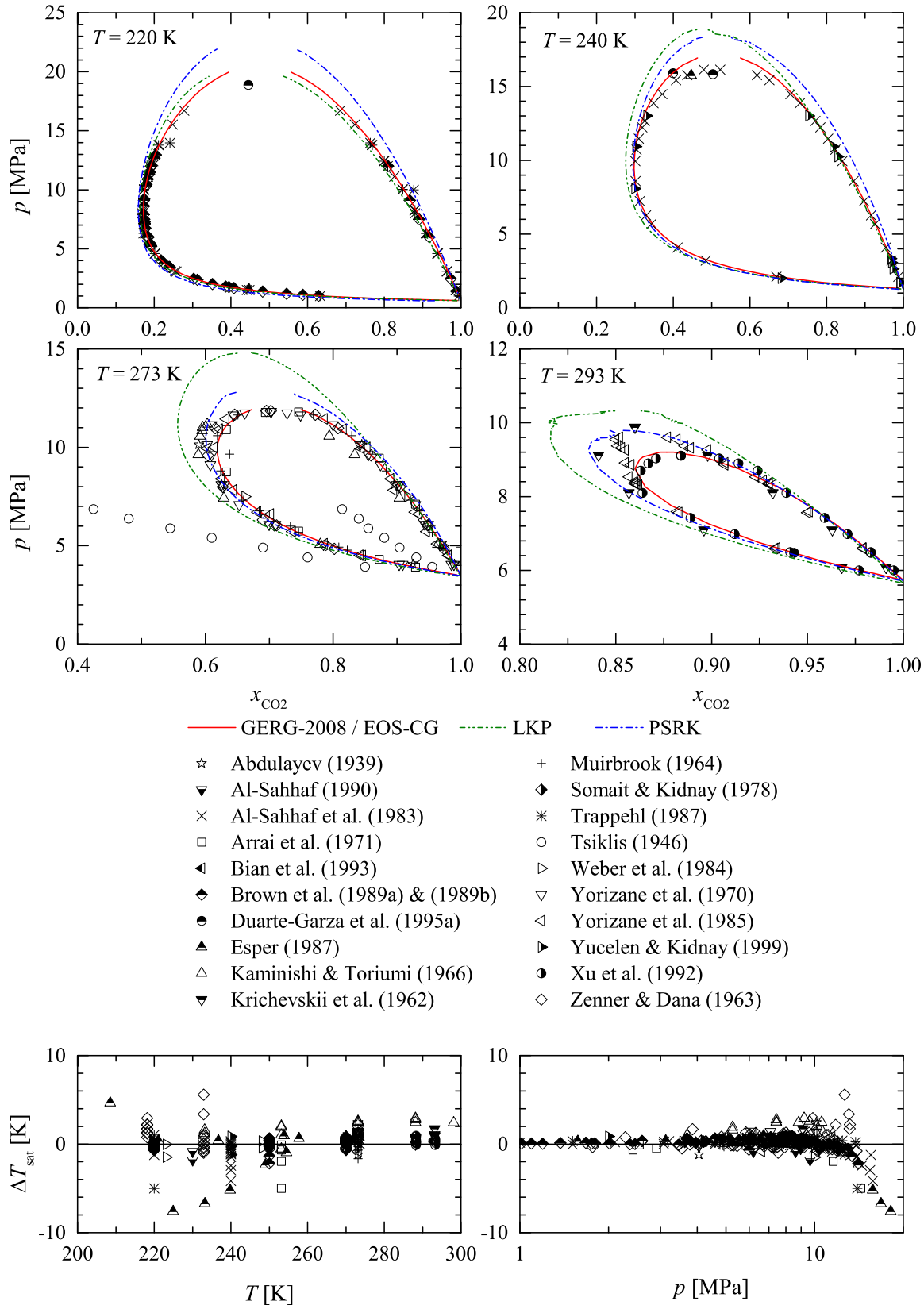


Figure A1.2: Top: Measured and calculated phase boundaries for selected isotherms. Bottom: Dew and bubble point temperature deviations between experimental data and the new mixture model over temperature and pressure for the system carbon dioxide + nitrogen.

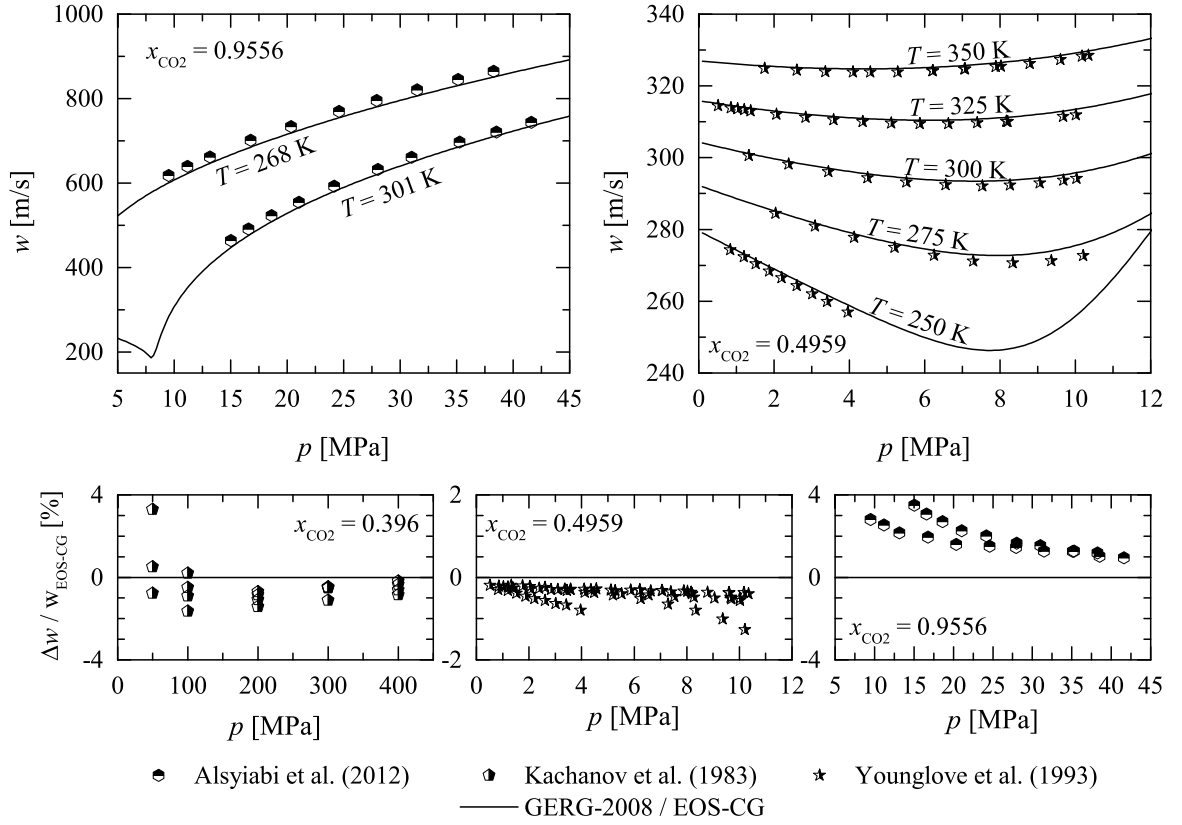


Figure A1.3: Deviations and absolute values of experimental speeds of sound and values calculated from the new mixture model for the system carbon dioxide + nitrogen.

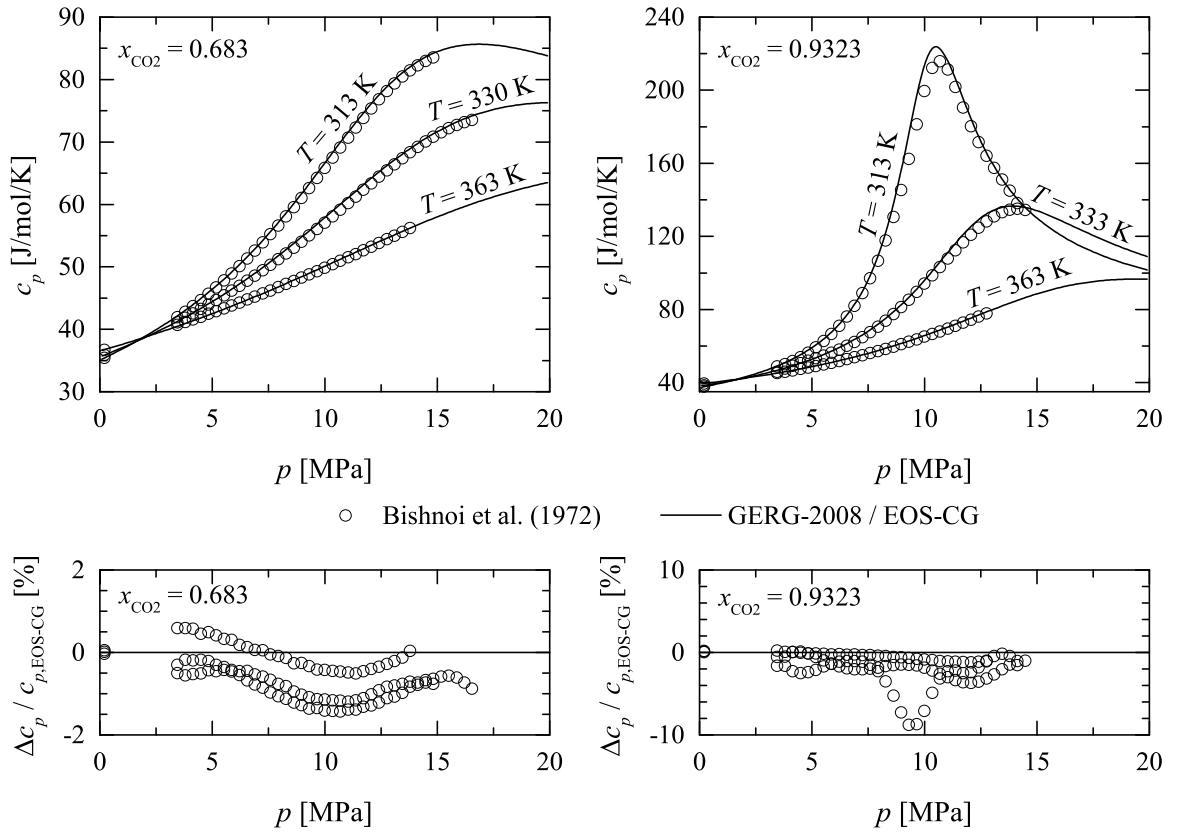


Figure A1.4: Deviations and absolute values of experimental isobaric heat capacities and values calculated from the new mixture model for the system carbon dioxide + nitrogen.

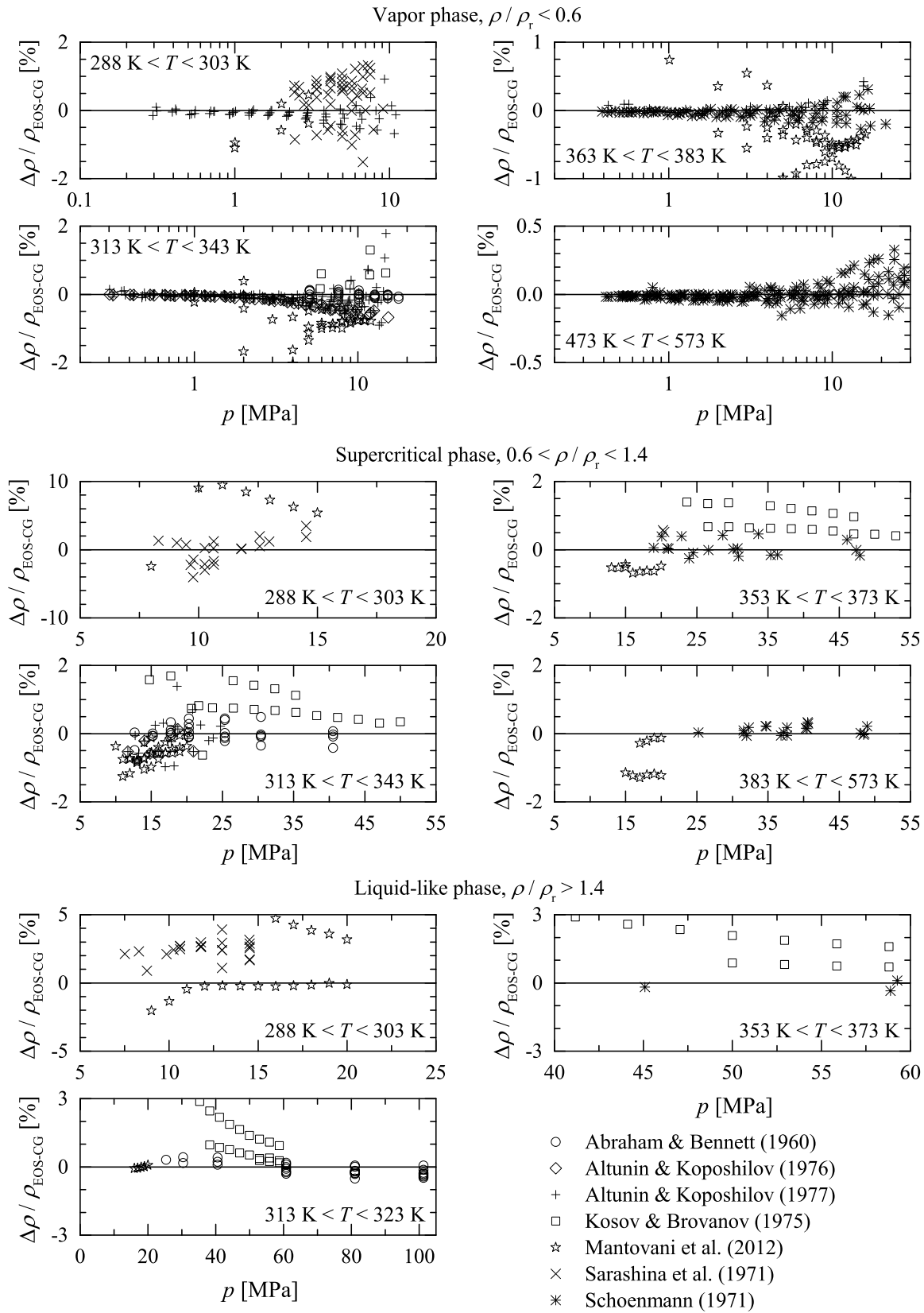


Figure A1.5: Deviations between the available experimental $p\rho T$ data and the new mixture model for the system carbon dioxide + argon.

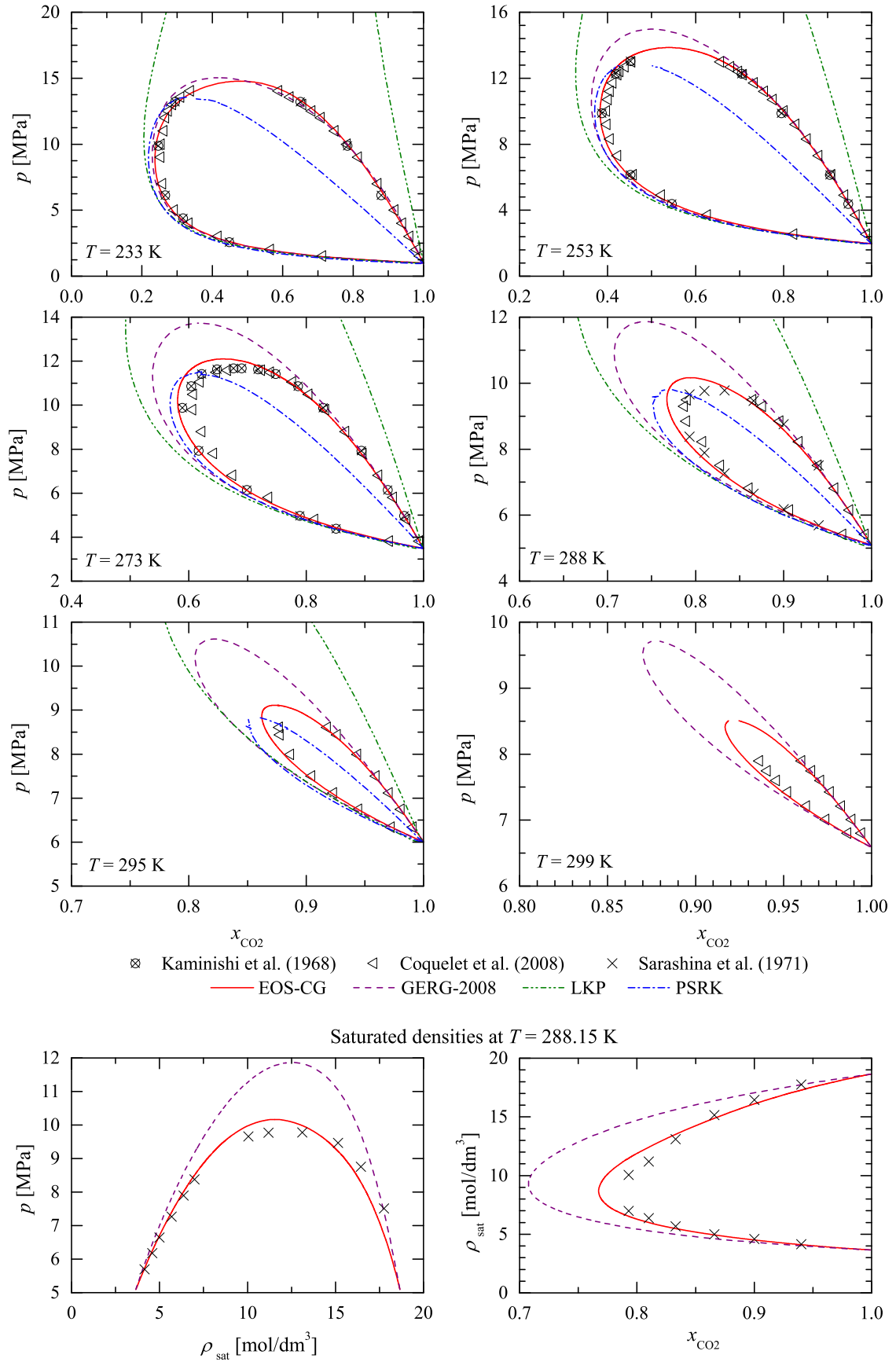


Figure A1.6: Phase boundaries and saturated densities: Experimental data and values calculated from the new mixture model (EOS-CG) and the GERG-2008 for the system carbon dioxide + argon.

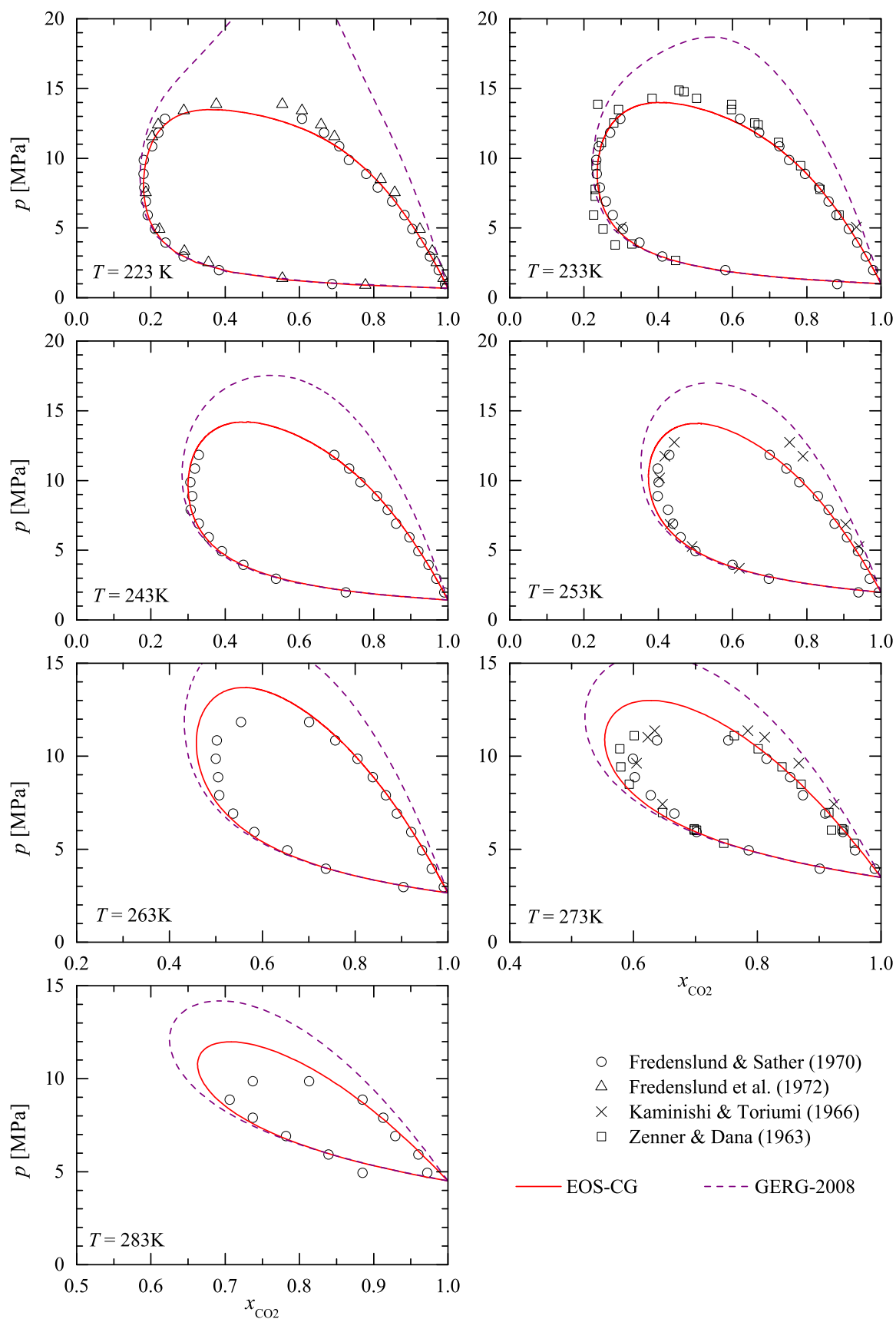


Figure A1.7: Experimental data and calculated values from the new mixture model and the GERG-2008 for the isothermal phase boundaries of the system carbon dioxide + oxygen.

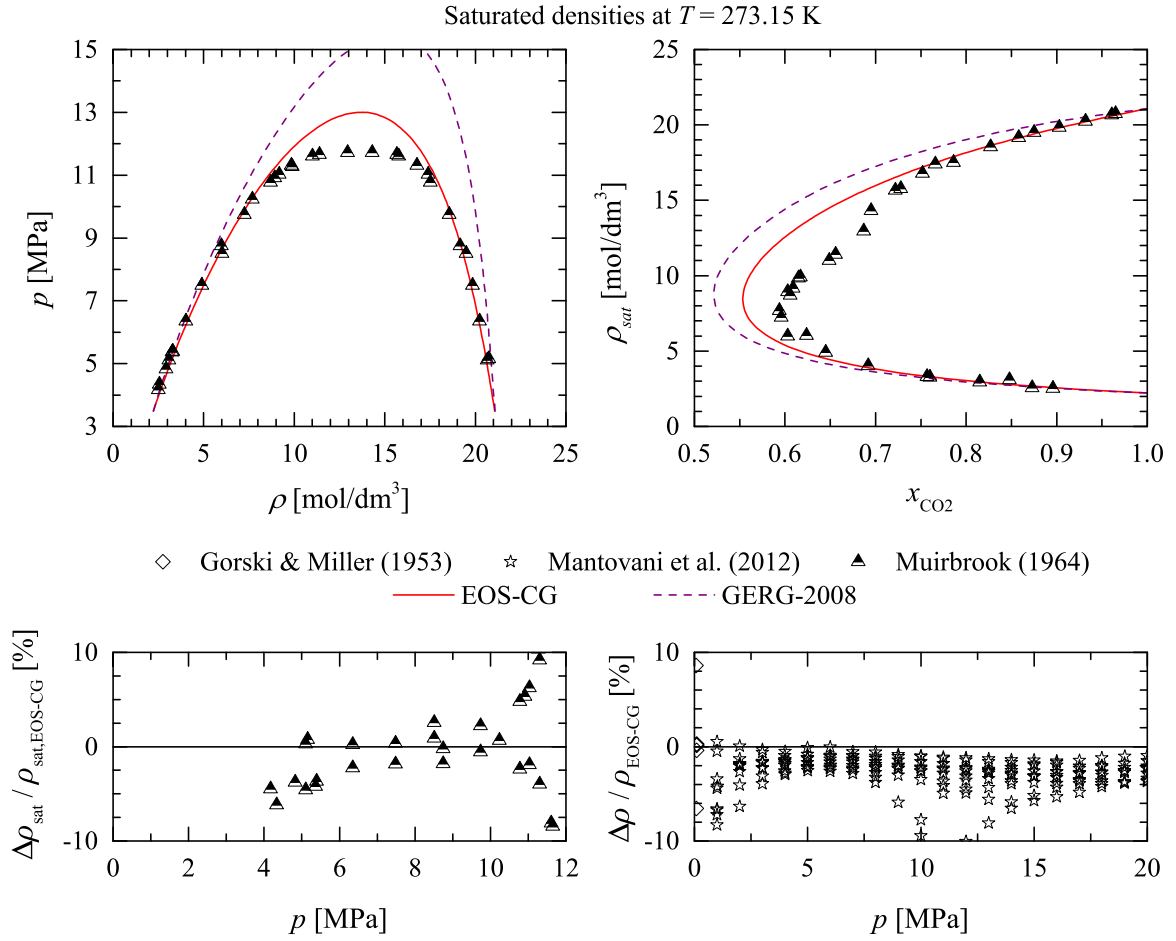


Figure A1.8: Densities of the saturated vapor and liquid and in the homogeneous phase for the system carbon dioxide + oxygen.

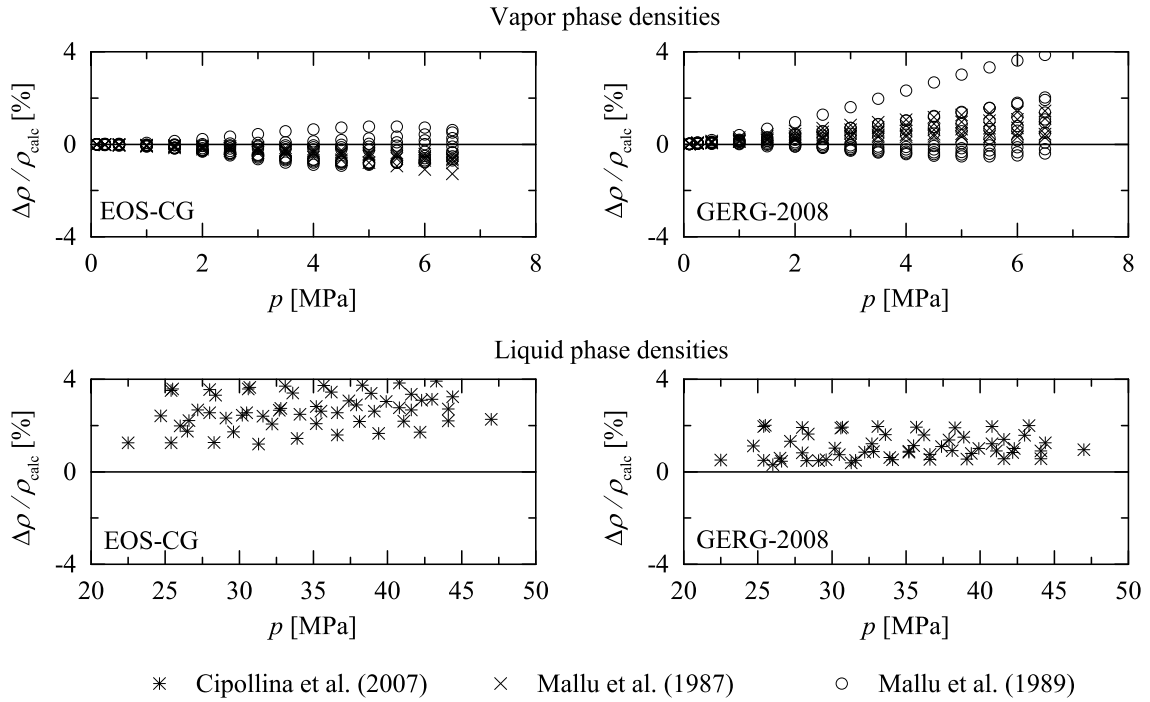


Figure A1.9: Deviations between the available experimental $p\rho T$ data and the new mixture model (left) and the GERG-2008 (right) for the system carbon dioxide + carbon monoxide.

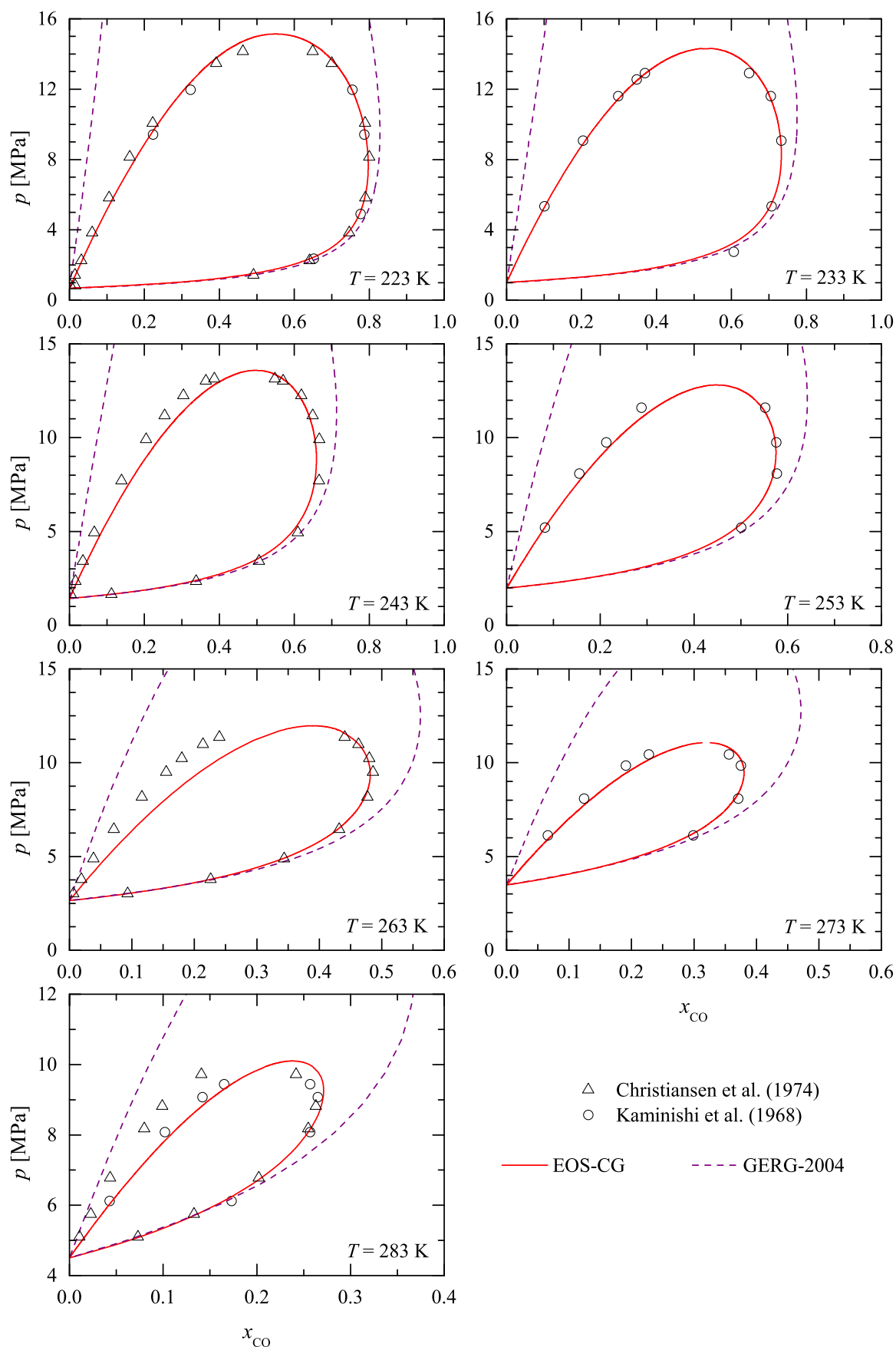


Figure A1.10: Experimental data and calculated values from the new mixture model and the GERG-2008 for the isothermal phase boundaries of the system carbon dioxide + carbon monoxide.

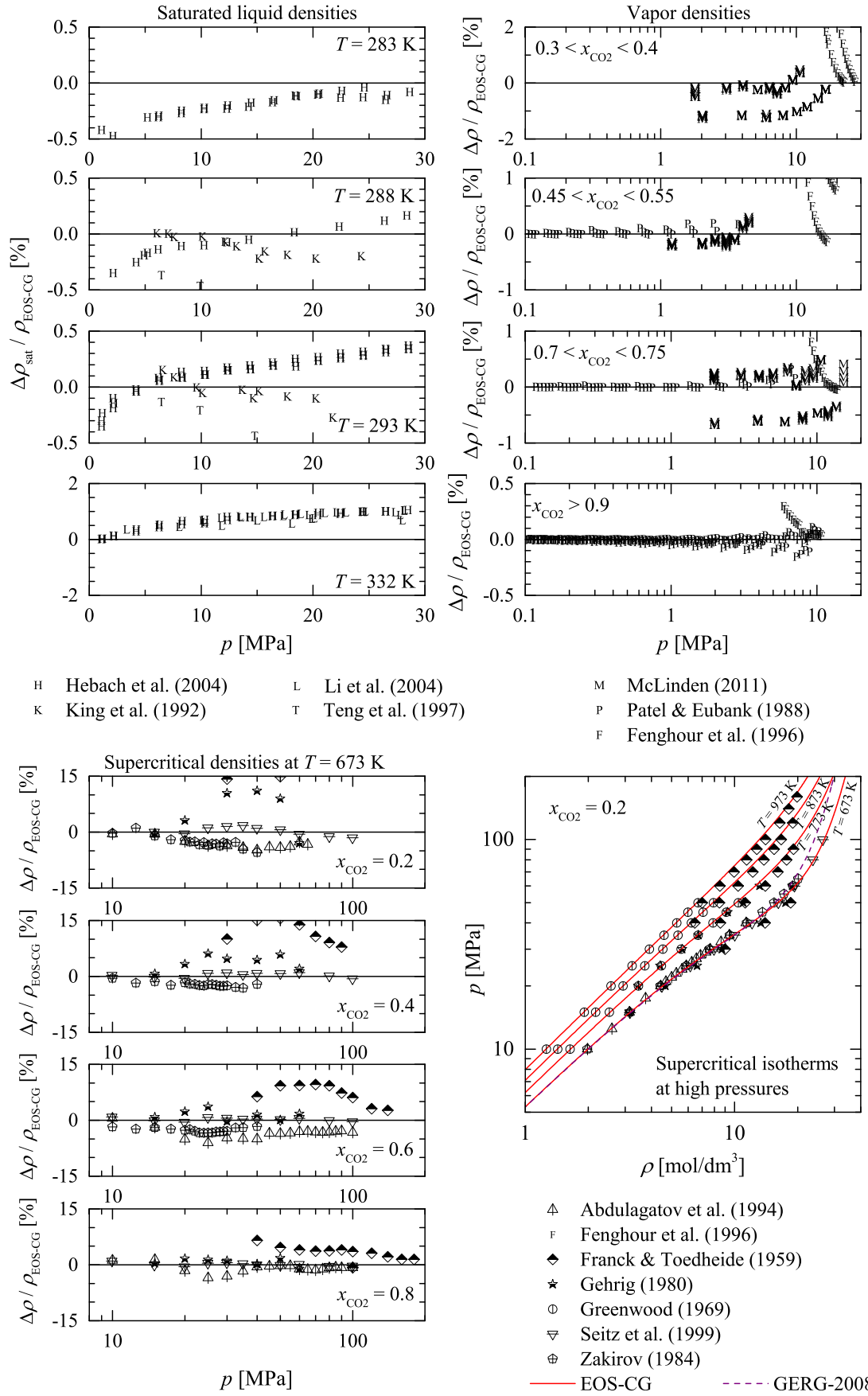


Figure A1.11: Deviations between selected experimental $p\rho T$ data and the new mixture model in the vapor, saturated liquid and supercritical phase. Bottom right: Pressure over density along isotherms in the supercritical state. Experimental data and models.

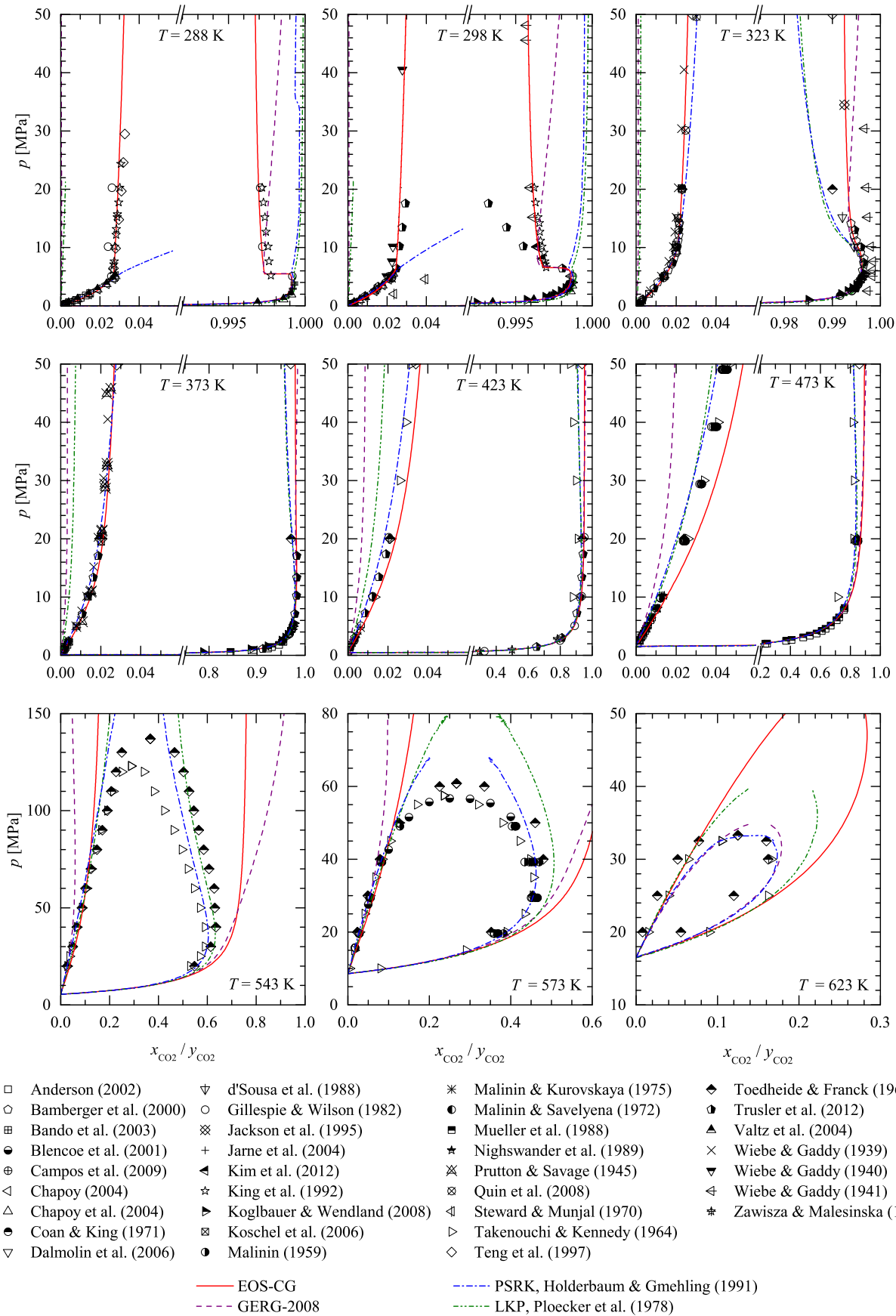


Figure A1.12: Experimental data and calculated values from the EOS-CG and other mixture models for the isothermal phase boundaries of the system water + carbon dioxide.

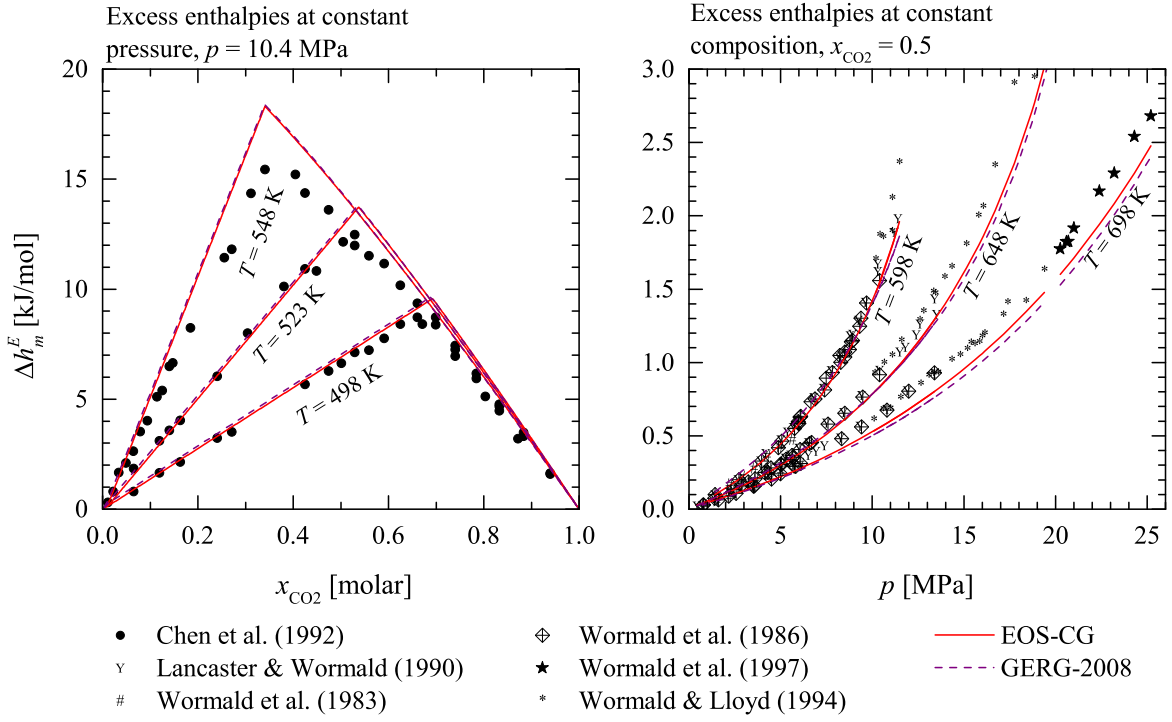


Figure A1.13: Experimental and calculated excess enthalpy values at constant pressure (left) and constant composition (right) for the system water + carbon dioxide.

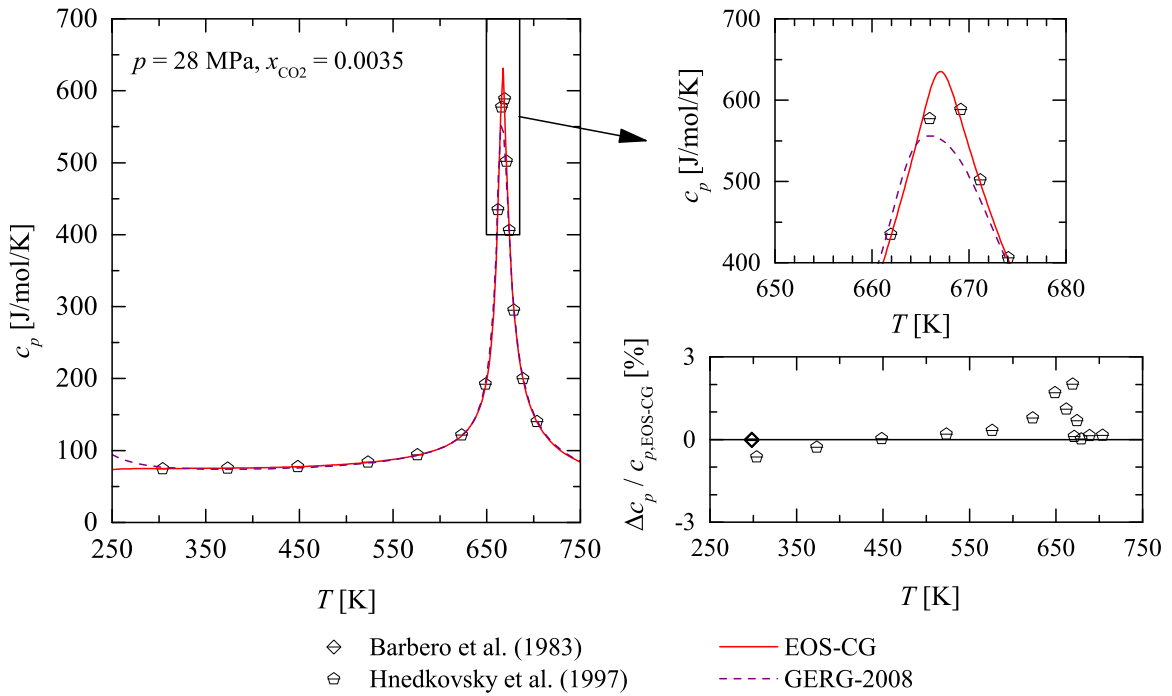


Figure A1.14: Experimental and calculated isobaric heat capacities and heat capacity deviations for the system water + carbon dioxide.

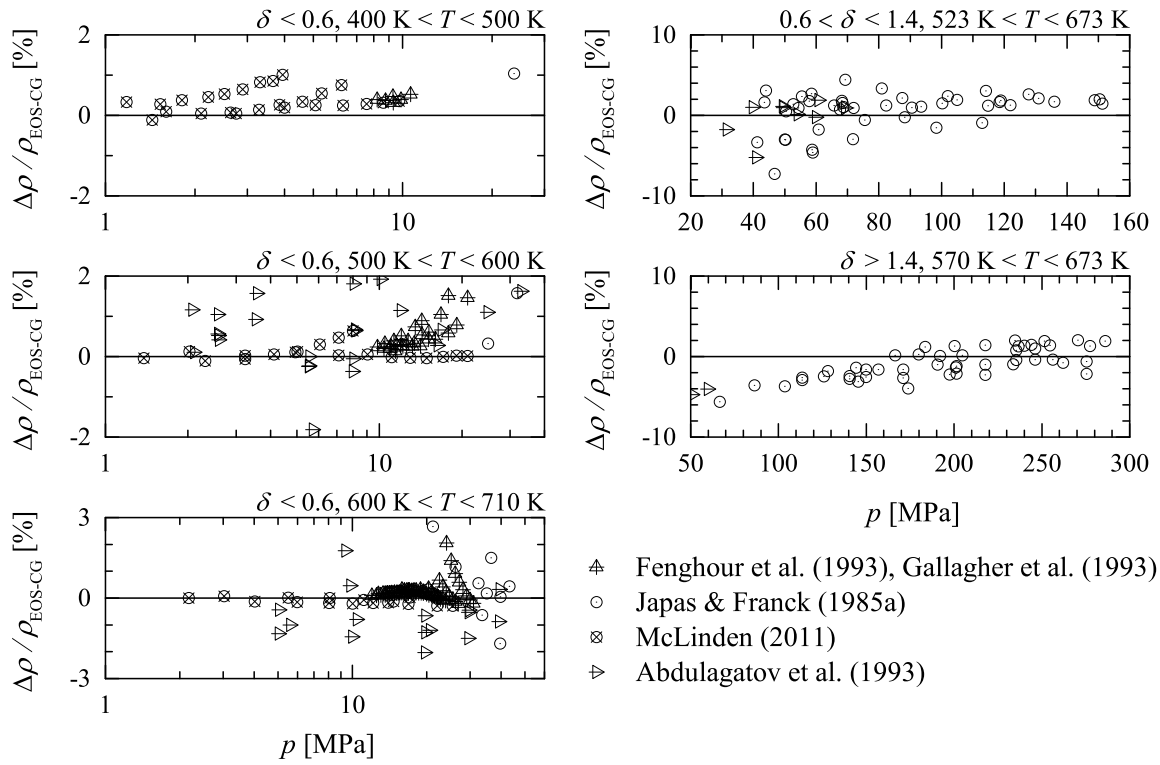


Figure A1.15: Deviations between experimental $p\rho T$ data and the new mixture model in the vapor, liquid-like, and supercritical phase for the system water + nitrogen.

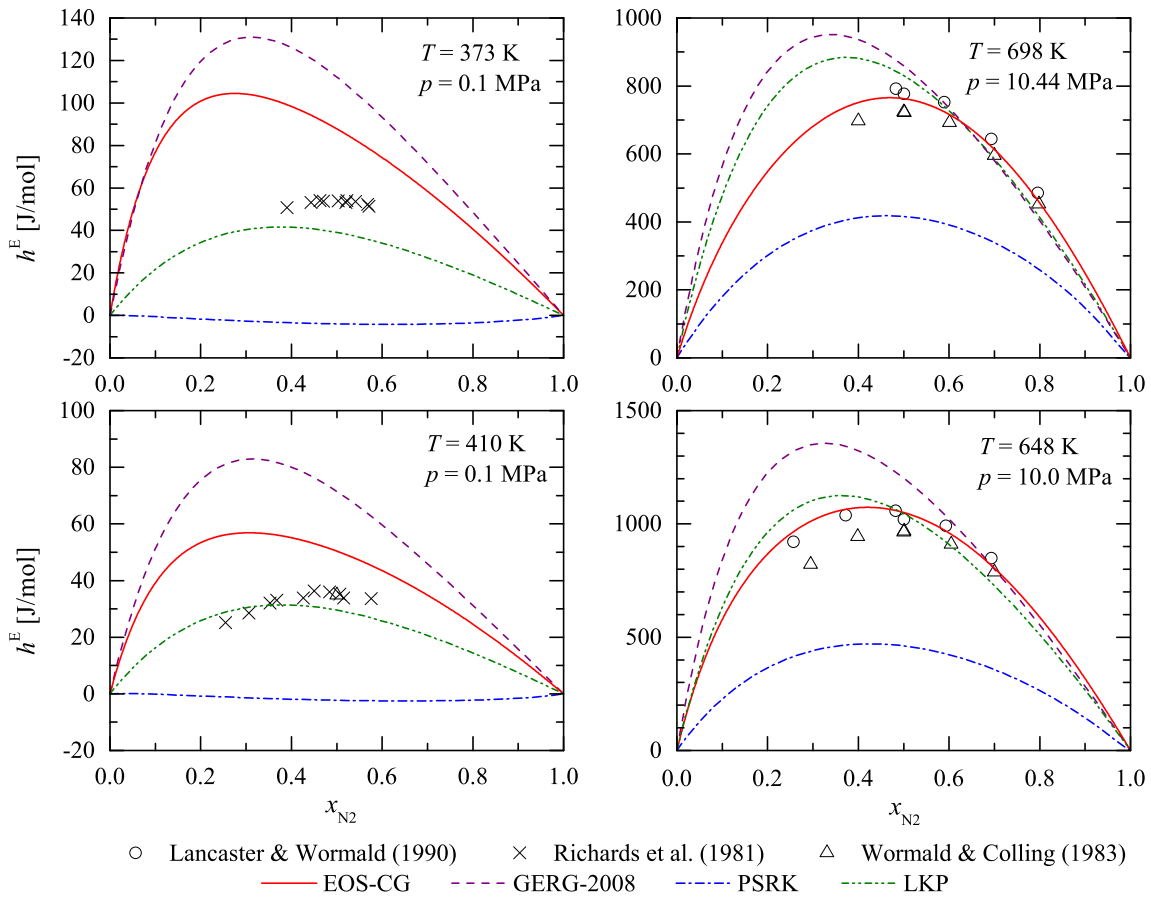


Figure A1.16: Experimental and calculated excess enthalpy values for the system water + nitrogen.

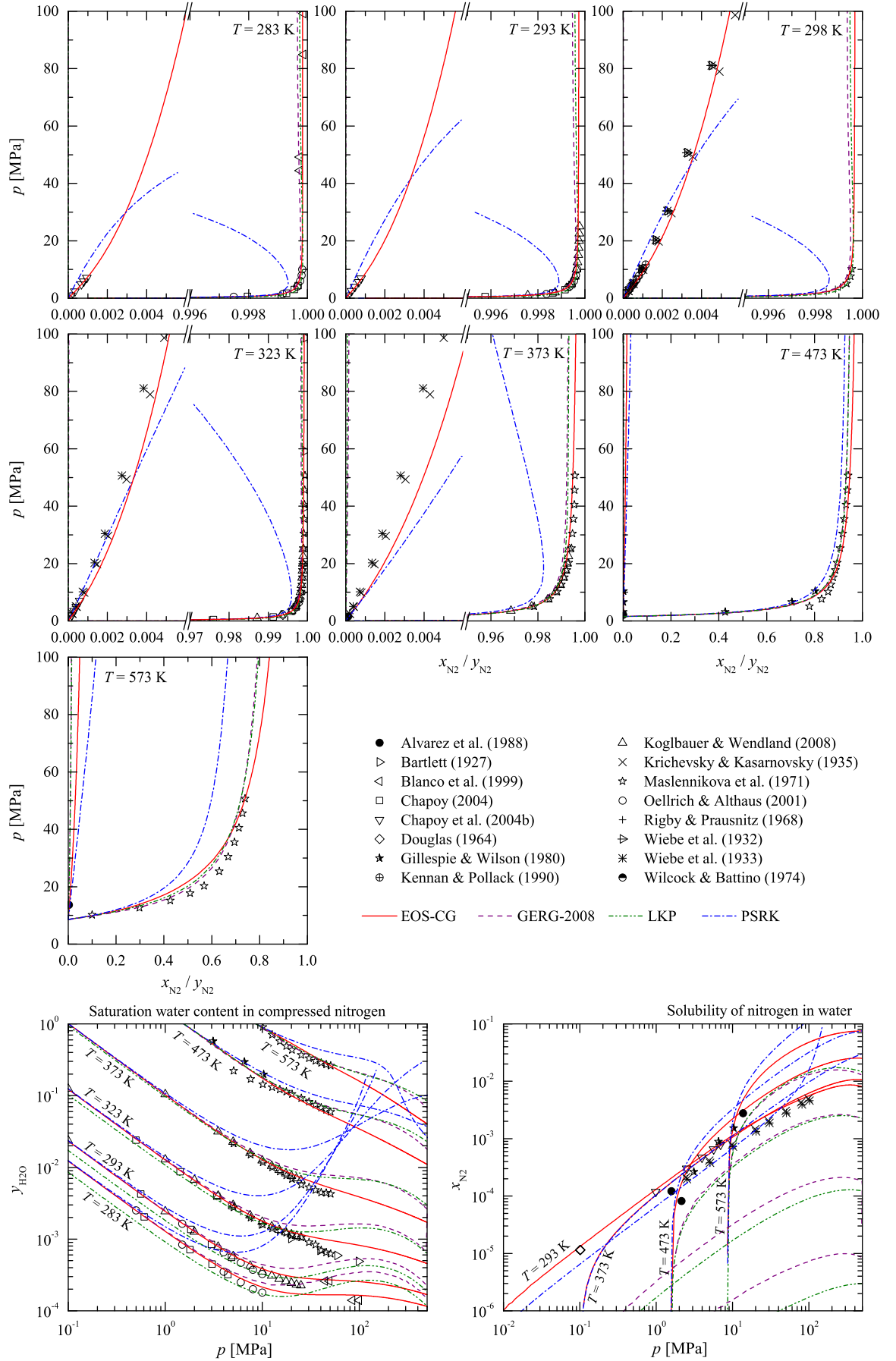


Figure A1.17: Experimental data and calculated values from the EOS-CG and other mixture models for the isothermal phase boundaries of the system water + nitrogen.

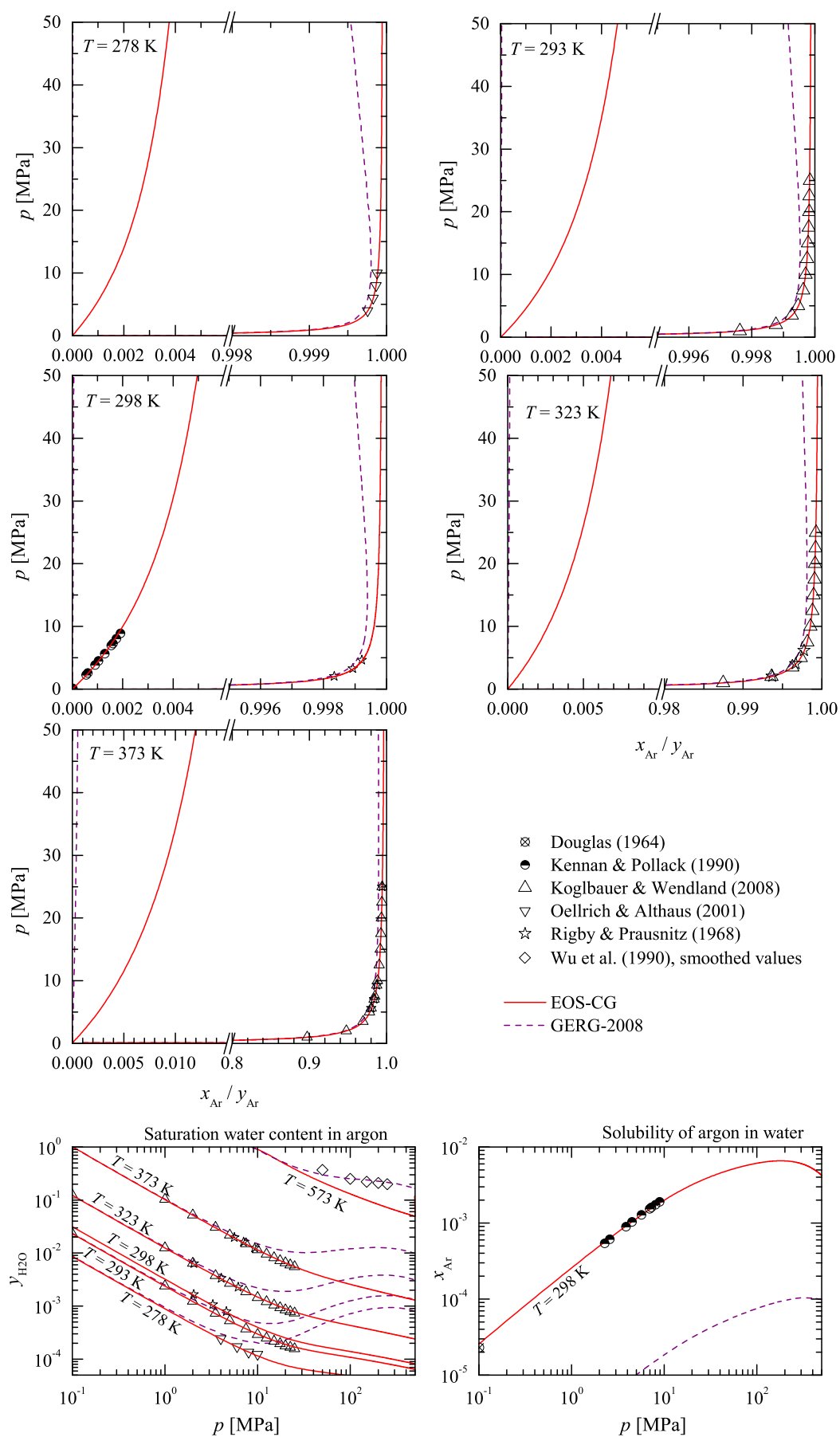


Figure A1.18: Experimental data and calculated values from the EOS-CG and other mixture models for the isothermal phase boundaries of the system water + argon.

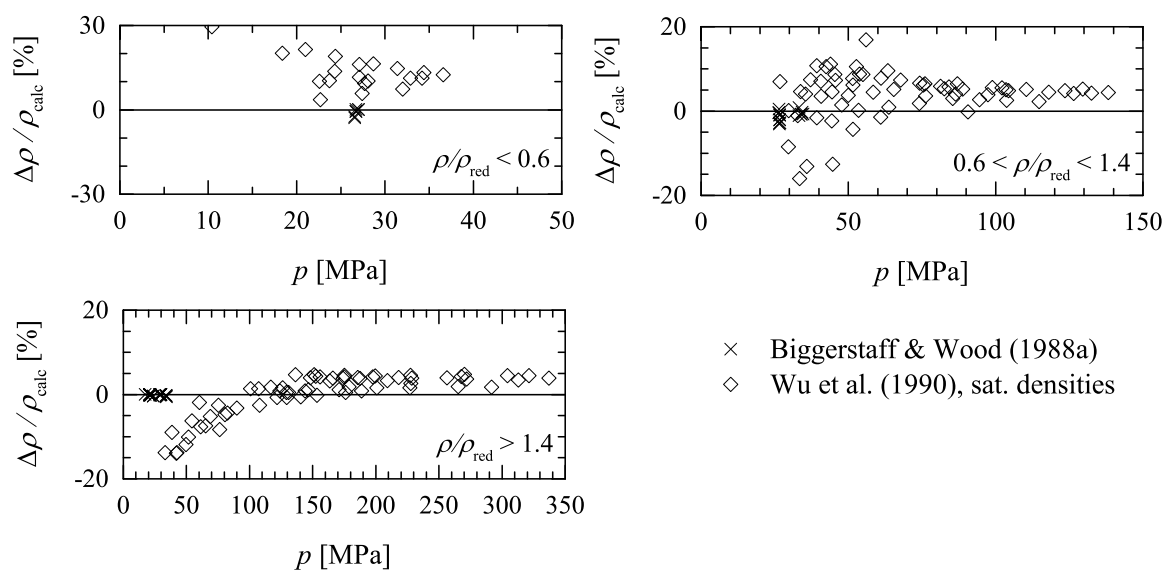


Figure A1.19: Deviations between experimental ppT data on the phase boundary and the new mixture model for the system water + argon.

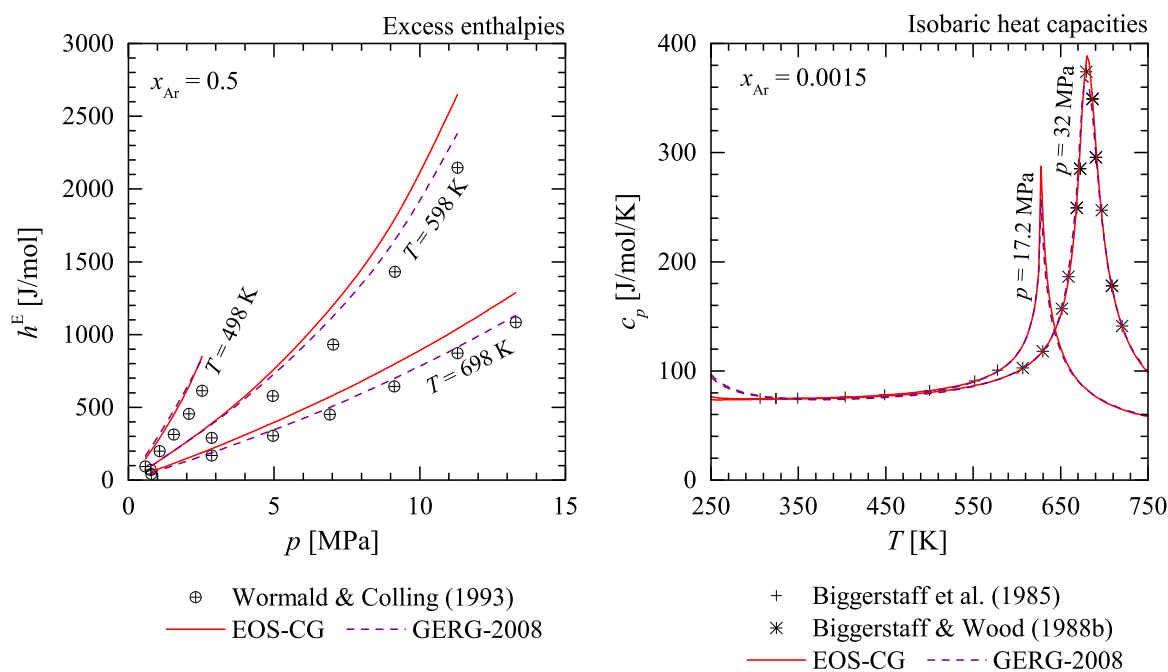


Figure A1.20: Experimental and calculated values for the system water + argon. Left: Excess enthalpies at equimolar composition and different isotherms. Right: Isobaric heat capacities of the water-rich phase at different isobars.

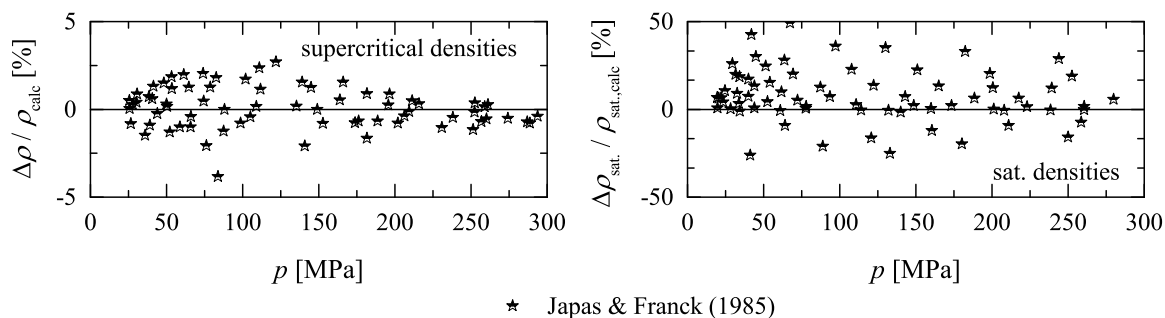


Figure A1.21: Deviations between experimental ppT data and the new mixture model in the supercritical phase and on the phase boundary for the system water + oxygen.

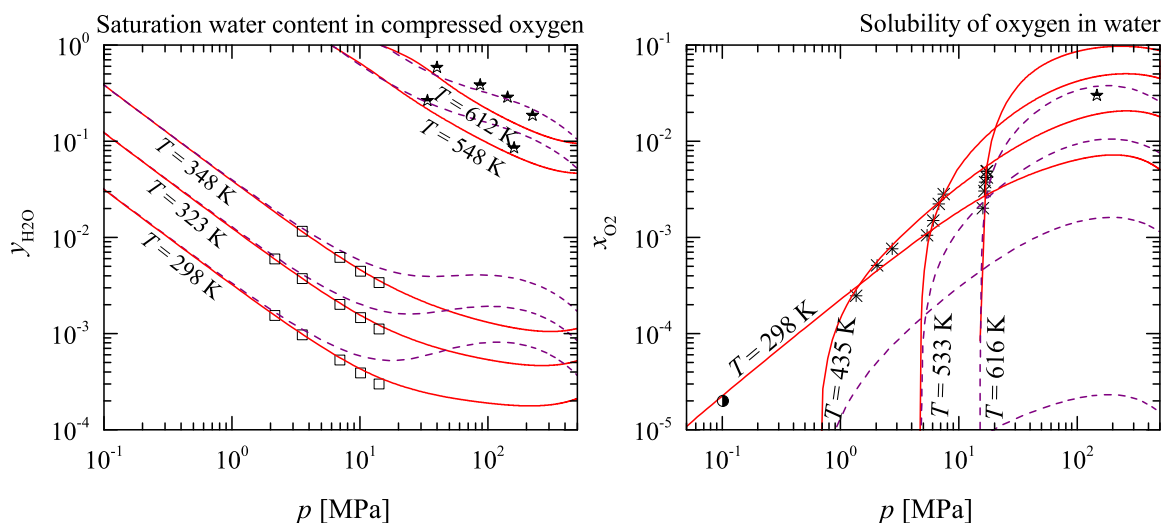


Figure A1.22: Experimental and calculated values of the saturation water content and oxygen solubility at several isotherms for the system water + oxygen.

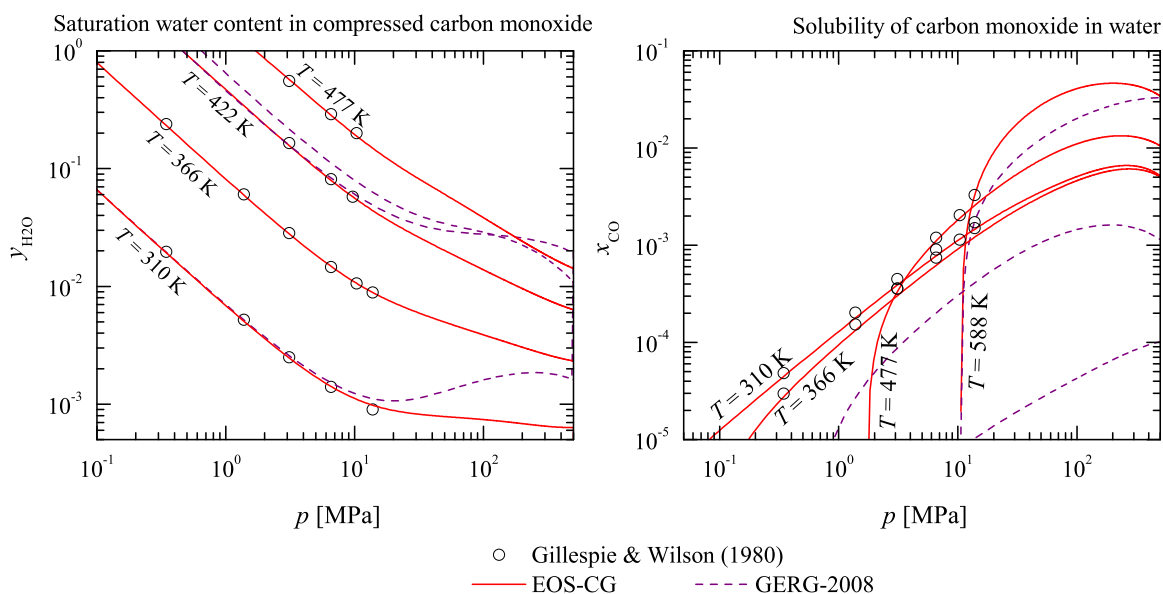


Figure A1.23: Experimental and calculated values of the saturation water content and CO solubility at several isotherms for the system water + carbon monoxide.

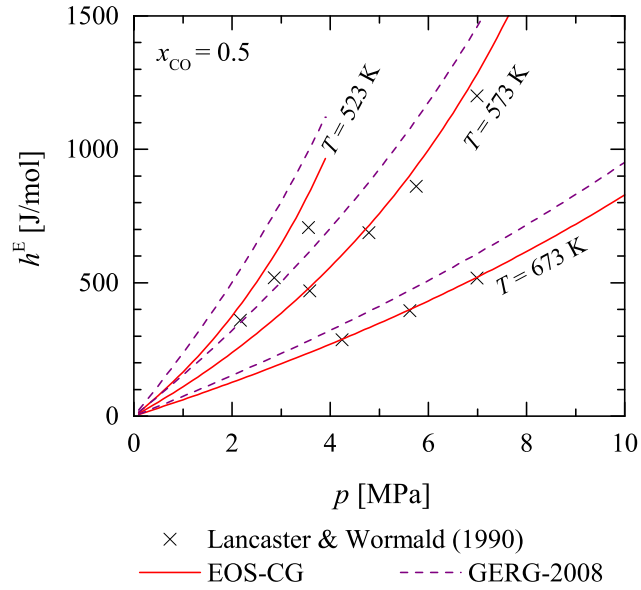


Figure A1.24: Experimental and calculated excess enthalpy values at $x_{CO} = 0.5$ and several isotherms for the system water + carbon monoxide.

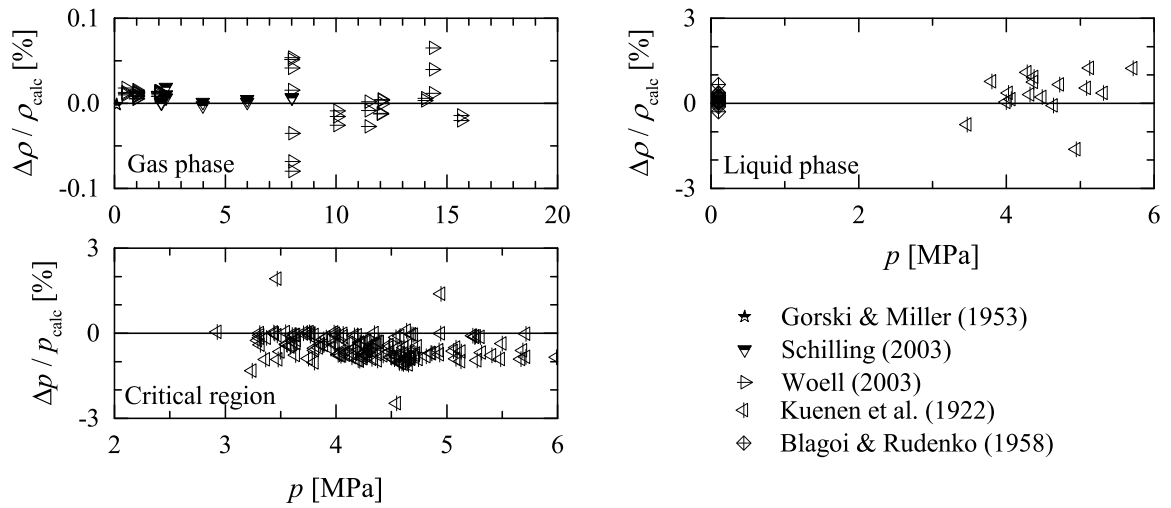


Figure A1.25: Deviations between experimental $p\rho T$ data and the new mixture model in the gas, supercritical, and liquid phase for the system nitrogen + oxygen.

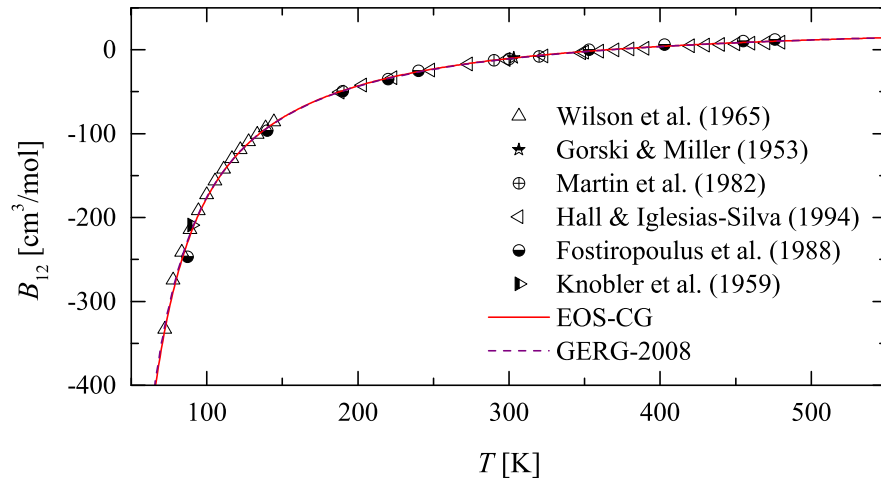


Figure A1.26: Experimental and calculated B_{12} values for the system nitrogen + oxygen.

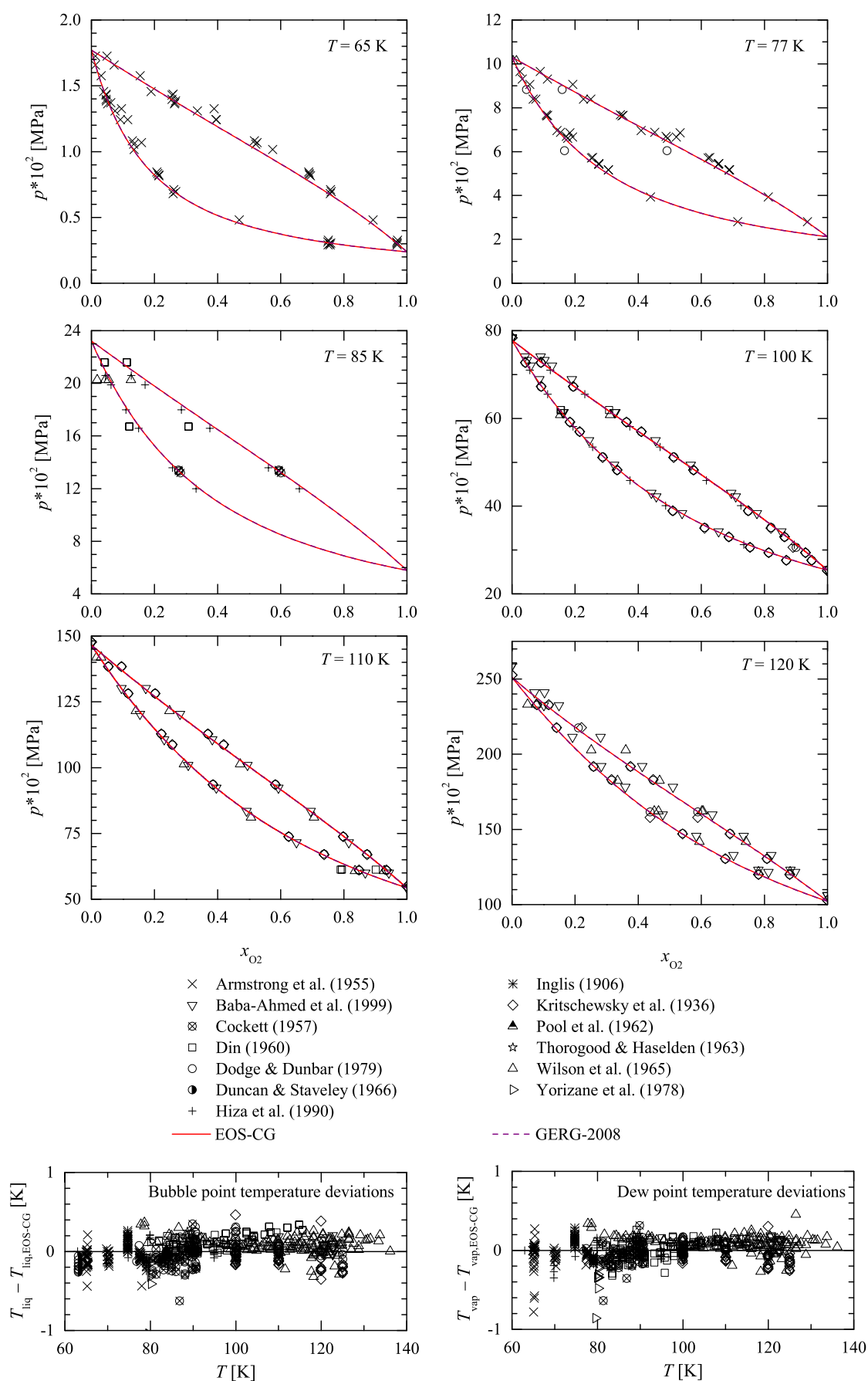


Figure A1.27: Top: Experimental data and calculated for the isothermal phase boundaries of the system nitrogen + oxygen. Bottom: Bubble and dew point temperature deviations.

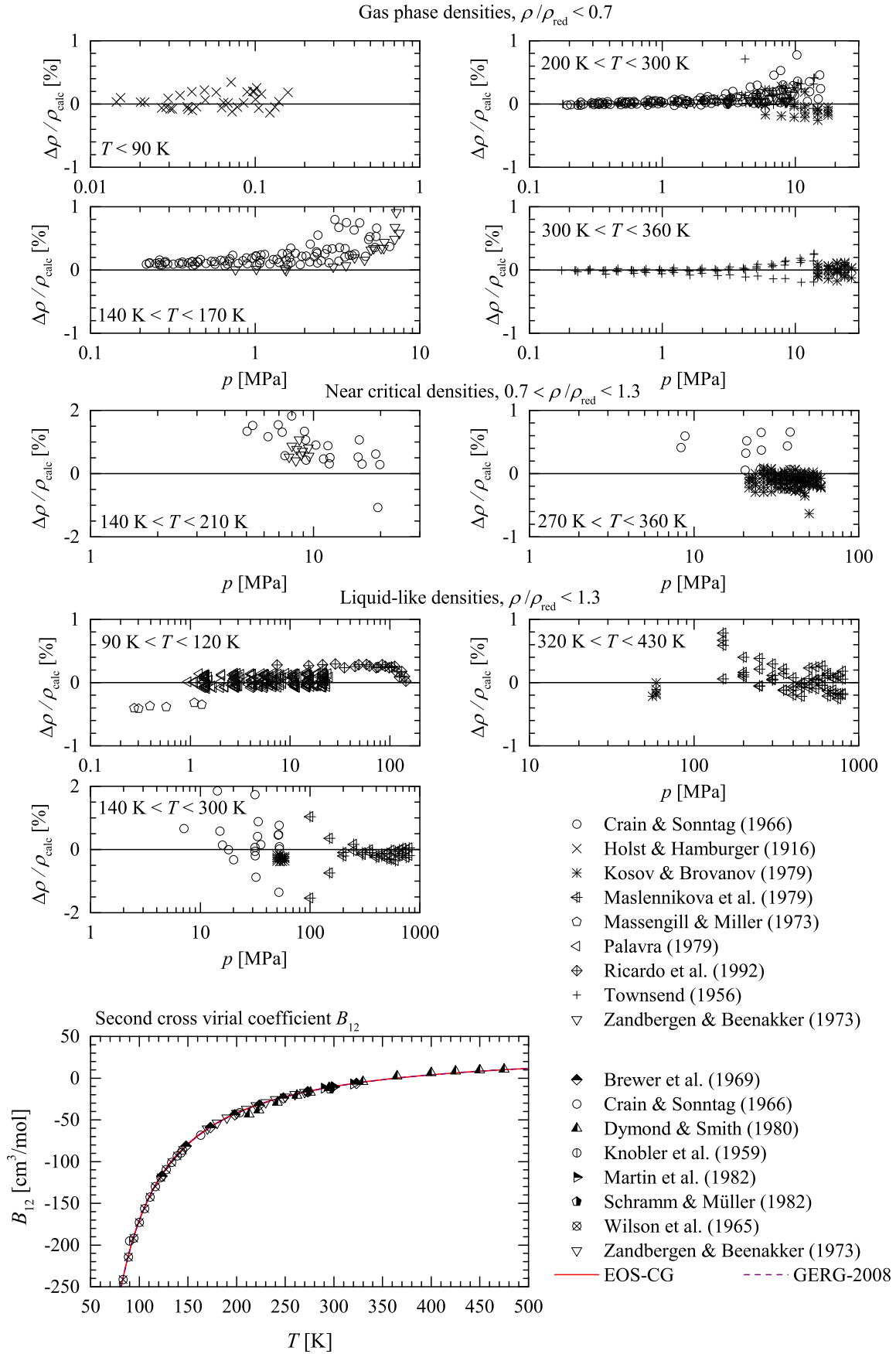


Figure A1.28: Top: Deviations between experimental $p\rho T$ data and the new mixture model in the gas, supercritical, and liquid phase. Bottom: Experimental and calculated B_{12} values for the system nitrogen + argon.

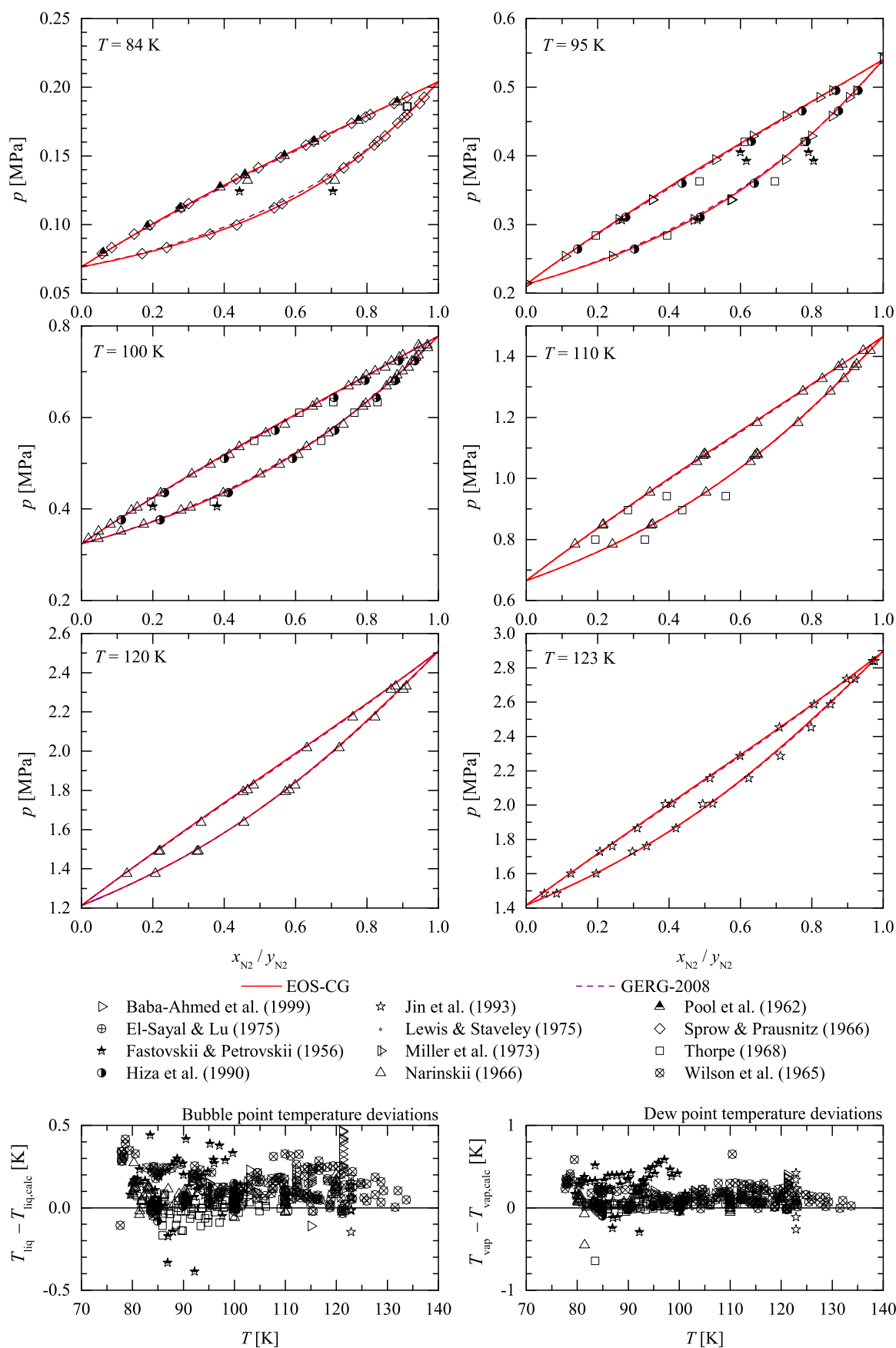


Figure A1.29: Top: Experimental data and calculated for the isothermal phase boundaries of the system nitrogen + argon. Bottom: Bubble and dew point temperature deviations.

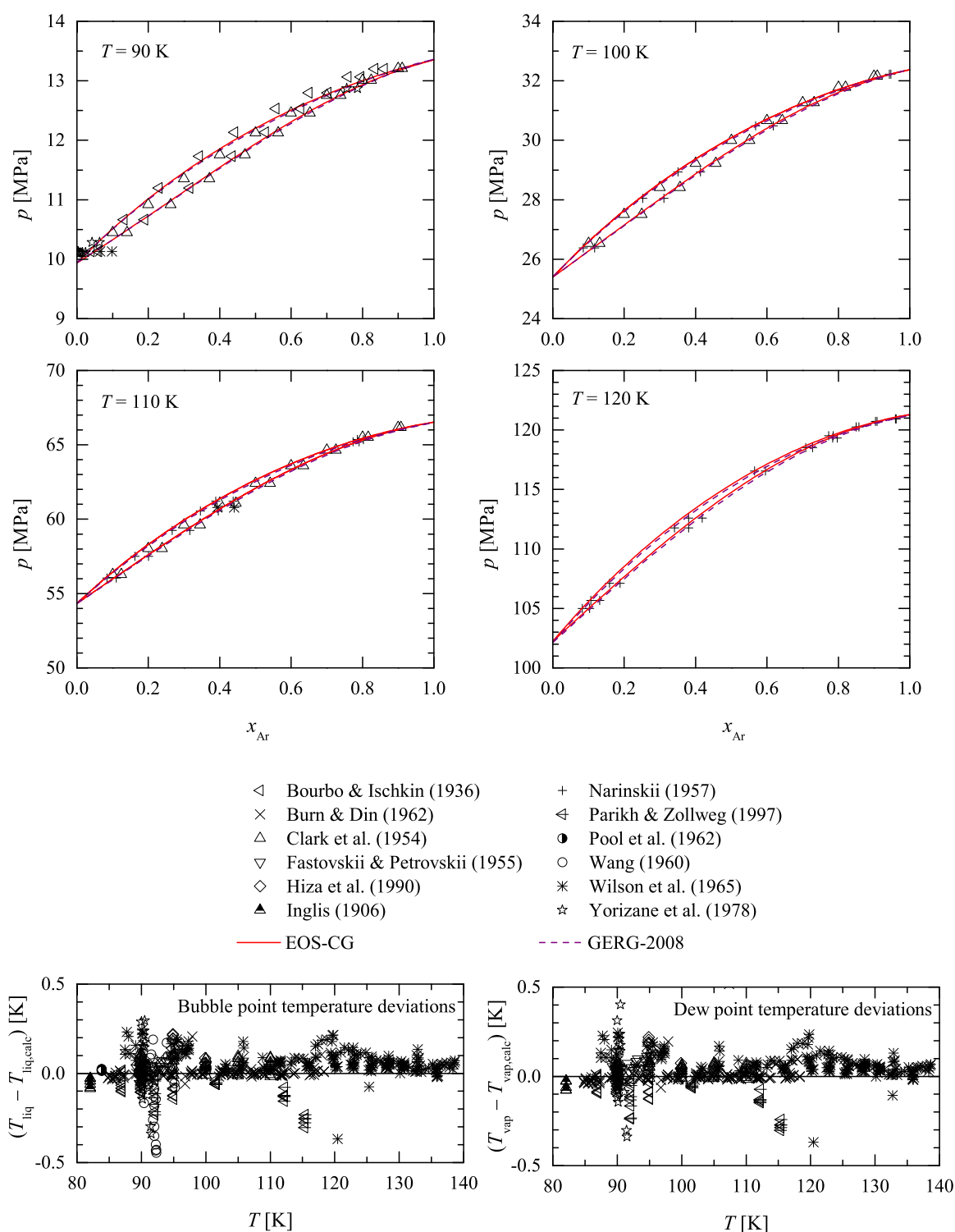


Figure A1.30: Top: Experimental data and calculated for the isothermal phase boundaries of the system oxygen + argon. Bottom: Bubble and dew point temperature deviations.

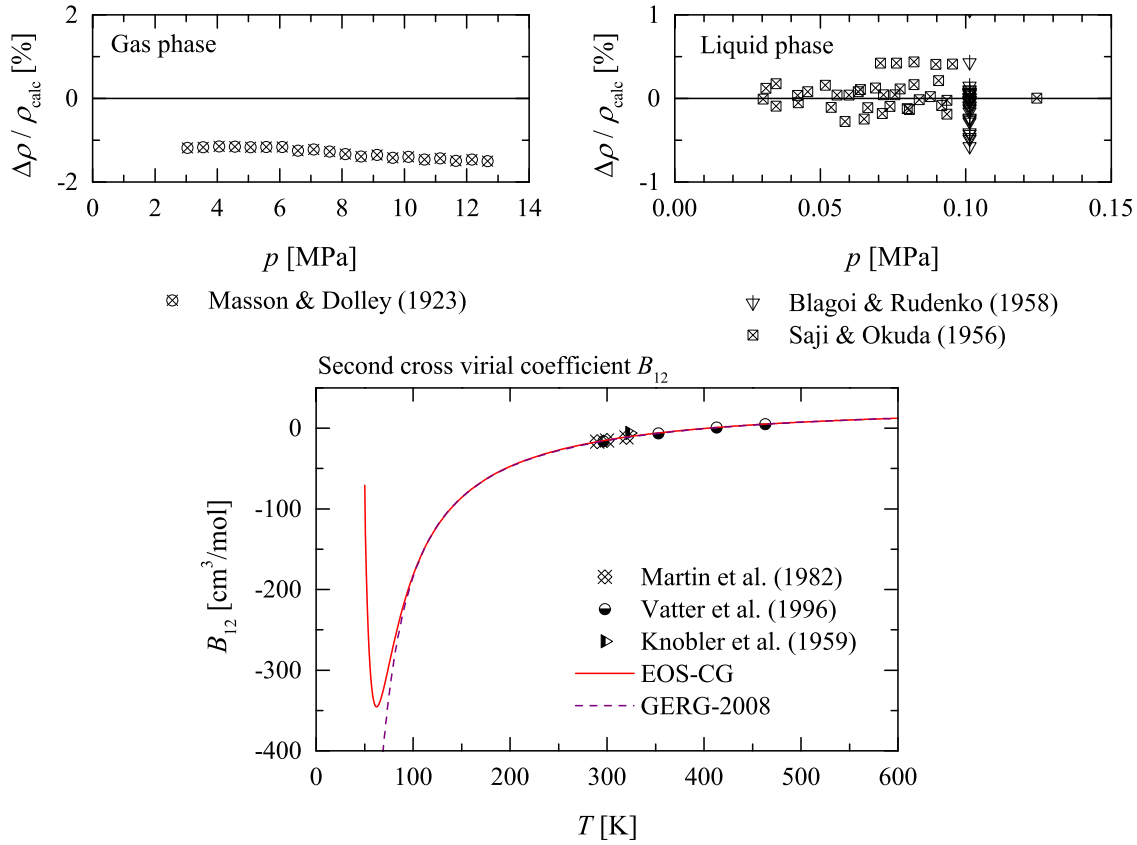


Figure A1.31: Top: Deviations between experimental ppT data and the new mixture model in the supercritical gas and liquid phase. Bottom: Experimental and calculated second cross virial coefficient (B_{12}) values for the system oxygen + argon

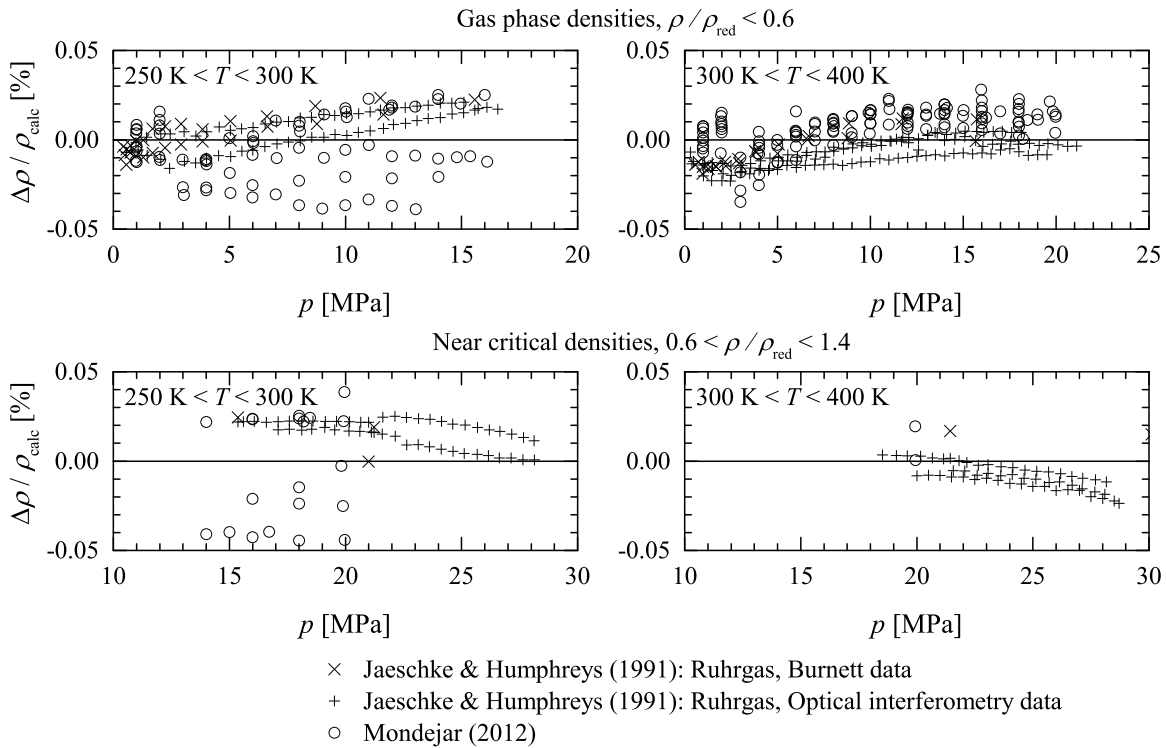


Figure A1.32: Deviations between experimental ppT data and the new mixture model in the supercritical gas phase up to near-critical densities for the system nitrogen + carbon monoxide.

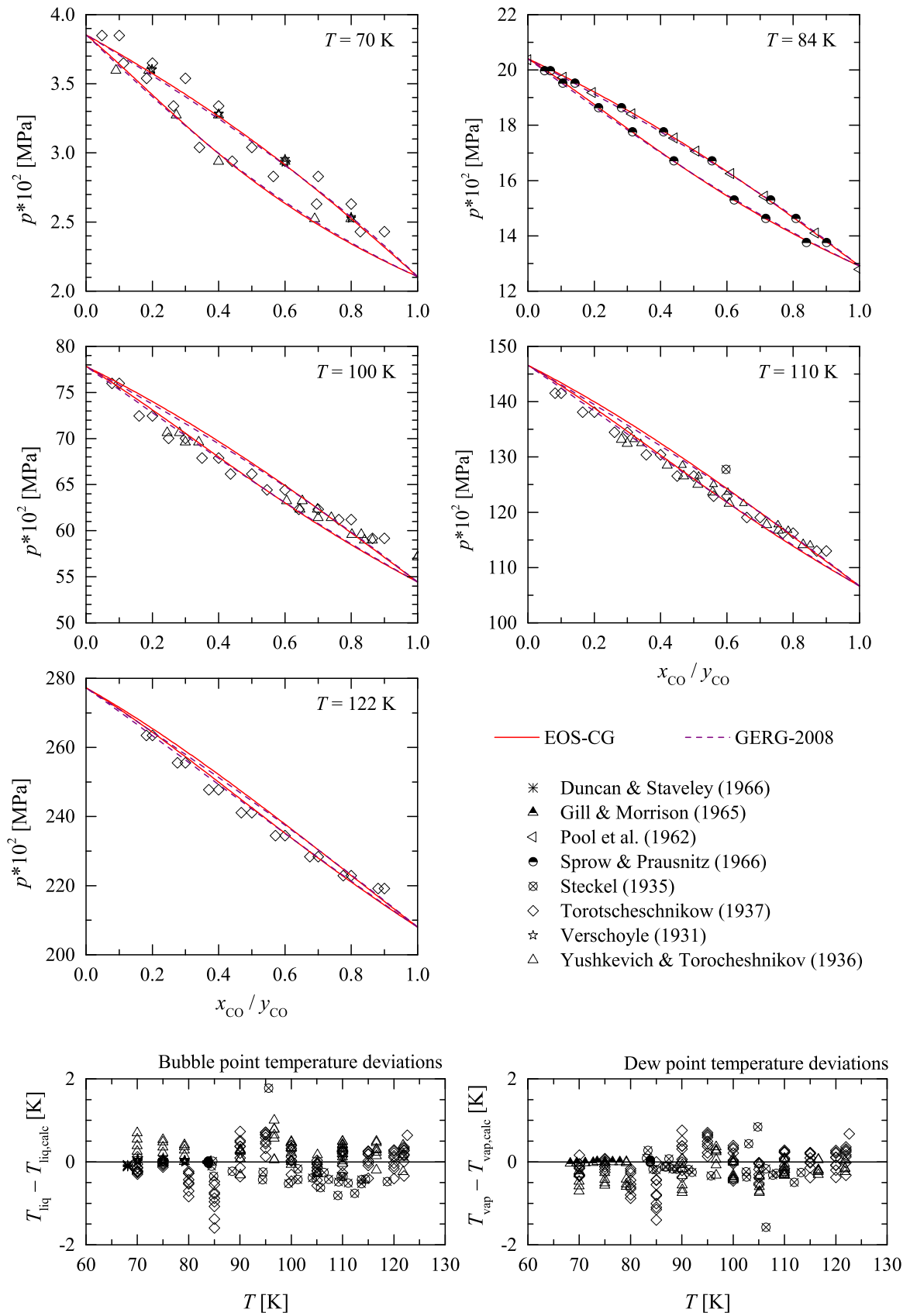


Figure A1.33: Top: Experimental data and calculated values for the isothermal phase boundaries of the system nitrogen + carbon monoxide. Bottom: Bubble and dew point temperature deviations.

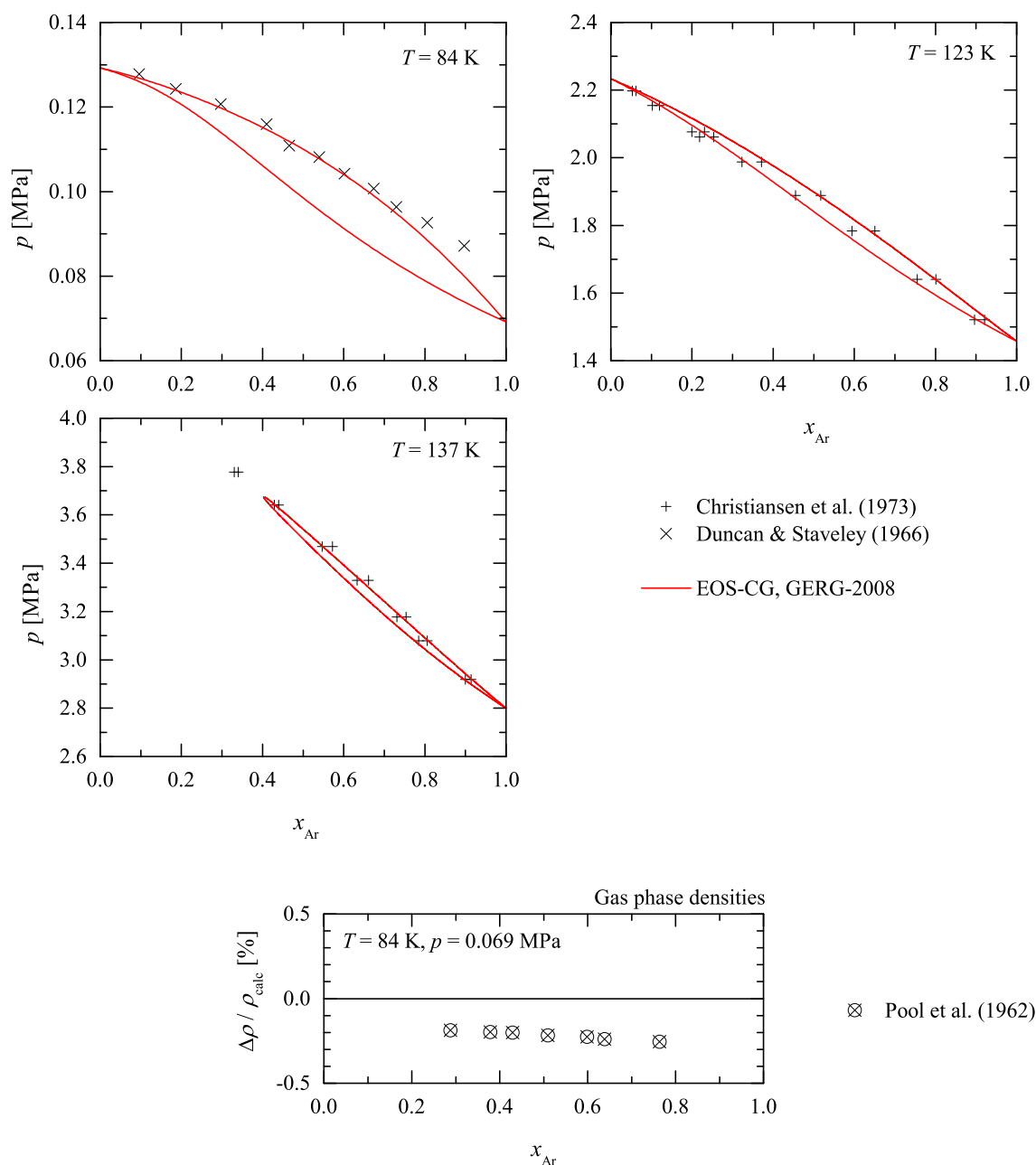


Figure A1.34: Top: Experimental data and calculated for the isothermal phase boundaries of the system argon + carbon monoxide. Bottom: Deviations between experimental $p\rho T$ data in the gas phase and the new mixture model.

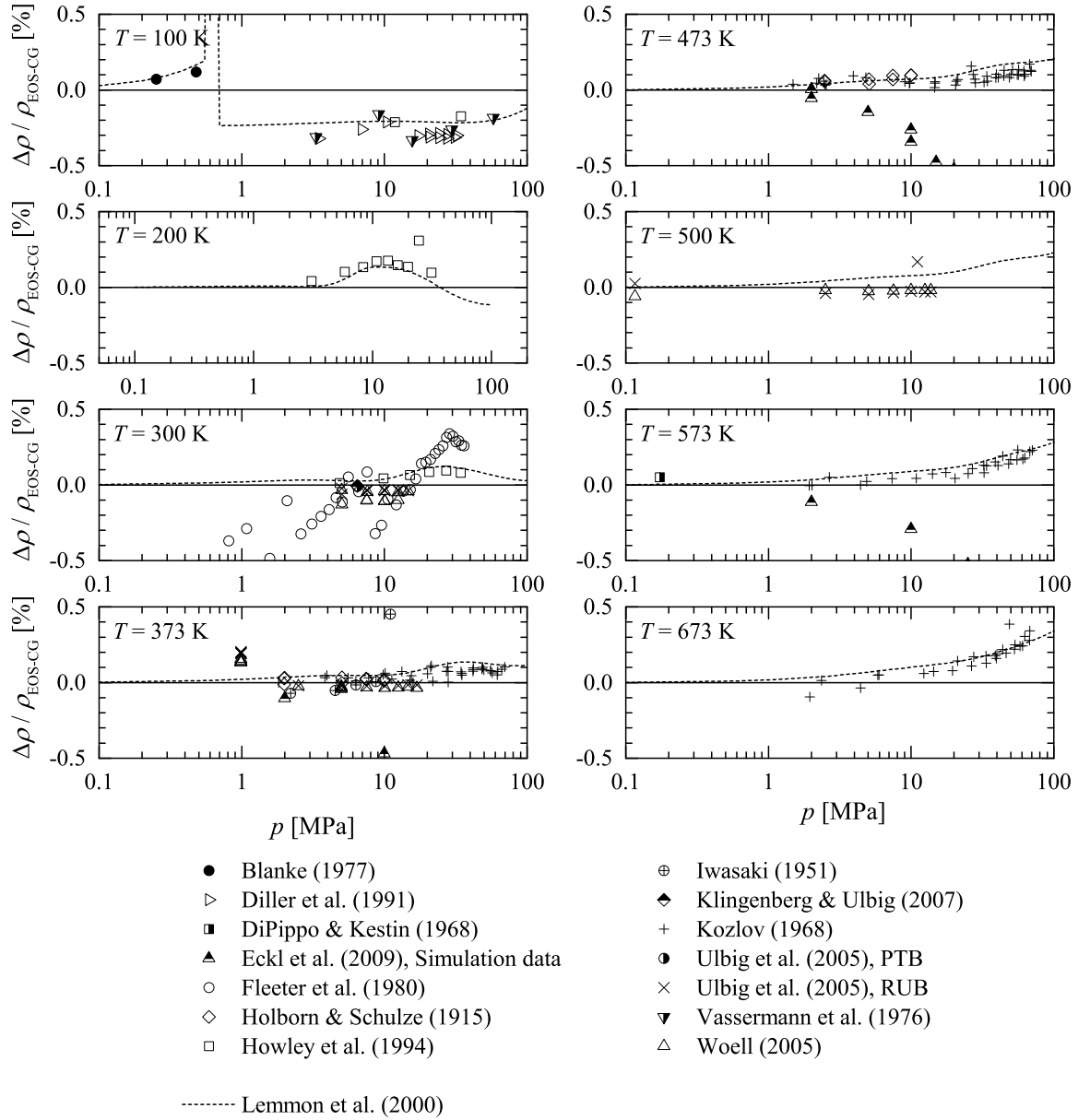


Figure A1.35: Density deviations for air at different isotherms between experimental data, the model by Lemmon *et al.* (2000), and the new mixture model.

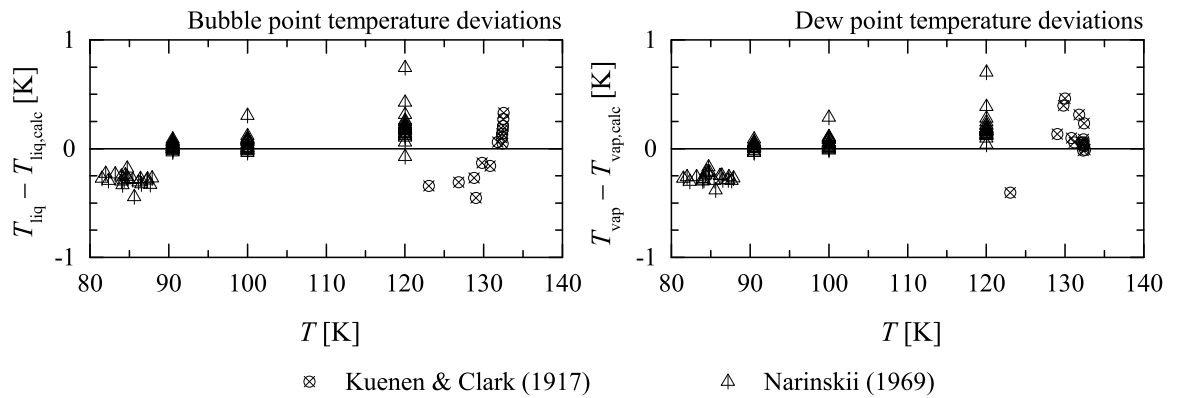


Figure A1.36: Bubble and dew point temperature deviations for air.

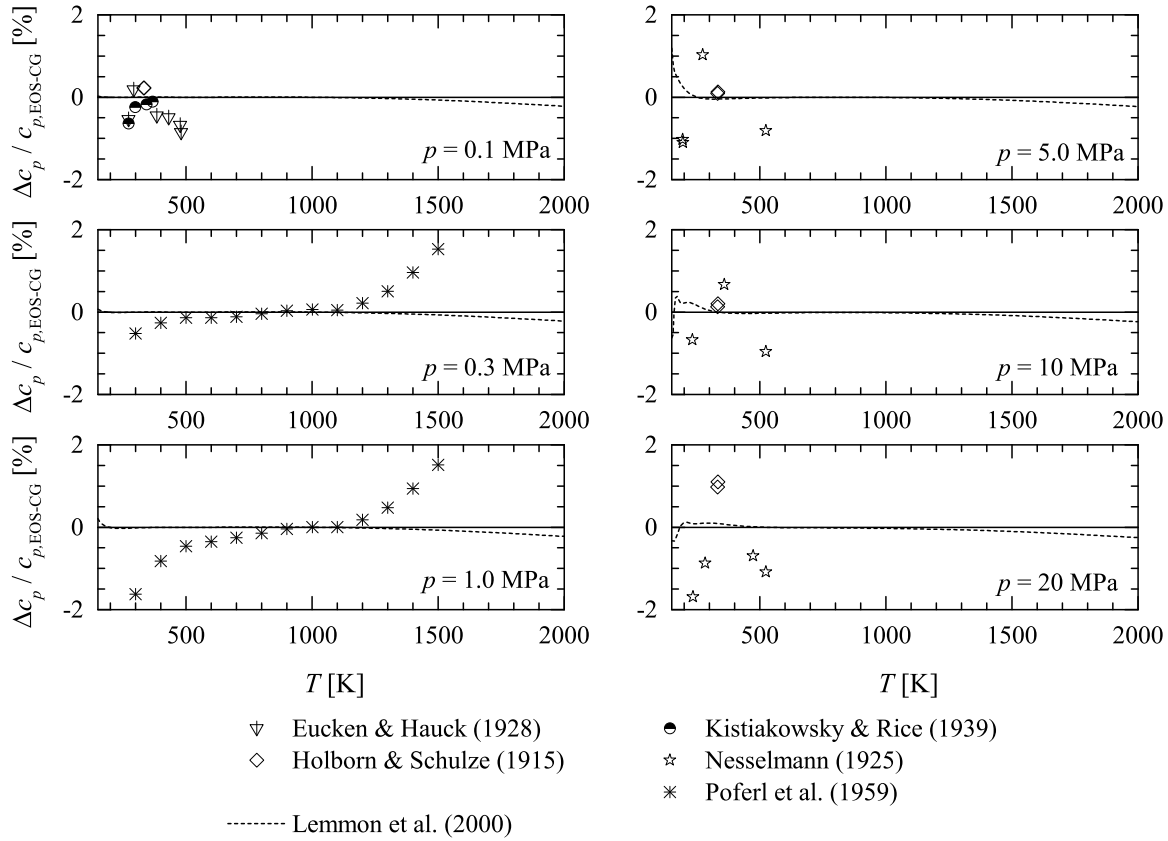


Figure A1.37: Deviations between experimental isobaric heat capacity data, the model by Lemmon *et al.* (2000) and values calculated from the new mixture model at different isobars for air.

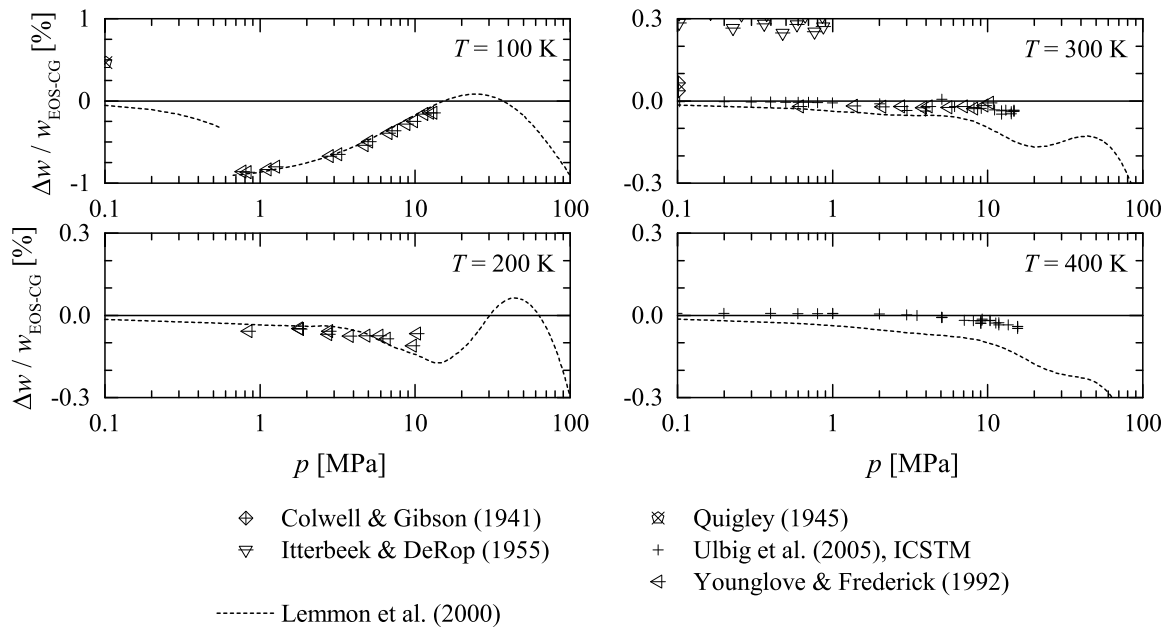


Figure A1.38: Deviations between experimental speed of sound data, the model by Lemmon *et al.* (2000) and values calculated from the new mixture model at different isotherms for air.

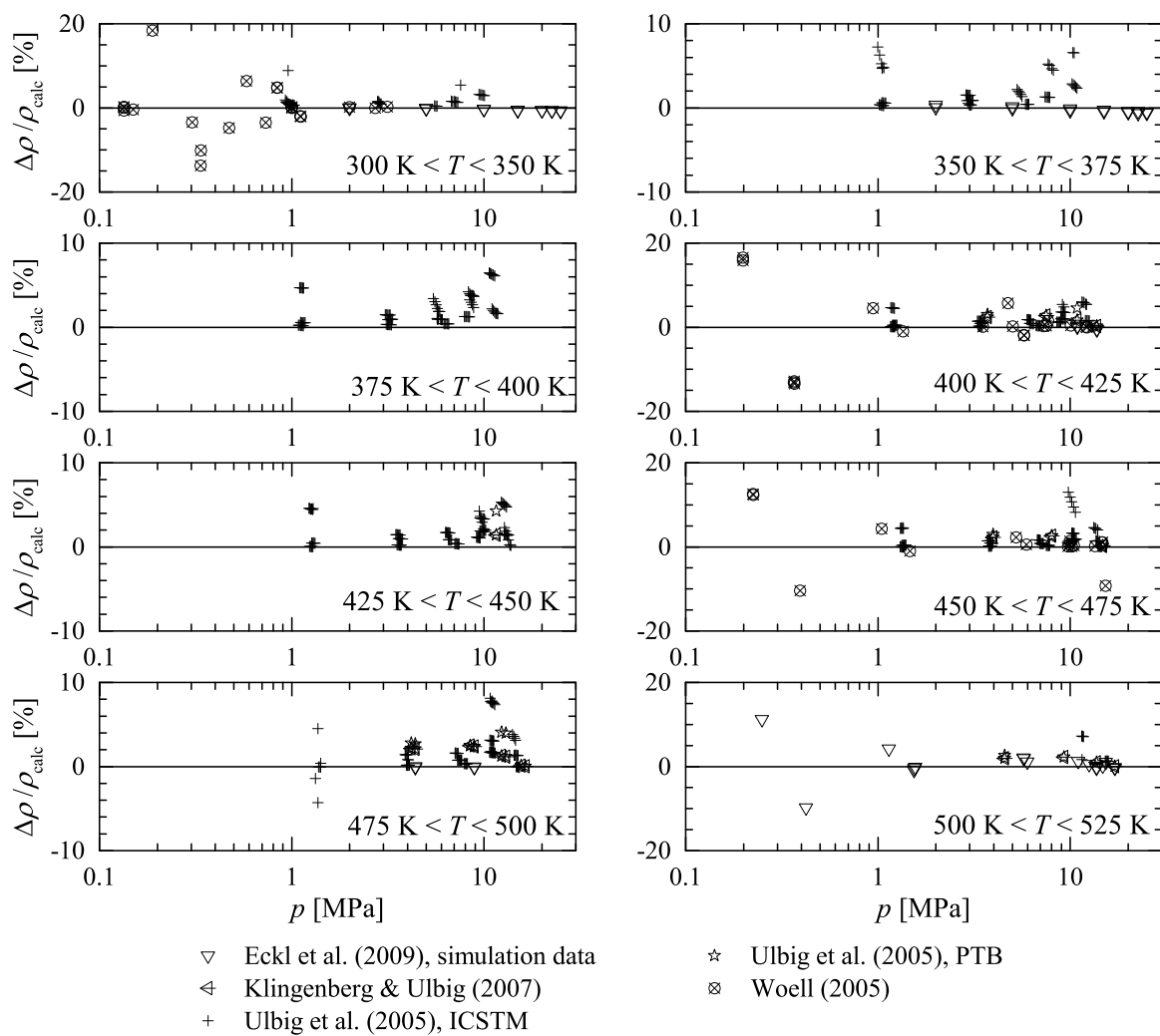


Figure A1.39: Deviations between experimental $p\rho T$ data and the new mixture model in the gas phase for humid air.

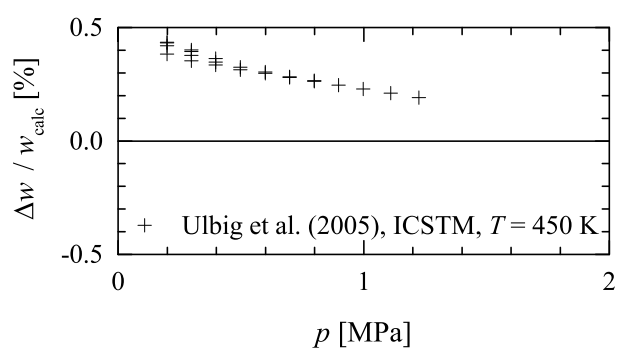


Figure A1.40: Deviations between experimental speed of sound data and the new mixture model for humid air.

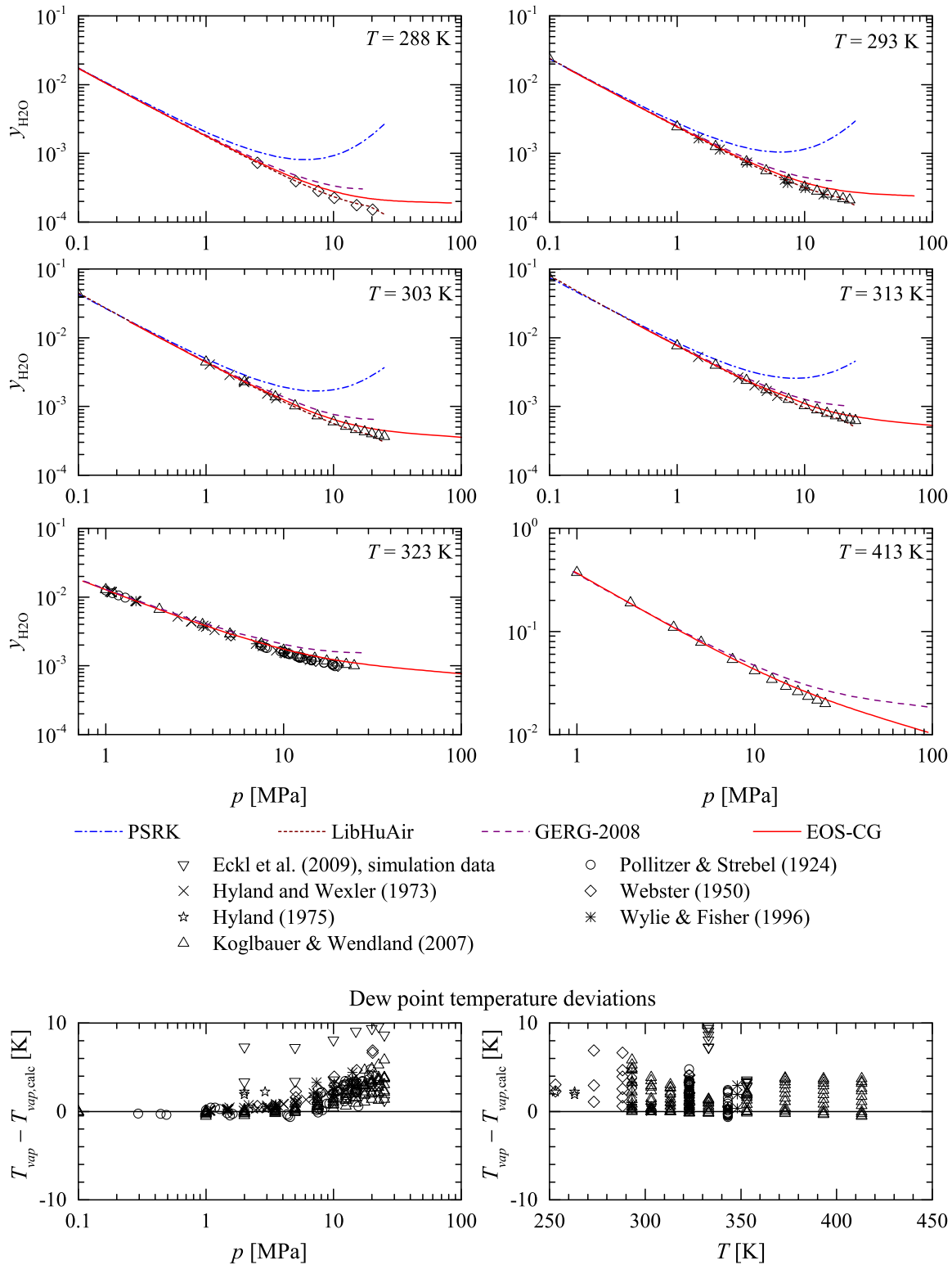


Figure A1.41: Top: Experimental and calculated values using different models of the saturated water content in humid air at different isotherms. Bottom: Dew point temperature deviations calculated with the new EOS-CG model.

A2 NUMERICAL REPRESENTATION OF EXPERIMENTAL DATA

In the following section a numerical, statistical representation of all experimental data collected for the development of the new mixture model is given. For each data set the number of points, temperature, pressure, and composition range are given, together with the *absolute average deviation* (AAD) between the data and the model. The AAD is calculated according to

$$\text{AAD} = \frac{1}{M} \sum_{m=1}^M |\Delta z_m|, \quad \text{A2.1}$$

Where M is the number of data points used for the calculation, and Δz_m is the relative or total deviation (depending on the property) between an experimental data point m and the model.

For VLE data the AAD is calculated either from the total deviations between experimental and calculated phase equilibrium compositions or the total deviations between experimental and calculated dew and bubble point temperatures, at given experimental pressure and phase composition. When experimental information on both phases in equilibrium is given, AAD values are calculated for both phases separately.

For $p\rho T$, speed of sound, heat capacity, Joule-Thomson, or excess enthalpy data the AAD is evaluated for three density regions separately, since often the accuracy of the mixture model is dependent on the density region. These regions are defined by the reduced density $\delta = \rho/\rho_r$, they read

$0 < \delta \leq 0.6$	typical gas phase densities, usually with the highest model accuracy,
$0.6 < \delta \leq 1.4$	extended critical region where the highest uncertainties have to be expected, both by experimental data and the model, and
$\delta > 1.4$	liquid or liquid-like supercritical region.

The AAD calculation includes all data points with the following exceptions: If the calculation of a data point failed, either due to numerical problems in the calculation software or because of the model (e.g. an experimental data point in a region where the model predicts a homogeneous state); if a data point is identified as an outlier (the deviation Δz_m is larger than ten times the AAD).

Table A2.1: Representation of experimental thermodynamic property data of binary mixtures by the EOS-CG mixture model.

xCO ₂ + (1 - x)H ₂ O										
Authors	N	N _y	N _x	N _{used}	T [K]	p [MPa]	y	x	AAD _y [%]	AAD _x [%]
VLE data										
Anderson (2002)	54	0	54	1	274 – 288	0.1 – 2.2		0.00 – 0.02		0.145
Bamberger <i>et al.</i> (2000)	29	29	29	14	323 – 353	4.0 – 14.1	0.99 – 1.00	0.01 – 0.02	0.060	0.023
Bando <i>et al.</i> (2003)	12	0	12	0	303 – 333	10.0 – 20.0		0.02 – 0.03		0.061
Bartholomé and Fritz (1956)	15	0	15	0	283 – 303	0.1 – 2.0		0.00		0.711
Blencoe <i>et al.</i> (2001)	8	0	8	0	573	27.6 – 56.7		0.05 – 0.40		11.667
Campos <i>et al.</i> (2009)	50	0	50	0	298 – 323	0.1 – 0.5		0		0.009
Chapoy (2004)	75	0	75	8	274 – 351	0.2 – 9.3		0.00 – 0.03		0.062
Chapoy <i>et al.</i> (2004a)	26	0	26	0	274 – 351	0.2 – 9.3		0.00 – 0.02		0.083
Coan and King (1971)	22	22	0	3	298 – 373	1.7 – 5.1	0.97 – 1.00		0.061	
Dalmolin <i>et al.</i> (2006)	49	0	49	0	288 – 323	0.1 – 0.5		0.00		0.041
Dhima <i>et al.</i> (1999)	7	0	7	0	344	10.0 – 100.0		0.02 – 0.03		0.126
D'Souza <i>et al.</i> (1988)	4	4	4	0	323 – 348	10.1 – 15.2	0.99	0.02	0.120	0.106
Gillespie and Wilson (1982)	40	40	40	1	288 – 533	0.7 – 20.3	0.32 – 1.00	0.00 – 0.51	0.306	0.159
Han <i>et al.</i> (2009)	28	0	28	0	313 – 343	4.3 – 18.3		0.01 – 0.02		0.035
Jackson <i>et al.</i> (1995)	2	2	0	0	323 – 348	34.5	0.99		0.066	
Jarne <i>et al.</i> (2004)	99	99	0	0	251 – 288	0.1 – 4.1	1.00		0.009	
Kim <i>et al.</i> (2012)	26	26	0	0	283 – 312	8.1 – 20.1	1.00		0.008	
King <i>et al.</i> (1992)	68	41	27	8	288 – 313	5.2 – 24.3	0.99 – 1.00	0.02 – 0.03	0.028	0.040
Koglbauer and Wendland (2008)	61	61	0	0	298 – 373	0.1 – 5.5	0.61 – 1.00		0.128	
Koschel <i>et al.</i> (2006)	8	0	8	0	323 – 373	2.1 – 20.2		0.01 – 0.02		0.063
Li <i>et al.</i> (2004)	6	0	6	0	332	3.3 – 19.9		0.01 – 0.02		0.058
Malinin and Kurovskaya (1975)	8	0	8	0	298 – 423	4.8		0.01 – 0.02		0.045
Malinin and Savelyeva (1972)	11	0	11	0	298 – 348	4.8		0.01 – 0.02		0.026
Malinin (1959)	116	0	116	1	473 – 603	9.8 – 58.8		0.01 – 0.85	15.829	
Mather and Franck (1992)	11	11	0	0	498 – 546	114.4 – 311.0	0.53 – 0.79		17.133	
Müller and Maurer (1982)	49	49	49	14	372 – 473	0.3 – 8.1	0.23 – 0.95	0.00 – 0.01	1.386	0.032
Nighswander <i>et al.</i> (1989)	33	0	33	0	352 – 471	2.0 – 10.2		0.00 – 0.02		0.041
Prupton and Savage (1945)	26	0	26	0	374 – 393	2.3 – 70.3		0.00 – 0.03		0.115
Qin <i>et al.</i> (2008)	7	0	7	0	323 – 375	10.6 – 49.9		0.02 – 0.03		0.100

Table A2.1 continued...

xCO₂ + (1 - x)H₂O continued										
Authors	N	N _y	N _x	N _{used}	T [K]	p [MPa]	y	x	AAD _y [%]	AAD _x [%]
VLE data continued										
Seo <i>et al.</i> (2011)	8	8	0	0	283–294	6.1–10.1	1.00		0.021	
Steward and Munjal (1970)	12	0	12	0	273–298	1.0–4.6		0.02–0.06		2.083
Takenouchi and Kennedy (1964)	121	121	121	22	383–623	10.0–150.0	0.08–0.96	0.00–0.29	15.436	1.360
Teng <i>et al.</i> (1997)	24	0	24	0	278–293	6.4–29.5		0.03		0.105
Tödheide and Franck (1963)	112	112	112	0	323–623	20.0–350.0	0.06–0.99	0.01–0.43	12.017	4.296
Trusler (2012)	42	42	42	9	298–448	1.1–17.6	0.30–1.00	0.00–0.03	0.384	0.130
Valtz <i>et al.</i> (2004)	52	29	47	8	278–318	0.5–8.0	0.97–1.00	0.00–0.03	0.053	0.047
Wiebe and Gaddy (1939)	29	0	29	0	323–373	2.5–70.9		0.00–0.03		0.154
Wiebe and Gaddy (1940)	42	0	42	0	285–313	2.5–50.7		0.01–0.03		0.186
Wiebe and Gaddy (1941)	39	39	0	0	298–348	0.1–70.9	0.75–1.00		0.436	
Zawisza and Malesinska (1981)	47	0	47	0	323–473	0.2–5.4		0.00–0.88		15.136
Zheng <i>et al.</i> (1997)	10	0	10	0	278–338	0.0–0.1		0.00		0.008
ppT data										
Authors	N	N _y	N _x	N _{used}	T [K]	p [MPa]	x	δ < 0.6	AAD [%]	
									0.6 < δ < 1.4	δ > 1.4
Abdulagatov <i>et al.</i> (1994)	72			0	673	10.0–40.0	0.00–0.60	2.063	2.258	0.074
Barbero <i>et al.</i> (1983) ^c	10			0	298	0.1	0.00			0.142
Crovetto (1991)	94			7	651–725	27.9–38.0	0.00–0.01		0.463	0.542
Fenghour and Wakeham (1996)	151			22	415–699	5.8–34.5	0.20–0.93	0.487		
Tödheide and Franck (1959)	303			0	673–1023	30.0–200.0	0.20–0.80	7.616	6.239	1.496
Gehrig (1980)	198			0	673–773	10.0–60.0	0.10–0.90	1.661	3.611	7.210
Greenwood (1969)	759			9	723–1023	5.0–50.0	0.00–0.99	0.713	1.123	
Hebach <i>et al.</i> (2004)	203			35	283–333	1.0–30.6	0.00–0.03			0.365
Hnedkovsky <i>et al.</i> (1996)	32			0	298–705	1.0–35.0	0.00	0.033	0.320	0.274
King <i>et al.</i> (1992)	27			5	288–298	6.0–24.3	0.02–0.03			0.103
Li <i>et al.</i> (2004)	35			0	332	0.4–28.6	0.00–0.02			0.664
McLinden (2011)	408			41	500–619	1.2–16.4	0.36–0.71	0.340		
Nighswander <i>et al.</i> (1989)	33			0	352–471	2.0–10.2	0.00–0.01			1.731
Patel and Eubank (1988)	296			25	323–498	0.0–10.2	0.50–0.98	0.022		

Table A2.1 continued...

$x\text{CO}_2 + (1-x)\text{N}_2$ continued										
Authors	N	N_y	N_x	N_{used}	T [K]	p [MPa]	y	x	AAD $_y$ [%]	AAD $_x$ [%]
VLE data continued										
Arai <i>et al.</i> (1971)	40	28	10	0	253–288	2.4–14.4	0.43–0.94	0.65–0.94	1.120	0.722
Bian <i>et al.</i> (1993)	13	8	8	0	301–303	7.2–7.9	0.96–0.99	0.97–0.99	0.102	0.138
Brown <i>et al.</i> (1989a)	18	18	18	0	250–270	2.6–14.1	0.38–0.76	0.70–0.99	0.774	0.169
Brown <i>et al.</i> (1989b)	59	59	15	0	220–270	1.0–13.0	0.17–0.82	0.81–0.99	0.215	0.254
Duarte-Garza <i>et al.</i> (1995a)	23	0	23	0	208–268	10.8–21.4		0.40–0.50		9.254
Esper <i>et al.</i> (1989)	11	11	0	0	208–257	0.7–18.2	0.45		3.690	
Kaminishi and Toriumi (1966)	22	20	18	0	233–298	3.7–12.7	0.24–0.92	0.63–0.97	2.231	2.360
Krichevskii <i>et al.</i> (1962)	22	11	11	0	288–303	6.1–9.1	0.79–0.99	0.90–0.99	0.882	0.502
Muirbrook (1964)	11	10	10	0	273	4.8–11.7	0.62–0.82	0.77–0.97	0.444	0.178
Somait and Kidnay (1978)	35	35	33	0	270	3.4–12.3	0.58–0.95	0.65–1.00	0.686	0.403
Trappehl (1987)	15	15	15	0	220	1.0–14.0	0.17–0.63	0.76–0.99	0.422	0.566
Tsiklis (1946)	7	7	7	0	273	3.9–6.9	0.42–0.85	0.81–0.95	15.848	8.061
Weber <i>et al.</i> (1984)	6	6	6	0	223–273	5.0–10.0	0.20–0.79	0.84–0.97	0.463	0.204
Xu <i>et al.</i> (1992)	18	17	17	0	288–293	6.0–9.7	0.80–0.98	0.85–0.99	0.404	0.383
Yorizane <i>et al.</i> (1970)	15	15	15	0	273	4.1–11.8	0.60–0.91	0.70–0.99	1.309	0.850
Yorizane <i>et al.</i> (1985)	34	28	28	0	273–298	4.5–11.4	0.60–0.94	0.79–0.98	0.543	0.373
Yucelen and Kidnay (1999)	19	9	16	0	240–270	1.7–13.0	0.30–0.92	0.75–0.99	0.731	0.239
Zenner and Dana (1963)	31	30	31	0	218–273	1.3–13.9	0.15–0.80	0.70–0.99	2.143	0.737
AAD [%]										
							x	$\delta < 0.6$	$0.6 < \delta < 1.4$	$\delta > 1.4$
Authors	N			N_{used}	T [K]	p [MPa]	x	$\delta < 0.6$	$0.6 < \delta < 1.4$	$\delta > 1.4$
pρT data										
Altunin and Chin (1972)	110			0	323–343	0.3–20.4	0.21–0.76	0.254	1.305	
Arai <i>et al.</i> (1971)	173			0	253–288	2.4–14.5	0.46–0.94	0.963	1.594	3.080
Bailey <i>et al.</i> (1989)	200			0	208–400	0.0–48.4	0.44	0.205	0.503	0.847
Brugge <i>et al.</i> (1989)	196			0	299–320	0.2–10.5	0.10–0.90	0.035		
Brugge <i>et al.</i> (1997)	749			0	225–450	1.0–69.1	0.10–0.90	0.196	0.298	0.156
Duarte-Garza <i>et al.</i> (1995a)	279			0	208–300	1.1–77.5	0.39–0.50	0.612	1.586	0.623
Duarte-Garza <i>et al.</i> (1995b)	947			0	225–450	0.2–69.1	0.10–0.90	0.112	0.296	0.159
Edwards and Roseveare (1972)	4			0	298	0.0–0.1	0.48	13.823		

Table A2.1 continued...

$x\text{CO}_2 + (1-x)\text{N}_2$ continued						
Authors	N	N_{used}	T [K]	p [MPa]	x	AAD [%] $\delta < 0.6$ $0.6 < \delta < 1.4$ $\delta > 1.4$
<i>ppT data continued</i>						
Ely <i>et al.</i> (1987)	79	0	250–329	2.2–33.0	0.98	0.115 0.152 0.099
Ely <i>et al.</i> (1989)	79	0	250–329	2.2–33.0	0.98	0.114 0.152 0.099
Esper <i>et al.</i> (1989)	307	0	208–320	0.0–48.4	0.44	0.062 0.346 0.703
Gorski and Miller (1953)	6	0	303	0.0–0.1	0.49–0.50	13.914
Hacura <i>et al.</i> (1988)	242	0	322–347	49.0–273.7	0.25–0.74	0.387 3.211
Haney and Bliss (1944)	44	0	298–398	7.5–50.6	0.25–0.50	0.170 0.231 0.162
Jaeschke and Humphreys (1991)	215	0	274–349	0.2–26.1	0.10–0.31	0.025 0.092
Jiang <i>et al.</i> (1990)	41	0	293	0.6–5.1	0.27–0.70	0.025
Kaminishi (1978)	48	0	243–333	2.7–19.6	0.90–0.95	0.321 23.061
Kosov and Brovanov (1975)	93	0	313–353	5.9–58.8	0.23–0.67	2.310 2.381 2.932
Kritschewsky and Markov (1940)	54	0	273–473	5.0–50.6	0.24–0.47	3.114 1.279 0.939
Mantovani <i>et al.</i> (2012)	197	0	303–383	1.0–20.0	0.90–0.95	1.211 1.121 0.802
Mondéjar (2012)	347	0	250–400	0.4–19.9	0.10–0.50	0.060 0.128
Rivkin (1975)	296	0	273–473	0.3–9.9	0.18–0.98	0.118
Seitz <i>et al.</i> (1994)	9	0	473	100	0.10–0.90	0.553
Seitz and Blencoe (1996)	51	0	673	19.9–99.9	0.10–0.90	0.624
Seitz <i>et al.</i> (1996)	192	0	323–573	9.9–99.9	0.10–0.90	0.560 0.448 0.285
Speed of sound						
Alsiyabi <i>et al.</i> (2012)	20	0	268–301	9.5–41.6	0.95	2.149
Kachanov <i>et al.</i> (1983)	19	0	297–422	50.0–400.0	0.39	0.891
Younglove <i>et al.</i> (1993)	65	0	249–350	0.5–10.3	0.49	0.405
Excess enthalpy						
Lee and Mather (1972)	666	0	283–353	1.0–12.1	0.10–0.90	12.731 3.785
Isobaric heat capacity						
Bishnoi <i>et al.</i> (1972)	203	0	313–363	0.1–16.5	0.68–0.93	0.824 2.009
2nd cross virial coefficient^a						
Cottrell <i>et al.</i> (1956)	3	0	303–363			3.768
Martin <i>et al.</i> (1982)	4	0	289–319			2.630

Table A2.1 continued...

$x\text{CO}_2 + (1 - x)\text{N}_2$ continued										
Authors	N	N_{used}	T [K]	p [MPa]	x	$\delta < 0.6$	$0.6 < \delta < 1.4$	$\delta > 1.4$	AAD [%]	
2nd cross virial coefficient cont.										
Pfefferle <i>et al.</i> (1955)	6	0	303						11.555	
$x\text{CO}_2 + (1 - x)\text{O}_2$										
Authors	N	N_v	N_x	N_{used}	T [K]	p [MPa]	y	x	AAD _{v} [%]	AAD _{x} [%]
VLE data										
Fredenslund <i>et al.</i> (1972)	11	9	10	0	223	0.9 – 13.4	0.19 – 0.78	0.61 – 1.00	1.621	3.560
Fredenslund and Sather (1970)	72	70	70	70	223 – 283	1.0 – 12.8	0.18 – 0.90	0.61 – 0.99	1.785	0.854
Zenner and Dana (1963)	33	27	23	0	218 – 273	2.2 – 13.5	0.15 – 0.75	0.60 – 0.97	1.705	2.373
Kaminishi and Toriumi (1966)	17	17	17	0	233 – 298	3.7 – 12.7	0.40 – 0.93	0.62 – 1.00	3.005	4.352
AAD [%]										
Authors	N	N_{used}	T [K]	p [MPa]	x	$\delta < 0.6$	$0.6 < \delta < 1.4$	$\delta > 1.4$		
$p\rho T$ data										
Gorski and Miller (1953)	6	0	303	0.0 – 0.1	0.49 – 0.50	2.694				
Mantovani <i>et al.</i> (2012)	196	65	303 – 383	1.0 – 20.0	0.87 – 0.93	2.206			3.997	2.736
Muirbrook (1964) ^c	33	0	273	4.1 – 11.7	0.59 – 0.96	6.284			10.816	3.403
Speed of sound										
Alsiyabi <i>et al.</i> (2012)	20	20	268 – 301	10.4 – 40.9	0.93				0.717	
2nd cross virial coefficient^a										
Cottrell <i>et al.</i> (1956)	3	0	303 – 363						3.034	
Martin <i>et al.</i> (1982)	3	0	289 – 319						1.106	
$x\text{CO}_2 + (1 - x)\text{Ar}$										
Authors	N	N_v	N_x	N_{used}	T [K]	p [MPa]	y	x	AAD _{v} [%]	AAD _{x} [%]
VLE data										
Coquelet <i>et al.</i> (2008)	62	62	62	61	233 – 299	1.5 – 14.0	0.25 – 0.99	0.59 – 0.99	1.330	0.668
Kaminishi <i>et al.</i> (1968)	19	19	15	0	233 – 273	2.6 – 13.2	0.25 – 0.85	0.65 – 0.97	1.359	0.420
Sarashina <i>et al.</i> (1971b)	12	8	4	0	288	5.7 – 9.8	0.79 – 0.94	0.83 – 0.94	1.158	0.608

Table A2.1 continued...

xCO ₂ + (1 - x)Ar continued									
Authors	N	N _{used}	T [K]	p [MPa]	x	δ < 0.6	AAD [%]		δ > 1.4
pT data									
Abraham and Bennett (1960)	91	36	323	5.0 – 101.3	0.12 – 0.83	0.075	0.167		0.234
Altunin and Koposhilov (1976)	60	12	313	0.3 – 20.9	0.35 – 0.81	0.216	0.417		
Altunin and Koposhilov (1977)	302	49	303 – 373	0.2 – 24.7	0.35 – 0.81	0.166	0.441		
Kosov and Brovanov (1975)	91	0	313 – 353	5.8 – 58.8	0.20 – 0.71	1.267	1.875		1.584
Mantovani et al. (2012)	194	0	303 – 383	1.0 – 20.0	0.83 – 0.96	0.971	1.387		1.152
Sarashina et al. (1971b) ^c	88	10	288	2.4 – 14.5	0.70 – 0.94	0.698	1.417		2.438
Schönmann (1971)	335	112	373 – 573	0.3 – 59.3	0.18 – 0.80	0.051	0.151		0.210
Joule–Thomson coefficient ^b									
Strakey et al. (1974)	84	67	233 – 383	0.0 – 20.2	0.46 – 0.75	0.075	0.097		0.052
2 nd cross virial coefficient ^a									
Bose and Cole (1970)	5	0	320 – 322				6.169		
Cottrell et al. (1956)	3	0	303 – 363				6.075		
Martin et al. (1982)	3	3	289 – 319				0.356		
Schönmann (1971)	3	3	373 – 573				0.772		
xCO ₂ + (1 - x)CO									
Authors	N	N _v	N _x	N _{used}	T [K]	p [MPa]	y	x	AAD _v [%] AAD _x [%]
VLE data									
Christiansen et al. (1974)	34	34	34	0	223 – 283	0.8 – 14.2	0.20 – 0.98	0.54 – 1.00	1.142 2.592
Kaminishi et al. (1968)	22	21	19	22	223 – 283	2.4 – 12.9	0.21 – 0.83	0.63 – 0.96	0.791 0.988
AAD [%]									
Authors	N			N _{used}	T [K]	p [MPa]	x	δ < 0.6	0.6 < δ < 1.4 δ > 1.4
pT data									
Cipollina et al. (2007)	56			14	308 – 343	22.5 – 47.0	0.86 – 0.95		2.646
Mallu et al. (1987)	75			19	323 – 423	0.1 – 6.5	0.57	0.288	
Mallu et al. (1989)	150			30	323 – 423	0.1 – 6.5	0.29 – 0.79	0.298	
2 nd cross virial coefficient ^a									
Brewer and Vaughn (1969)	2			2	223 – 273				9.075
Cottrell et al. (1956)	3			0	303 – 363				9.110

Table A2.1 continued...

$x\text{CO}_2 + (1-x)\text{CO}$ continued									
Authors	N	N_{used}	T [K]	p [MPa]	x	$\delta < 0.6$	$0.6 < \delta < 1.4$	$\delta > 1.4$	
2nd cross virial coefficient^a cont.									
Mallu <i>et al.</i> (1987)	3	3	323–423				2.992		
$x\text{H}_2\text{O} + (1-x)\text{N}_2$									
Authors	N	N_v	N_x	N_{used}	T [K]	p [MPa]	y	x	AAD [%]
VLE data									
Alvarez <i>et al.</i> (1988)	31	0	31	0	336–636	0.5–25.6		0.00–0.01	0.106
Bartlett (1927)	5	5	0	5	323	9.9–98.7	1.00		0.029
Blanco <i>et al.</i> (1999)	52	52	0	0	249–283	4.2–109.6	1.00		0.006
Chapoy (2004)	35	35	0	9	282–363	0.4–5.0	0.87–1.00		0.028
Chapoy <i>et al.</i> (2004b)	52	0	52	15	274–363	0.9–7.2		0.00	0.003
Cosgrove and Walkley (1981)	8	0	8	0	278–313	0.1		0.00	0.000
Cuccaro <i>et al.</i> (2012)	16	16	0	0	241–270	0.1	1.00		0.022
Douglas (1964)	38	0	38	2	276–302	0.1		0.00	0.000
Eicheleberger (1955)	6	0	6	0	338	7.0–20.2		0.00	0.022
Gillespie and Wilson (1980)	16	16	16	0	310–588	0.3–13.8	0.14–1.00		0.023
Japas and Franck (1985a)	97	97	0	0	479–657	15.5–270.5	0.01–0.87		37.318
Kennan and Pollack (1990)	7	0	7	7	298	4.5–11.7		0.00	0.006
Koglbauer and Wendland (2008)	116	114	0	13	293–373	0.1–25.0	0.29–1.00		0.030
Kosyakov <i>et al.</i> (1977)	22	21	0	0	233–273	1.0–10.1	1.00		0.001
Krichevsky and Kasarnovsky (1935)	32	0	32	15	298–373	2.5–98.7		0.00–0.01	0.032
Maslennikova <i>et al.</i> (1971)	134	134	0	0	298–623	5.1–50.7	0.03–1.00		2.046
Mohammadi <i>et al.</i> (2005)	35	35	0	0	282–363	0.4–5.0	0.87–1.00		0.028
Oellrich and Althaus (2001)	43	43	0	11	248–293	0.5–10.0	1.00		0.030
O'Sullivan and Smith (1966)	6	0	6	0	324	10.1–60.8		0.00	0.083
O'Sullivan and Smith (1970)	18	0	18	0	324–398	10.1–61.6		0.00	0.003
Pray <i>et al.</i> (1952)	5	0	5	0	533–588	5.7–13.4		0.00	0.093
Rigby and Prausnitz (1968)	13	13	0	7	298–373	2.1–10.2	0.98–1.00		0.020
Saddington and Krase (1934)	18	18	0	0	323–503	10.1–30.4	0.42–1.00		2.906
Smith <i>et al.</i> (1962)	5	0	5	0	303	1.1–5.9		0.00	0.002

$$x\text{H}_2\text{O} + (1-x)\text{N}_2 \text{ continued}$$

Authors	N	N_v	N_x	N_{used}	T [K]	p [MPa]	y	x	AAD_y [%]	AAD_x [%]
VLE data continued										
Wiebe <i>et al.</i> (1932)	8	0	8	0	298	2.5–101.3		0.00–0.01		0.021
Wiebe <i>et al.</i> (1933)	32	0	32	0	298–373	2.5–101.3		0.00–0.01		0.051
Wilcock and Battino (1974)	1	0	1	0	298	0.1		0.00		0.000
Excess enthalpy										
Abdulagatov <i>et al.</i> (1993)	55			30	523–663	2.0–69.2	0.06–0.94	1.278	1.467	4.384
Fenghour <i>et al.</i> (1993)	101			25	428–706	8.2–30.9	0.35–0.95	0.328		
Gallagher <i>et al.</i> (1993b)	101			0	428–706	8.2–30.9	0.35–0.95	0.328		
Japas and Franck (1985a)	111			72	479–672	15.5–286.1	0.10–0.86	1.433	2.059	1.718
McLinden (2011)	61			52	499–619	1.1–25.4	0.31–0.70	0.231		
2nd cross virial coefficient^a										
Lancaster and Wormald (1990)	97			20	448–698	0.4–12.5	0.24–0.79	7.000		
Richards <i>et al.</i> (1981)	58			10	373–423	0.1	0.25–0.68	35.833		
Wormald and Colling (1983)	94			0	448–698	0.3–12.5	0.29–0.79	14.421		
Wormald and Lancaster (1988)	6			0	373–423	0.0–0.1	0.5	30.592		
Hall and Iglesias-Silva (1994)	4			0	298–373			–		
Tulegenov <i>et al.</i> (2007)	53			0	223–663			–		
$x\text{H}_2\text{O} + (1-x)\text{O}_2$										
Authors	N	N_v	N_x	N_{used}	T [K]	p [MPa]	y	x	AAD_y [%]	AAD_x [%]
VLE data										
Cosgrove and Walkley (1981)	8	0	8	8	278–313	0.1		1.00		<0.001
Douglas (1964)	15	0	15	0	281–302	0.1		1.00		<0.001
Japas and Franck (1985b)	117	57	60	16	471–656	19.5–279.8	0.06–0.99		14.327	3.333
Pray <i>et al.</i> (1952)	18	0	18	7	435–616	1.4–17.4		1.00		0.026
Wylie and Fisher (1996a)	14	14	0	6	298–348	2.2–14.1	0.00–0.01		0.007	

Table A2.1 continued...

xH₂O + (1 - x)O₂ continued									
Authors	<i>N</i>	<i>N_{used}</i>	<i>T</i> [K]	<i>p</i> [MPa]	<i>x</i>	$\delta < 0.6$	AAD [%]		
							$0.6 < \delta < 1.4$	$\delta > 1.4$	
<i>pT</i> data									
Japas and Franck (1985b) ^c	146	34	471 – 672	19.5 – 324.0	0.05 – 0.89	17.220	15.984	10.978	
2nd cross virial coefficient^a									
Hall and Iglesias-Silva (1994)	4	0	298 – 373				–	–	
Wheatley and Harvey (2007)	16	0	100 – 2000				–	–	
Wylie and Fisher (1996a)	3	0	298 – 348				–	–	
xH₂O + (1 - x)Ar									
Authors	<i>N</i>	<i>N_v</i>	<i>N_x</i>	<i>N_{used}</i>	<i>T</i> [K]	<i>p</i> [MPa]	<i>y</i>	<i>x</i>	AAD [%]
VLE data									
Cosgrove and Walkley (1981)	6	0	6	0	278 – 303	0.1		1.00	0.001
Crovetto <i>et al.</i> (1982)	8	0	8	0	306 – 568	1.7 – 9.7		1.00	0.130
Douglas (1964)	30	0	30	6	277 – 302	0.1		1.00	0.001
Kennan and Pollack (1990)	9	0	9	9	298	2.3 – 8.9		0.99 – 1.00	0.003
Koglbauer and Wendland (2008)	116	116	0	6	293 – 373	0.1 – 25.0	0.00 – 0.71		0.018
Morrison and Johnstone (1954)	13	0	13	0	283 – 347	0.1		1.00	0.001
Oellrich and Althaus (2001)	19	19	0	4	258 – 288	1.5 – 10.0	0.00		<0.001
Rigby and Prausnitz (1968)	12	12	0	12	298 – 373	2.0 – 9.3	0.00 – 0.02		0.016
Wu <i>et al.</i> (1990)	173	21	172	0	476 – 662	10.4 – 337.2	0.20 – 0.76	0.20 – 0.98	20.304
									25.962
AAD [%]									
Authors	<i>N</i>	<i>N_{used}</i>	<i>T</i> [K]	<i>p</i> [MPa]	<i>x</i>	$\delta < 0.6$	$0.6 < \delta < 1.4$	$\delta > 1.4$	
<i>pT</i> data									
Biggerstaff and Wood (1988a)	84	18	322 – 716	17.2 – 34.5	0.99	0.916	1.131	0.104	
Wu <i>et al.</i> (1990)	152	60	476 – 662	10.4 – 337.2	0.20 – 0.95	15.427	5.731	3.981	
Excess enthalpy									
Wormald and Lancaster (1988)	6	0	373 – 423	0.1	0.50	41.457			
Wormald and Colling (1993)	46	8	448 – 698	0.4 – 13.3	0.50	27.139			
Isobaric heat capacity									
Biggerstaff and Wood (1988b)	23	8	606 – 720	31.5 – 32.3	0.99	0.034	0.573	1.155	
Biggerstaff <i>et al.</i> (1985)	27	8	305 – 577	16.6 – 17.5	0.99			0.404	

Table A2.1 continued...

xH ₂ O + (1 - x)Ar continued									
Authors	<i>N</i>	<i>N_{used}</i>	<i>T</i> [K]	<i>p</i> [MPa]	<i>x</i>	AAD [%]			
2 nd cross virial coefficient ^a									
Hodges <i>et al.</i> (2002)	21	0	100–2000						–
Wormald and Lancaster (1988)	6	0	373–423						–
xH ₂ O + (1 - x)CO									
Authors	<i>N</i>	<i>N_y</i>	<i>N_x</i>	<i>N_{used}</i>	<i>T</i> [K]	<i>p</i> [MPa]	<i>y</i>	<i>x</i>	AAD _{<i>y</i>} [%] AAD _{<i>x</i>} [%]
VLE data									
Gillespie and Wilson (1980)	18	18	18	16	310–588	0.3–13.8	0.00–0.55	0.91–1.00	0.372 0.011
AAD [%]									
Authors	<i>N</i>	<i>N_{used}</i>	<i>T</i> [K]	<i>p</i> [MPa]	<i>x</i>	δ < 0.6 0.6 < δ < 1.4 δ > 1.4			
Excess enthalpy									
Lancaster and Wormald (1990)	22	11	473–698	0.7–12.1	0.50	10.365			
Wormald and Lancaster (1988)	4	0	363–403	0.0	0.50	19.793			
2 nd cross virial coefficient ^a									
Wheatley and Harvey (2009)	14	0	200–2000						–
xN ₂ + (1 - x)O ₂									
Authors	<i>N</i>	<i>N_y</i>	<i>N_x</i>	<i>N_{used}</i>	<i>T</i> [K]	<i>p</i> [MPa]	<i>y</i>	<i>x</i>	AAD _{<i>y</i>} [K] AAD _{<i>x</i>} [K]
VLE data									
Armstrong <i>et al.</i> (1955)	70	70	70	0	64–77	0.0–0.1	0.24–0.99	0.03–0.95	0.098 0.098
Baba-Ahmed <i>et al.</i> (1999)	45	41	41	0	100–122	0.3–2.9	0.13–1.00	0.06–1.00	0.070 0.062
Cockett (1957)	62	62	62	0	81–91	0.1	0.21–0.94	0.07–0.81	0.104 0.130
Din (1960)	119	119	119	0	79–115	0.1–1.0	0.19–0.97	0.10–0.89	0.417 0.475
Dodge and Dunbar (1927)	49	49	49	0	76–125	0.1–3.0	0.13–0.96	0.05–0.91	0.117 0.121
Duncan and Staveley (1966)	9	0	9	0	63	0.0		0.10–0.80	0.181 0.181
Hiza <i>et al.</i> (1990)	47	42	47	0	62–99	0.0–0.7	0.19–0.97	0.07–0.88	0.090 0.081
Inglis (1906)	37	35	35	0	74–79	0.0–0.1	0.10–1.00	0.03–1.00	0.459 0.117
Kritschewsky & Torotsch. (1936)	42	38	38	0	99–125	0.3–3.2	0.13–1.00	0.05–1.00	0.109 0.143
Pool <i>et al.</i> (1962)	9	0	9	0	83	0.1–0.2		0.10–0.90	0.043 0.043
Thorogood and Haselden (1963)	13	13	13	0	88–90	0.1	0.01–0.27	0.00–0.08	0.115 0.152

Table A2.1 continued...

$xN_2 + (1-x)O_2$ continued										
Authors	N	N_y	N_x	N_{used}	T [K]	p [MPa]	y	x	AAD _y [K]	AAD _x [K]
VLE data continued										
Wilson <i>et al.</i> (1965)	138	138	138	0	77–136	0.1–2.6	0.11–1.00	0.05–0.99	0.110	0.111
Yorizane <i>et al.</i> (1978)	10	10	10	0	79–80	0.0–0.1	0.37–0.93	0.11–0.85	0.335	0.424
									AAD [%]	
								$\delta < 0.6$	$0.6 < \delta < 1.4$	$\delta > 1.4$
$xN_2 + (1-x)Ar$										
Authors	N	N_y	N_x	N_{used}	T [K]	p [MPa]	x	y	AAD _y [K]	AAD _x [K]
$p\rho T$ data										
Blagoi and Rudenko (1958)	19			0	66–79	0.1	0.10–0.79			0.186
Gorski and Miller (1953)	5			0	303	0.1	0.49–0.50	0.002		
Kuonen <i>et al.</i> (1922)	153			0	135–293	2.9–5.9	0.25–0.50	0.940	10.288	0.608
Schilling (2003)	11			0	293	2.1–8.0	0.79	0.006		
Wöll (2003)	49			0	233–333	0.5–15.6	0.79	0.018		
Isobaric heat capacity										
Perkins and Cieszkiewicz (1991)	1922			0	64–304	0.2–70.4	0.24–0.50	18.016	7.286	9.714
2nd cross virial coefficient^a										
Fostiropoulos <i>et al.</i> (1988)	10			0	87–475				3.788	
Gorski and Miller (1953)	1			0	303				0.033	
Hall and Iglesias-Silva (1994)	20			0	188–480				1.146	
Martin <i>et al.</i> (1982)	3			0	289–319				0.587	
Wilson <i>et al.</i> (1965)	14			0	72–144				3.810	
$xN_2 + (1-x)Ar$										
Authors	N	N_y	N_x	N_{used}	T [K]	p [MPa]	y	x	AAD _y [K]	AAD _x [K]
VLE data^d										
Baba-Ahmed <i>et al.</i> (1999)	43	43	43	19	95–121	0.3–2.5	0.11–0.94	0.06–0.91	0.198	0.194
Elshayal and Lu (1975)	7	0	7	0	100	0.4–0.7	0.14–0.91	0.14–0.91	0.062	0.062
Fastovskii and Petrovskii (1956)	50	50	50	0	79–102	0.1–0.4	0.11–0.97	0.05–0.90	0.299	0.201
Hiza <i>et al.</i> (1990)	28	28	28	12	84–99	0.1–0.7	0.22–0.94	0.10–0.89	0.038	0.059
Jin <i>et al.</i> (1993)	13	13	13	0	122	1.5–2.7	0.09–0.92	0.05–0.90	0.155	0.089
Lewis and Staveley (1975)	6	6	6	0	84	0.1–0.2	0.48–0.91	0.23–0.81	0.030	0.034
Miller <i>et al.</i> (1973)	14	7	7	0	112	0.8–1.5	0.17–0.90	0.11–0.85	0.154	0.155
Narinskii (1966)	98	98	98	0	80–119	0.1–2.3	0.05–0.98	0.02–0.96	0.066	0.076

Table A2.1 continued...

xN ₂ + (1 - x)Ar continued										
Authors	N	N _v	N _x	N _{used}	T [K]	p [MPa]	y	x	AAD _y [K]	AAD _x [K]
VLE data ^d continued										
Pool <i>et al.</i> (1962)	10	0	10	0	83	0.1 – 0.2		0.06 – 0.88		0.022
Sprow and Prausnitz (1966)	17	17	17	4	83	0.1 – 0.2	0.17 – 0.96	0.06 – 0.91	0.022	0.024
Thorpe (1968)	68	68	68	0	80 – 115	0.1 – 1.1	0.18 – 0.96	0.10 – 0.91	0.056	0.042
Wilson <i>et al.</i> (1965)	183	183	183	0	77 – 133	0.1 – 2.6	0.10 – 1.00	0.05 – 1.00	0.285	0.318
AAD [%]										
							x	δ < 0.6	0.6 < δ < 1.4	δ > 1.4
Authors										
pρT data										
Crain and Sonntag (1966)	264			0	143 – 273	0.1 – 52.4	0.20 – 0.80	0.196	1.449	0.551
Holst and Hamburger (1916)	41			0	73 – 90	0.0 – 0.1	0.31 – 0.80	0.198		
Kosov and Brovanov (1979)	201			0	293 – 353	5.9 – 58.8	0.16 – 0.80	0.099	0.131	0.294
Maslennikova <i>et al.</i> (1979)	88			0	298 – 423	100.0 – 800.0	0.26 – 0.74			0.284
Massengill and Miller (1973)	6			0	89 – 113	0.2 – 1.3	0.50			0.376
Palavra (1979)	203			31	93 – 106	0.9 – 24.9	0.31 – 0.69			0.071
Ricardo <i>et al.</i> (1992)	21			3	119	7.4 – 145.2	0.52			0.232
Townsend (1956)	144			24	298 – 323	0.1 – 13.9	0.16 – 0.84	0.072		
Zandbergen and Beenakker (1967)	55			0	170 – 292	0.7 – 9.5	0.19 – 0.74	0.096	0.720	
2 nd cross virial coefficient ^a										
Brewer and Vaughn (1969)	9			0	123 – 323				0.831	
Crain and Sonntag (1966)	4			0	143 – 273				1.718	
Dymond and Smith (1980)	12			0	213 – 474				2.687	
Elshayal and Lu (1975)	3			0	353 – 463				0.215	
Knobler <i>et al.</i> (1959)	1			0	90				12.599	
Martin <i>et al.</i> (1982)	3			0	289 – 319				0.453	
Schramm and Mueller (1982)	1			0	296				2.532	
Wilson <i>et al.</i> (1965)	14			0	72 – 144				1.717	
Zandbergen and Beenakker (1967)	11			0	170 – 270				0.179	

Table A2.1 continued...

xN₂ + (1 - x)CO										
Authors	N	N _y	N _x	N _{used}	T [K]	p [MPa]	y	x	AAD _y [K]	AAD _x [K]
VLE data^d										
Duncan and Staveley (1966)	10	0	9	7	68	0.0		0.20 – 1.00		0.095
Gill and Morrison (1966)	8	0	7	4	68 – 77	0.0 – 0.1		0.03		0.017
Pool <i>et al.</i> (1962)	10	0	9	8	83	0.1 – 0.2		0.13 – 1.00		0.017
Spro and Prausnitz (1966)	8	8	8	8	83	0.1 – 0.2	0.16 – 0.95	0.10 – 0.93	0.015	0.019
Steckel (1935)	48	0	48	0	83 – 118	0.2 – 2.3		0.11 – 0.83	0.315	0.452
Torotscheschnikow (1937)	109	108	109	0	70 – 122	0.0 – 2.7	0.12 – 0.95	0.00 – 0.90	0.335	0.325
Verschoye (1932)	24	0	24	8	70 – 79	0.0 – 0.1		0.20 – 0.80		0.031
Yushkevich and Torochechn. (1936)	75	65	65	0	70 – 121	0.0 – 2.8	0.11 – 1.00	0.14 – 1.00	0.287	0.300
Authors	N			N _{used}	T [K]	p [MPa]	x	$\delta < 0.6$	$0.6 < \delta < 1.4$	$\delta > 1.4$
pρT data										
Jaeschke and Humphreys (1991)	343			52	273 – 353	0.3 – 30.1	0.96	0.009	0.013	
Mondéjar (2012)	215			215	250 – 400	0.9 – 19.9	0.85 – 0.95	0.013	0.027	
2nd cross virial coefficient^a										
McElroy and Buchanan (1995)	8			0	303 – 348				1.203	
xO₂ + (1 - x)Ar										
Authors	N	N _y	N _x	N _{used}	T [K]	p [MPa]	y	x	AAD _y [K]	AAD _x [K]
VLE data^d										
Bourbo and Ischkin (1936)	27	27	27	0	87 – 95	0.1 – 0.2	0.12 – 0.94	0.14 – 0.96	0.058	0.069
Burn and Din (1962)	140	140	140	6	84 – 118	0.1 – 1.0	0.08 – 0.88	0.09 – 0.90	0.021	0.021
Clark <i>et al.</i> (1954)	45	45	45	0	90 – 110	0.1 – 0.7	0.09 – 0.88	0.10 – 0.90	0.042	0.053
Fastovskii and Petrovskii (1956)	24	24	24	0	89 – 96	0.1 – 0.2	0.13 – 0.72	0.17 – 0.79	0.103	0.088
Hiza <i>et al.</i> (1990)	12	12	12	4	94 – 99	0.2 – 0.3	0.19 – 0.86	0.21 – 0.90	0.104	0.160
Inglis (1906)	6	6	6	0	82	0.0 – 0.1	0.79 – 1.00	0.86 – 1.00	0.509	0.054
Narinskii (1957)	55	55	55	0	90 – 120	0.1 – 1.2	0.03 – 0.95	0.04 – 0.97	0.042	0.044
Parikh and Zollweg (1997)	24	24	24	4	92 – 115	0.1 – 0.9	0.07 – 0.97	0.08 – 0.98	0.137	0.134
Pool <i>et al.</i> (1962)	20	0	20	0	83 – 89	0.1		0.10 – 0.90		0.723
Wang (1960)	35	0	35	0	90 – 95	0.1 – 0.2		0.00 – 0.98		0.145
Wilson <i>et al.</i> (1965)	200	200	200	29	87 – 138	0.1 – 2.6	0.02 – 0.99	0.02 – 1.00	0.085	0.086

Table A2.1 continued...

xO₂ + (1 - x)Ar continued									
Authors	N	N _y	N _x	N _{used}	T [K]	p [MPa]	y	x	AAD _y [K] AAD _x [K]
VLE data^d continued									
Yorizane <i>et al.</i> (1978)	58	58	58	0	89 – 91	0.1	0.21 – 1.00	0.24 – 1.00	0.082 0.080
Authors	N	N _y	N _x	N _{used}	T [K]	p [MPa]	x	δ < 0.6	AAD [%] 0.6 < δ < 1.4 δ > 1.4
ppT data									
Blagoi and Rudenko (1958)	36			8	70 – 88	0.1	0.12 – 0.90		0.192
Masson and Dolley (1923)	20			0	298	3.0 – 12.6	0.50	1.306	
Saji and Okuda (1965)	37			0	78 – 87	0.0 – 0.1	0.00 – 0.99		0.146
2nd cross virial coefficient^a									
Martin <i>et al.</i> (1982)	3			0	289 – 319				0.408
Vatter <i>et al.</i> (1996)	5			0	296 – 463				1.185
xO₂ + (1 - x)CO									
<i>No experimental data available</i>									
xAr + (1 - x)CO									
Authors	N	N _y	N _x	N _{used}	T [K]	p [MPa]	y	x	AAD _y [K] AAD _x [K]
VLE data^d									
Christiansen <i>et al.</i> (1973)	16	14	14	0	123 – 137	1.5 – 3.5	0.05 – 0.90	0.06 – 0.92	0.154 0.109
Duncan and Staveley (1966)	11	0	11	0	83	0.1		0.10 – 0.90	0.192
Authors	N	N _y	N _x	N _{used}	T [K]	p [MPa]	x	δ < 0.6	AAD [%] 0.6 < δ < 1.4 δ > 1.4
ppT data									
Pool <i>et al.</i> (1962)	7			0	83	0.0	0.28 – 0.76	8.187	

^a The deviation is given in [cm³/mol].^b The deviation is given in [MPa/K].^c Densities of the saturated vapor or liquid.^d Deviations are given in differences in dew point and bubble point temperature in [K].

N: Number of data points in the data set.

N_y, N_x: Number of data points for the saturated vapor and liquid phase (VLE data). Only the data points are listed, where the VLE calculation converged.N_{used}: Number of data points used in the fitting of the mixture model.

Table A2.2: Representation of experimental thermodynamic property data of multi-component mixtures by the EOS-CG mixture model.

$x_1\text{CO}_2 + x_2\text{N}_2 + x_3\text{O}_2$									
Authors	N	N_y	N_x	T [K]	p [MPa]	y_1	x_1	AAD $_y$ [%]	AAD $_x$ [%]
VLE data^a									
Muirbrook and Prausnitz (1965)	12	12	12	273	5.2 – 10.6	0.60 – 0.78	0.81 – 0.96	1.281	0.122
Zenner and Dana (1963)	64	64	64	218 – 273	5.2 – 13.1	0.15 – 0.61	0.64 – 0.93	0.982	0.695
Saturated densities									
Muirbrook and Prausnitz (1965)	23	11	12	273	5.2 – 10.6	0.60 – 0.78	0.81 – 0.96	3.757	0.437
Humid Air: $x_1\text{N}_2 + x_2\text{O}_2 + x_3\text{Ar} + x_4\text{H}_2\text{O}$									
Authors	N	N_y	N_x	T [K]	p [MPa]	y_1	y_4	AAD $_y$ [K]	AAD $_x$ [K]
VLE data^b									
Eckl <i>et al.</i> (2009)	28	28	0	333 – 353	2.0 – 25.0	0.74 – 0.78	<0.01 – 0.05	13.584	
Hyland (1975)	7	7	0	253 – 343	2.0 – 3.5	0.77 – 0.78	<0.01 – 0.01	1.543	
Hyland and Wexler (1973)	29	29	0	303 – 323	1.1 – 10.3	0.77 – 0.78	<0.01 – 0.01	0.989	
Koglbauer and Wendland (2007)	114	114	0	293 – 413	0.1 – 25.0	0.41 – 0.78	<0.01 – 0.48	2.627	
Pollitzer and Strebel (1924)	52	52	0	323 – 343	0.3 – 19.5	0.70 – 0.78	<0.01 – 0.11	2.808	
Webster (1950)	22	17	0	238 – 323	2.5 – 20.3	0.78	<0.01 – 0.00	4.934	
Wylie and Fisher (1996b)	15	15	0	293 – 348	1.5 – 14.1	0.77 – 0.78	<0.01 – 0.01	2.699	
AAD [%]									
Authors	N			T [K]	p [MPa]	x_1	$\delta < 0.6$	$0.6 < \delta < 1.4$	$\delta > 1.4$
$p\rho T$ data									
Eckl <i>et al.</i> (2009)	40			333 – 524	2.0 – 25.0	0.73 – 0.78	0.275	0.626	
Japas and Franck (1985b)	18			620 – 672	27.0– 279.5	0.15 – 0.16	35.658	14.373	11.349
Klingenberg and Ulbig (2007)	22			423 – 524	3.7 – 17.0	0.74 – 0.77	1.360		
Ulbig <i>et al.</i> (2005)	569			317 – 524	0.9 – 17.0	0.61 – 0.77	1.954		
Abdulagatov <i>et al.</i> (1993)	59			300 – 500	0.1 – 15.2	0.75 – 0.77	1.772		
Speed of sound data									
Ulbig <i>et al.</i> (2005)	23			450	0.1 – 1.2	0.63	0.332		
Air: $x_1\text{N}_2 + x_2\text{O}_2 + x_3\text{Ar}$									
Authors	N	N_y	N_x	T [K]	p [MPa]	y_1	x_1	AAD $_y$ [K]	AAD $_x$ [K]
VLE data^b									
Kuenen and Clark (1917)	32	16	14	123 – 132	2.4 – 3.8	0.78	0.78	0.159	0.189
Narinskii (1969) ^a	115	82	83	81 – 120	0.1 – 2.2	0.08 – 0.94	0.04 – 0.86	1.675	2.288

Table A2.2 continued ...

Air: $x_1\text{N}_2 + x_2\text{O}_2 + x_3\text{Ar}$ continued						
Authors	N	T [K]	p [MPa]	x_1	$\delta < 0.6$	AAD [%] $0.6 < \delta < 1.4$ $\delta > 1.4$
<i>pT</i> data						
Amagat (1893)	78	273 – 318	0.1 – 303.9	0.78	0.081	0.216
Blanke (1977)	110	60 – 169	0.0 – 4.9	0.78	0.227	3.197
DiPippo and Kestin (1968)	30	296 – 773	0.0 – 0.1	0.78	0.412	
Diller <i>et al.</i> (1991)	64	70 – 130	3.4 – 32.2	0.78		0.275
Eckl <i>et al.</i> (2009)	81	213 – 1273	2.0 – 200.0	0.78	0.338	0.895
Eucken and Hauck (1928)	16	137 – 164	5.4 – 16.2	0.78		12.985
Fleeter <i>et al.</i> (1980)	33	300	0.8 – 36.1	0.78	0.175	0.252
Holborn and Schultze (1915)	42	273 – 473	1.9 – 10.0	0.78	0.035	
Howley <i>et al.</i> (1994)	286	67 – 399	1.0 – 35.1	0.78	0.110	0.139
Iwasaki (1951)	28	323 – 423	2.1 – 19.8	0.78	0.321	
Kestin and Leidenfrost (1959)	18	293 – 298	0.0 – 6.9	0.78	0.049	
Kestin and Whitelaw (1964)	42	297 – 523	0.1 – 14.4	0.78	0.066	
Klingenberg and Ulbig (2007)	32	300 – 501	0.8 – 18.5	0.78	0.041	
Kozlov (1968)	345	287 – 873	1.2 – 72.2	0.78	0.079	0.128
Latto and Saunders (1973)	26	100 – 398	0.1 – 14.5	0.78	1.548	1.429
Magee (1994)	226	66 – 298	1.7 – 34.6	0.78	0.097	0.136
Michels <i>et al.</i> (1954a)	157	273 – 348	0.7 – 228.2	0.78	0.068	0.113
Michels <i>et al.</i> (1954b)	199	118 – 248	0.5 – 102.2	0.78	0.156	0.394
Penning (1923)	62	128 – 293	2.5 – 6.2	0.78	0.169	
Rogovaya and Kaganer (1960)	10	273	4.7 – 8.5	0.78	0.084	
Romberg (1971)	124	84 – 122	0.0 – 1.9	0.78	0.075	
Scott <i>et al.</i> (1981)	43	309 – 375	0.8 – 23.8	0.78	0.071	0.066
Ulbig <i>et al.</i> (2005)	187	295 – 546	0.1 – 18.5	0.78	0.124	
Vassermann <i>et al.</i> (1976)	109	77 – 198	2.6 – 59.8	0.78		0.245
Wöll (2005)	88	298 – 500	0.1 – 16.8	0.78	0.220	
Speed of sound						
Abbey and Barlow (1948)	6	293	0.0 – 0.1	0.78	0.391	
Boyer (1951)	11	273	0.0	0.78	1.504	

Table A2.2 continued...

Air: $x_1\text{N}_2 + x_2\text{O}_2 + x_3\text{Ar}$ continued						
Authors	N	T [K]	p [MPa]	x_1	$\delta < 0.6$	AAD [%] $0.6 < \delta < 1.4$ $\delta > 1.4$
Speed of sound continued						
Colwell and McGraw (1938)	9	297 – 299	0.1	0.78	0.063	
Colwell and Gibson (1941)	7	273	0.0	0.78	0.100	
Ewing and Goodwin (1993)	13	255	0.0 – 6.8	0.78	0.008	
Hardy <i>et al.</i> (1942)	7	273 – 296	0.0 – 0.1	0.78	1.786	
King and Partington (1930)	11	1137–1439	0.1	0.78	1.985	
Quigley (1945)	29	91 – 258	0.1	0.78	0.304	
Shilling and Partington (1928)	28	273–1572	0.1	0.78	1.432	
Tucker (1943)	6	292 – 346	0.0	0.78	2.453	
Ulbig <i>et al.</i> (2005)	107	300 – 450	0.0 – 16.3	0.78	0.016	
van Isterbeek and de Rop (1955)	44	229 – 312	0.1 – 1.3	0.78	0.211	
Younglove and Frederick (1992)	169	90 – 299	0.3 – 13.8	0.78	0.126	0.392
Isobaric heat capacity						
Eucken (1913)	6	271 – 480	0.1	0.78	0.530	
Holborn and Jakob (1914)	6	332	0.0 – 19.6	0.78	0.394	
Holborn and Jakob (1917)	7	333	0.0 – 29.4	0.78	0.453	0.360
Kistiakowsky and Rice (1939)	4	271 – 366	0.1	0.78	0.292	
Nesselmann (1925)	19	193 – 523	4.9 – 19.6	0.78	1.083	2.899
Pofel <i>et al.</i> (1959)	46	299 – 2499	0.3 – 1.0	0.78	3.897	
Isochoric heat capacity^c						
Chashkin <i>et al.</i> (1966)	57	127 – 137	ρ [mol/dm ³] 10.9	0.78	103.258	
Eucken and Hauck (1928)	16	137 – 164	18.0 – 18.9	0.78		5.589
Magee (1994)	227	66 – 298	2.0 – 32.9	0.78	0.558	0.452
2nd virial coefficient B^d						
Hilsenrath (1955)	61	49 – 1501			3.562	
Levelt Sengers <i>et al.</i> (1972)	54	100 – 1399			0.323	

^a The deviation of the composition of the first component in the saturated vapor and liquid phase is calculated and given in [mole %].^b The deviation of the dew and bubble point temperature is calculated and given in [K].^c The isochoric heat capacity is calculated at given temperature and density. Instead of the pressure range the density range is given in [mol/dm³].^d The deviation of the 2nd virial coefficient of the mixture is calculated and given in [cm³/mol]

Lebenslauf

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