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Abstract

A new mixture model for thermodynamic properties of CO_2-rich mixtures common for Carbon Capture and Storage applications was developed and presented by *Gernert (2013)*. The model allows calculations of mixtures containing carbon dioxide, water, nitrogen, oxygen, argon, and carbon monoxide. The structure of the model is compatible to other accurate mixture models in terms of the reduced Helmholtz energy, and in particular to the GERG-2008 equation of state for natural gas mixtures developed by *Kunz and Wagner (2012)*, which uses a very similar mathematical structure. This way a description of multicomponent mixtures containing further components becomes possible.

Within WP 1.2 a thorough validation of the new model was carried out. This validation was based on detailed comparisons with selected experimental data and other established models. For the components that were identified as most relevant for applications covered by IMPACTS, particular attention was paid to the comparison of the new mixture model with the GERG-2008 equation of state.

In comparisons to existing experimental data the model by *Gernert (2013)* proves to be the (so far) best fit to all reliable data points. The representation of the data and the extrapolation behavior are comparable or better for all binary mixtures than for GERG-2008. Significant improvements were achieved in the description of thermodynamic properties for binary mixtures with water.

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1 INTRODUCTION

The aim of the IMPACTS project is to investigate the impact of impurities in CO_2-rich mixtures on Carbon Capture and Storage (CCS) applications. This requires extensive knowledge of the thermodynamic properties of these mixtures. Calculating thermodynamic properties requires accurate equations of state that provide a mathematical description of the physical behavior of the mixtures.

As a member of Work Package 1.2 ("Thermophysical behavior of CO_2 mixtures") the thermodynamics group of Ruhr-University Bochum (RUB) is developing a reference equation of state for a specified list of mixture-components found to be relevant in CCS applications. This list of components was defined in WP 1.1 and at the WP 1.2 workshop held at RUB in January 2013. The current version of the reference model was developed by Johannes Gernert and is presented in his PhD thesis, which has already been distributed via the IMPACTS eRoom (see *Gernert, 2013*). The model is referred to as "equation of state for combustion gases and combustion gas like mixtures" (EOS-CG) and allows for calculations of mixtures containing carbon dioxide, water, nitrogen, oxygen, argon, and carbon monoxide.

The purpose of this report is a detailed validation of the EOS-CG mixture model. This validation is based on comparisons with the available experimental data and other selected models, in particular with the GERG-2008 equation of state for natural gas mixtures developed by *Kunz and Wagner (2012),* which is based on a very similar mathematical structure.

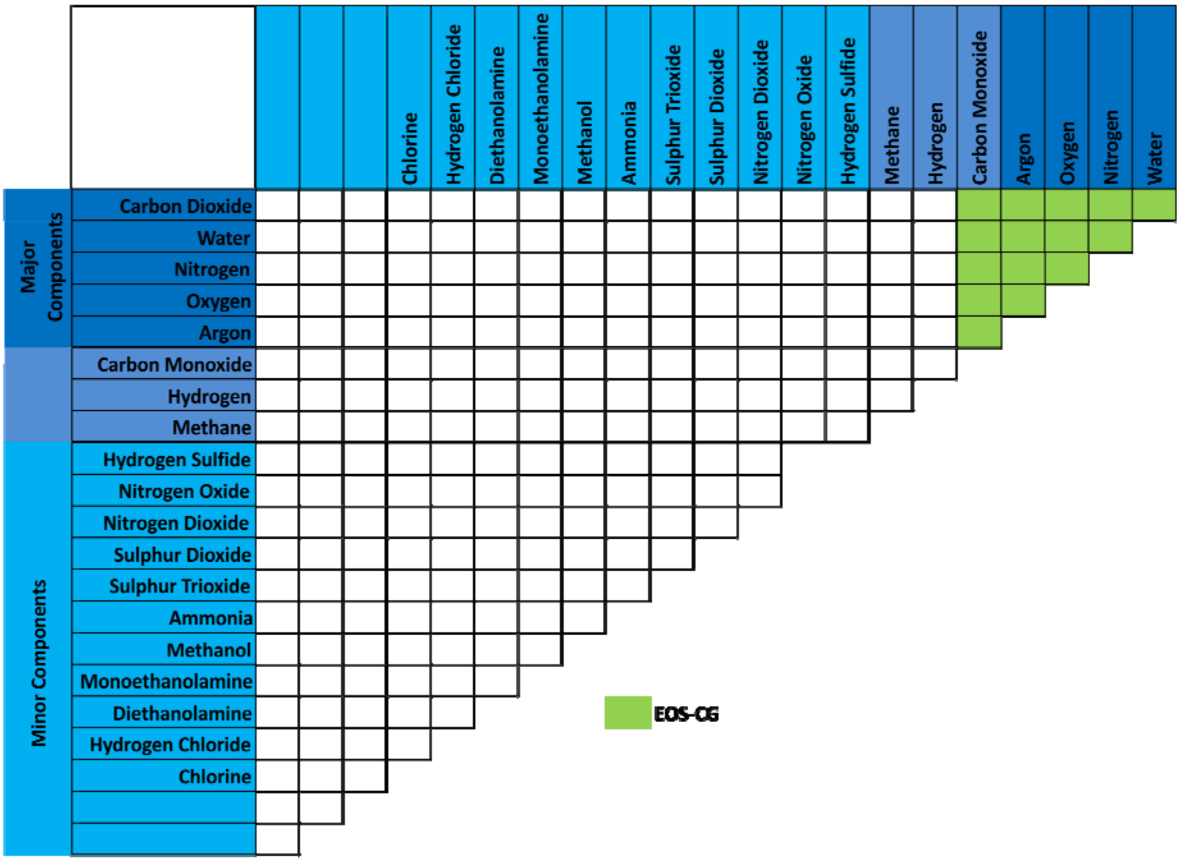
For the comprehension of the present report some basic information on the validity and mathematical structure of the model are essential. This information is given in chapter 2. Comparisons of the new mixture model with experimental data and other models are discussed in the third chapter. The report concludes with a summary of the validation results and an outlook to future work.

2 THE EQUATION OF STATE FOR COMBUSTION GASES AND COMBUSTION GAS LIKE MIXTURES

The reference model for thermodynamic properties of CCS mixtures validated in this work is referred to as “equation of state for combustion gases and combustion gas like mixtures” (EOS-CG). The model is presented in detail in the PhD thesis of *Gernert (2013),* which has already been distributed via the IMPACTS eRoom. For the comprehension of the present report some basic information on the validity and mathematical structure of the model is essential. The components and mixtures considered in the EOS-CG mixture model are given in section 2.1. The general structure of the model is described in section 2.2.

2.1 Components and Mixtures considered in the Model

The EOS-CG mixture model is proposed for mixtures of carbon dioxide, water, nitrogen, oxygen, argon, and carbon monoxide. Thus, it covers 15 of the binary mixtures found to be relevant within the IMPACTS project. The list of binary mixtures contains the ten systems considered as “mixtures of major components” plus five mixtures including carbon monoxide (one of the three secondary components) and major components. The complete matrix of binary mixtures considered relevant for IMPACTS is shown in Figure 2.1.



					Chlorine	Hydrogen Chloride	Diethanolamine	Monoethanolamine	Methanol	Ammonia	Sulphur Trioxide	Sulphur Dioxide	Nitrogen Dioxide	Nitrogen Oxide	Hydrogen Sulfide	Methane	Hydrogen	Carbon Monoxide	Argon	Oxygen	Nitrogen	Water
Major Components	Carbon Dioxide																	🟩	🟩	🟩	🟩	🟩
	Water																	🟩	🟩	🟩	🟩	
	Nitrogen																	🟩	🟩	🟩		
	Oxygen																	🟩	🟩			
	Argon																	🟩				
	Carbon Monoxide																					
	Hydrogen																					
	Methane																					
Minor Components	Hydrogen Sulfide																					
	Nitrogen Oxide																					
	Nitrogen Dioxide																					
	Sulphur Dioxide																					
	Sulphur Trioxide																					
	Ammonia																					
	Methanol																					
	Monoethanolamine																					
	Diethanolamine																					
	Hydrogen Chloride																					
	Chlorine																					

🟩 EOS-CG

Figure 2.1: Matrix of relevant binary mixtures.

2.2 General Structure

The general structure of the EOS-CG mixture model is equivalent to the structure of the GERG-2004 equation of state for natural gas mixtures developed by *Kunz et al. (2007)*. It is a so called "fundamental equation of state". Equations of this type allow for a calculation of all thermodynamic properties simply by combining their derivatives. The most commonly used form is explicit in the Helmholtz free energy a. The functional form depends on the independent variables density ρ, temperature T, and molar composition $\bar{x}$. In practical applications it is common to work with dimensionless equations. Written in a dimensionless reduced form the general structure of the EOS-CG mixture model reads:

$$\frac{a(\rho,T,\bar{x})}{RT}=\alpha(\delta,\tau,\bar{x})=\alpha^{\mathrm{o}}(\rho,T,\bar{x})+\alpha^{\mathrm{r}}(\delta,\tau,\bar{x}) \tag{2.1}$$

with α as the reduced Helmholtz free energy, δ as the reduced mixture density and τ as the inverse reduced mixture temperature according to

$$\delta=\frac{\rho}{\rho_{\mathrm{r}}(\bar{x})} \text{ and } \tau=\frac{T_{\mathrm{r}}(\bar{x})}{T}. \tag{2.2}$$

The functional form as formulated in equation (2.1) is split in two parts. The first part α^{o} describes the behavior of the hypothetical mixture of ideal gases whereas α^{r} represents the residual Helmholtz energy that results from molecular interactions in the real mixture. The ideal-gas part of the equation is given as:

$$\alpha^{\mathrm{o}}(\rho,T,\bar{x})=\sum_{i=1}^{N}x_i\left[\alpha_{\mathrm{o},i}^{\mathrm{o}}\left(\delta_{\mathrm{o},i},\tau_{\mathrm{o},i}\right)+\ln x_i\right] \tag{2.3}$$

where N is the number of components in the mixture and $\alpha_{\mathrm{o},i}^{\mathrm{o}}$ 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 ideal-gas Helmholtz free energy of each component is calculated at the reduced density $\delta_{\mathrm{o},i}$ and temperature $\tau_{\mathrm{o},i}$. For pure fluids, density and temperature are usually reduced by their values at the critical point. Therefore, the reduced parameters are defined as:

$$\delta_{\mathrm{o},i}=\frac{\rho}{\rho_{\mathrm{c},i}} \text{ and } \tau_{\mathrm{o},i}=\frac{T_{\mathrm{c},i}}{T}. \tag{2.4}$$

The residual part of the Helmholtz free energy of the mixture reads:

$$\alpha^{\mathrm{r}}(\rho,T,\bar{x})=\sum_{i=1}^{N}x_i\alpha_{\mathrm{o},i}^{\mathrm{r}}(\delta,\tau)+\Delta\alpha^{\mathrm{r}}(\delta,\tau,\bar{x}). \tag{2.5}$$

In this equation $\alpha_{\mathrm{o},i}^{\mathrm{r}}$ is the residual, reduced Helmholtz free energy of the component i, whereas δ and τ are the reduced density and temperature (of the pure component) according to equation (2.4) and $\Delta\alpha^{\mathrm{r}}$ is the so-called departure function, which is defined as:

$$\Delta\alpha^{\mathrm{r}}(\delta,\tau,\bar{x})=\sum_{i=1}^{N}\sum_{j=i+1}^{N}x_ix_jF_{ij}\alpha_{ij}^{\mathrm{r}}(\delta,\tau). \tag{2.6}$$

The departure function includes the binary specific departure function α_{ij}^{r} for the components i and j and the weighing factor F_{ij}, which enables the use of generalized departure functions for a group of binary systems (see *Lemmon and Jacobsen, 1999*).

The binary specific departure function is an empirical model that is only loosely tied to physical information. Its mathematical structure contains polynomials, exponential terms and so-called special exponential terms. These special terms were first introduced by *Klimeck (2000)* to reach a more accurate description of phase boundaries than by means of simple exponential terms, especially in the critical region. The complete functional form can be written as:

$$\begin{aligned}\alpha_{ij}^{\mathrm{r}}(\delta,\tau) = {} & \sum_{k=1}^{K_{\mathrm{pol},ij}} n_{ij,k}\delta^{d_{ij,k}}\tau^{t_{ij,k}} + \sum_{k=K_{\mathrm{pol},ij}+1}^{K_{\mathrm{pol},ij}+K_{\mathrm{exp},ij}} n_{ij,k}\delta^{d_{ij,k}}\tau^{t_{ij,k}} \exp\left(-\delta^{l_{ij,k}}\right) \\ & + \sum_{k=K_{\mathrm{pol},ij}+K_{\mathrm{exp},ij}+1}^{K_{\mathrm{pol},ij}+K_{\mathrm{exp},ij}+K_{\mathrm{spec},ij}} n_{ij,k}\delta^{d_{ij,k}}\tau^{t_{ij,k}} \exp\left[-\eta_{ij,k}\left(\delta-\varepsilon_{ij,k}\right)^2-\beta_{ij,k}\left(\delta-\gamma_{ij,k}\right)\right].\end{aligned} \tag{2.7}$$

The number of terms is chosen by the correlator while fitting the equation to experimental thermodynamic properties of the binary mixture of the components i and j. 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 varied by a fitting algorithm to obtain the best agreement between the experimental data and the properties calculated from the equation of state. The parameters η_{ij}, ε_{ij}, β_{ij}, and γ_{ij} are mathematically connected and cannot be treated as independent parameters in the fitting process. In the development of the EOS-CG model ε_{ij} and γ_{ij} were fixed and only η_{ij} and β_{ij} were fitted (see *Gernert, 2013*).

The reduced mixture temperature τ and density δ were defined in equation (2.2). From this equation it becomes obvious that the temperature T and density ρ are not reduced by their values at the critical point for mixture calculations. This is evident because each component in the mixture has different critical parameters and the overall critical point of the mixture is quite difficult to determine. For this reason *Kunz et al. (2007)* formulated the reducing functions $T_{\mathrm{r}}(\bar{x})$ and $\rho_{\mathrm{r}}(\bar{x})$ that span a composition-dependent surface between the critical parameters for density and temperature of the pure components in the mixture. These functions are defined as:

$$T_{\mathrm{r}}(\bar{x}) = \sum_{i=1}^{N} x_i^2 T_{\mathrm{c},i} + \sum_{i=1}^{N-1}\sum_{j=j+1}^{N} 2x_i x_j \beta_{T,ij}\gamma_{T,ij} \frac{x_i+x_j}{\beta_{T,ij}^2 x_i + x_j}\left(T_{\mathrm{c},i}T_{\mathrm{c},j}\right)^{0,5} \tag{2.8}$$

and

$$\frac{1}{\rho_{\mathrm{r}}(\bar{x})} = \sum_{i=1}^{N} x_i^2 \frac{1}{\rho_{\mathrm{c},i}} + \sum_{i=1}^{N-1}\sum_{j=j+1}^{N} 2x_i x_j \beta_{v,ij}\gamma_{v,ij} \frac{x_i+x_j}{\beta_{v,ij}^2 x_i + x_j}\frac{1}{8}\left(\frac{1}{\rho_{\mathrm{c},i}^{1/3}}+\frac{1}{\rho_{\mathrm{c},j}^{1/3}}\right)^3. \tag{2.9}$$

The reducing functions contain the binary parameters β and γ, which are fitted to experimental data and obey the symmetry rules as given by:

$$\beta_{T,ij} = \frac{1}{\beta_{T,ji}}, \quad \beta_{v,ij} = \frac{1}{\beta_{v,ji}} \quad \text{and} \quad \gamma_{T,ij} = \gamma_{T,ji}, \quad \gamma_{v,ij} = \gamma_{v,ji}. \tag{2.10}$$

The general structure of the mixture model includes two functional forms that represent the contribution of the pure fluids ($\alpha_{\mathrm{o},i}^{\mathrm{o}}$ and $\alpha_{\mathrm{o},i}^{\mathrm{r}}$) and three functional forms which represent the contribution of the mixture ($\rho_{\mathrm{r}}\left(\bar{x}\right)$, $T_{\mathrm{r}}\left(\bar{x}\right)$, and α_{ij}^{r}). For the description of the pure fluid contributions *Kunz et al. (2007)*, the originators of the GERG-2004 equation of state, which was an almost identical precursor of the GERG-2008 model discussed in this report, developed new Helmholtz equations of state. These equations of state are slightly less accurate than the corresponding reference equations of state, but have a significantly smaller number of terms. Frequently, equations with a smaller number of terms show a more reasonable extrapolation behavior and are more practical for calculations in the two-phase region – two important advantages for the calculation of mixture properties. In the EOS-CG model the pure fluid contributions are described by means of the reference equations of state. Thus, the transition from mixture to pure fluid calculations is consistent on the level of the best available equations of state. Another important reason for this decision is that the pure fluid equation of state for water used in the GERG-2004 / -2008 model shows considerable deviations from the IAPWS-95 reference equation by *Wagner and Pruß (2002)*, particularly in the liquid region. As mentioned earlier GERG-2004 and -2008 were originally developed for the description of natural gas mixtures, which contain only small amounts of water. Consequently, the inaccuracy in the calculation of properties of water is acceptable for this application. When calculating properties for mixtures with higher water content (like in CCS mixtures) this aspect becomes more relevant. The reference equations of state included in the EOS-CG mixture model are given in Table 2.1.

Table 2.1: Equations of state used for the pure fluid components in the EOS-CG mixture model.

Component	**Formula**	**Pure fluid equation used in EOS-CG mixture model**
Carbon dioxide	CO_2	Reference equation of state by *Span und Wagner (1996)*
Water	H_2O	Reference equation of state by *Wagner and Pruß (2002)*
Nitrogen	N_2	Reference equation of state by *Span et al. (2000)*
Oxygen	O_2	Reference equation of state by *Schmidt and Wagner (1985)*
Argon	Ar	Reference equation of state by *Tegeler et al. (1999)*
Carbon monoxide	CO	Short industrial equation of state by *Lemmon and Span (2006)*

The calculation of properties from the Helmholtz free energy mixture model will not be described in this work; it was discussed in detail in the PhD thesis of *Gernert (2013)*. His work also presents all parameters of the reducing functions and the binary departure functions of the 15 binary systems included in the EOS-CG model.

3 COMPARISON OF THE EOS-CG MIXTURE MODEL WITH EXPERIMENTAL DATA AND OTHER MODELS

The EOS-CG mixture model as introduced in section 2 will be validated based on comparisons with available experimental data and other selected models. Of particular interest are the comparisons with the GERG-2008 model developed by *Kunz and Wagner (2012)* – an extended version of the GERG-2004 model (see *Kunz et al.*, *2007*) covering mixtures of 21 instead of 18 components. The GERG-2008 model uses essentially the same mathematical structure as EOS-CG. For binary mixtures with water some additional comparisons are made with the cubic equation of state of *Holderbaum and Gmehling (1991)* (the so called Predictive Soave-Redlich-Kwong (PSRK) EOS) and with the virial equation of *Plöcker et al. (1978)* (the so called Lee-Kesler-Ploecker (LKP) EOS).

The representation of experimental data is mainly discussed by means of deviation plots or absolute plots showing the shape of specific properties depending on e.g. temperature, pressure or molar composition. The relative deviations illustrated in the plots are defined as:

$$\Delta z_{\mathrm{rel}} = 100 \cdot \left(\frac{z_{\mathrm{exp}} - z_{\mathrm{calc}}}{z_{\mathrm{calc}}} \right) \tag{3.1}$$

with z_{exp} as the experimental value of the state property z and z_{calc} as the respective value calculated from the mixture model. Absolute deviations are given by:

$$\Delta z_{\mathrm{tot}} = z_{\mathrm{exp}} - z_{\mathrm{calc}}. \tag{3.2}$$

Comparisons of the model with a complete data set are mainly based on the average absolute deviation (AAD), which is defined as the arithmetic average of the absolute value of all deviations of the M data points of a data set. The AAD value is calculated according to:

$$\mathrm{AAD} = \frac{1}{M} \sum_{m=1}^{M} \left| \Delta z_{\mathrm{rel},m} \right|. \tag{3.3}$$

Due to the large amount of available experimental information not all data can be discussed in this report. Thus, the validation of the EOS-CG mixture model is mainly based on a discussion of selected $p\rho T$ and $pTxy$ data. Additional plots, comments and special characteristics of some binary mixtures can be found in the PhD thesis of *Gernert (2013)*, in which the new mixture model is introduced.

3.1 Binary Mixtures with Carbon Dioxide

Due to the comparable shape and range of their two-phase regions it is reasonable to validate the representation of binary mixtures of CO_2 with nitrogen, oxygen, argon and CO in one section. The two-phase region of each mixture is limited by the critical temperature of CO_2 ($T_{\mathrm{c,CO2}} \approx 304$ K) as the upper boundary. The lower boundary is the freezing point of CO_2, which depends on the pressure and can be obtained from the sublimation or melting line. The pressure range of this region extends from the triple point pressure of CO_2 ($p_{\mathrm{tp,CO2}} \approx 0.52$ MPa) to about 20 MPa depending on the binary system and the composition. If the CO_2 content in the mixture is lower than about 5 mole-% the mixture will not split into two fluid phases but CO_2 will dissolve completely in the other component. If such a CO_2-poor mixture is cooled down below the sublimation or freezing temperature of pure CO_2 it will form a solid phase in equilibrium with a vapor phase.

3.1.1 Carbon Dioxide + Nitrogen

After a careful evaluation of the available experimental data, *Gernert (2013)* adopted the parameters of the functional form for the system carbon dioxide + nitrogen from the GERG-2008 without any new fitting. The existing parameters were considered as the optimal fit to the data and the physical behavior of the equation was found to be reasonable.

The number of publications presenting experimental $p\rho T$ data is plentiful, including measurements over a wide density range, the major part of the composition range, and for temperatures from 200 K to 700 K. In the vapor phase, the best agreement between the model and the experimental data was reached for the highly accurate measurements of *Jaeschke and Humphreys (1991)*. The data is reproduced with an AAD of 0.025 % and a maximum deviation of about $\pm 0.1\,\%$. In the supercritical region, there are less accurate data points of e.g. *Brugge et al. (1997)*, *Bailey et al. (1989)* and some recent measurements of *Mondéjar et al. (2012)*. The model represents these data with maximum deviations less than $\pm 1\,\%$. In the liquid-like phase the uncertainty of the model is estimated to be $\pm 0.5\,\%$. A selection of deviation plots for the vapor and liquid-like phase is given in Figure 3.1.

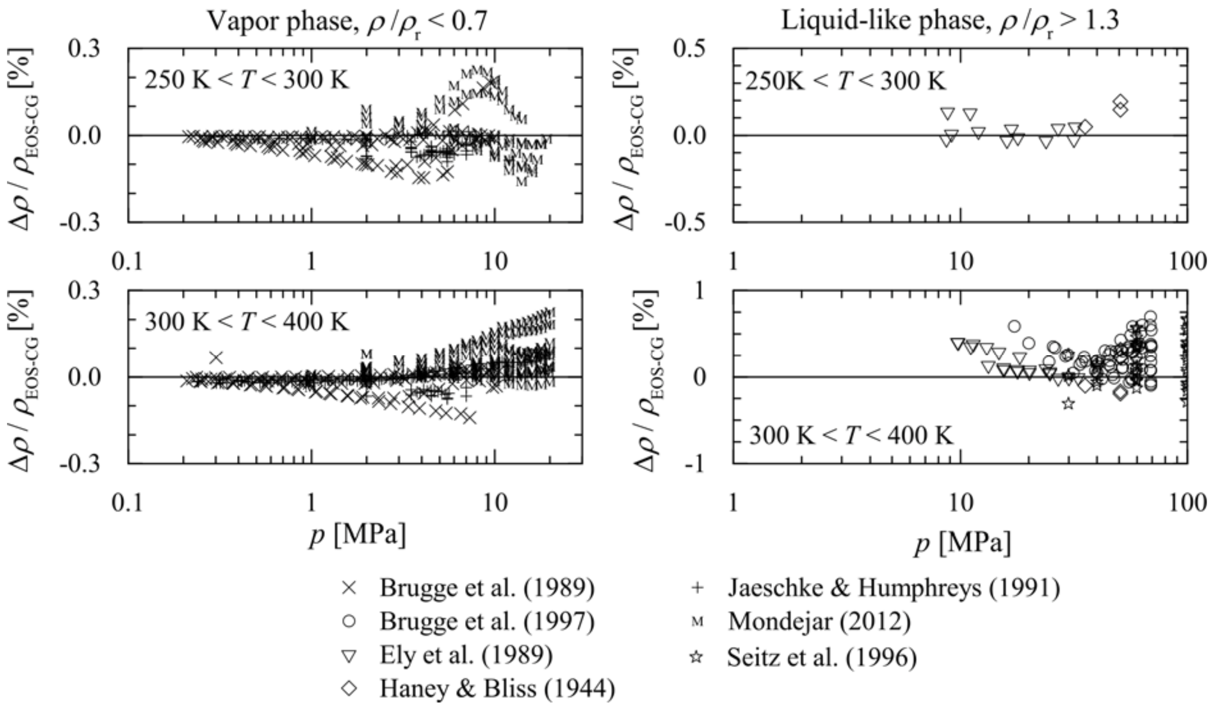


Figure 3.1: Deviations between selected $p\rho T$ data and the new mixture model for the system carbon dioxide + nitrogen.

The phase boundaries of the system carbon dioxide + nitrogen are presented in more than 20 publications including measurements over the whole fluid range except for pressures close to the critical pressure. Thus, the model shows good representation of the existing data up to about 0.8 p_c (see Figure 3.2).

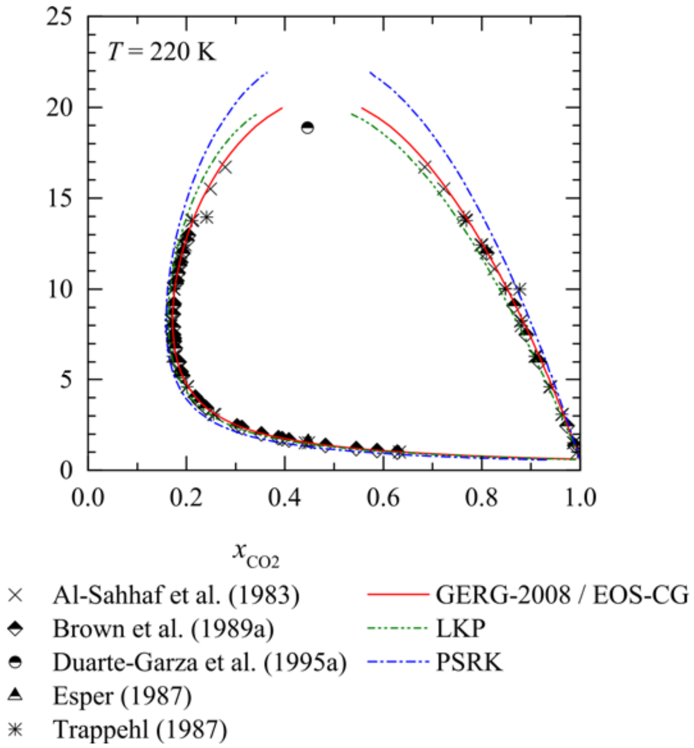


Figure 3.2: Experimental and calculated phase boundaries of the system carbon dioxide + nitrogen at 220 K.

The figure illustrates that at higher pressures the few available data points suggest that the model overestimates the bubble pressure line by up to 1 MPa. At given composition and pressure (up to 10 MPa) the experimental dew and bubble point temperatures are mainly reproduced within $\pm 1\,\mathrm{K}$. For a given temperature and pressure the experimental phase composition are recalculated within ± 0.5 mole-% in the saturated liquid phase and ± 0.8 mole-% in the gas phase.

Experimental speed of sound data for binary mixtures is generally spare. However, for the mixture of carbon dioxide and nitrogen three data sets are available. The accurate data of *Younglove et al. (1993)* include measurements up to 10 MPa and are reproduced within $\pm 1\,\%$. The remaining two data sets are significantly less accurate and will therefore not be discussed in this report.

Recently, the binary mixture model for carbon dioxide + nitrogen included in EOS-CG was employed in some pipeline simulations at SINTEF Energi AS, Norway. During these calculations it became apparent, that some isotherms are difficult to evaluate for metastable conditions, because common density solver algorithms like the ones implemented in the TREND or REFPROP software packages (see *Span et al.*, *2012* and *NIST*, *2013*) do not find a meaningful density value and are therefore not able to predict the two phases. This problem is described in more detail in the memo of *Aursand and Aashammer Gjennestad (2013)*.

Due to some adjustments by RUB, the density solver employed in the new Version 1.1 of TREND (see *Span et al.*, *2013*) now accepts density solutions in the problematic region and computes the correct phase split. However, essentially the observed problems have to be considered a shortcoming of the model, which needs to be addressed in future work. This might also include modifications of the employed pure fluid equations of state, since first studies suggest that the problem is caused by an unreasonable (in the sense of problematic for application in mixture models) behavior of the pure fluid equations in their two-phase regions.

3.1.2 Carbon Dioxide + Argon

The amount and accuracy of the experimental data for the binary system carbon dioxide + argon was considered sufficient to fit not only the reducing functions $T_{\mathrm{r}}(\bar{x})$ and $1/\rho_{\mathrm{r}}(\bar{x})$ but also the specific binary departure function. Due to the quite similar behavior of this system and the binary mixtures of carbon dioxide + nitrogen, the parameters of the departure function for carbon dioxide + nitrogen were used as starting values in the fitting process. The functional form was fitted to experimental vapor-liquid equilibrium (VLE), $p\rho T$ and Joule-Thomson coefficient data.

The $p\rho T$ data base contains seven references that cover the vapor, liquid-like and supercritical regions for temperatures between 288 K and 573 K and pressures up to 100 MPa. In general, these data are not as accurate as the best measurements for the system carbon dioxide + nitrogen. The model represents the data of *Altunin and Koposhilov (1976)*, *Altunin and Koposhilov (1977)*, and *Schönmann (1971)* with acceptable deviations, namely $\pm 0.5\,\%$ in the gas phase at elevated temperatures or low pressures, and $\pm 1\,\%$ near the phase boundary. The measurements of *Kosov and Brovanov (1975)* and *Mantovani et al. (2012)* already show considerable deviations at low pressures. Therefore, *Gernert (2013)* considered these data as not accurate enough to be included in the fitting process. This evaluation seems to be reasonable with regard to the inconsistency of these measurements in the liquid phase. Deviation plots for the experimental data in the liquid and vapor phase are shown in Figure 3.3.

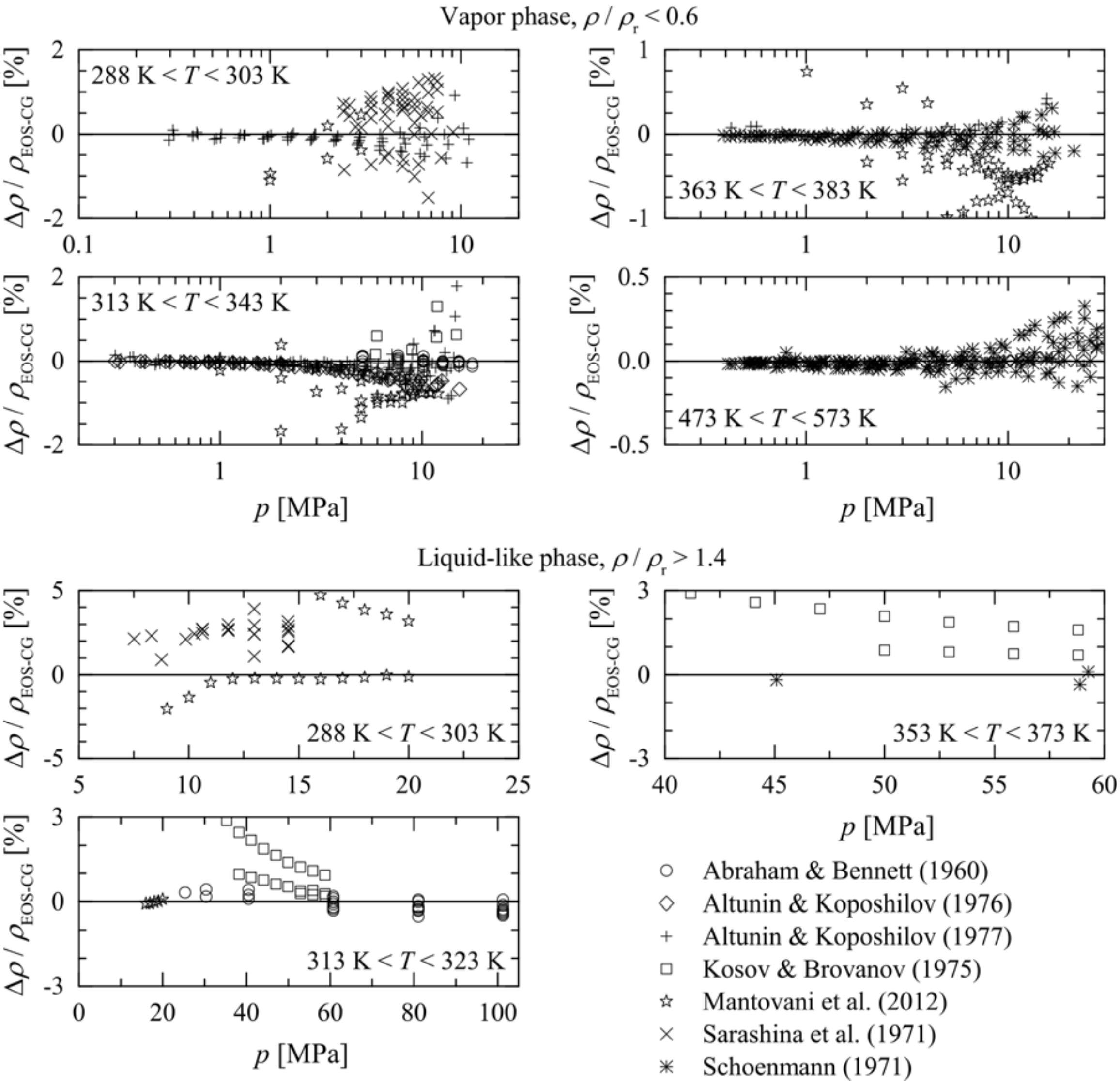


Figure 3.3: Deviations between selected $p\rho T$ data in the gas and liquid phase and the new mixture model for the system carbon dioxide + argon.

More detailed comparisons of the EOS-CG mixture model with experimental $p\rho T$ data for carbon dioxide + argon are included in the work of *Gernert (2013)*.

Experimental data for phase boundaries of the system carbon dioxide + argon are given in three references. The most recent one by *Coquelet et al. (2008)* presents *pTxy* measurements that were found to be the most accurate ones available. The right plot in Figure 3.4 illustrates that fitting the functional form of the mixture model to these data significantly improved the representation of phase boundaries (particularly at higher temperatures and pressures) compared to the GERG-2008 model.

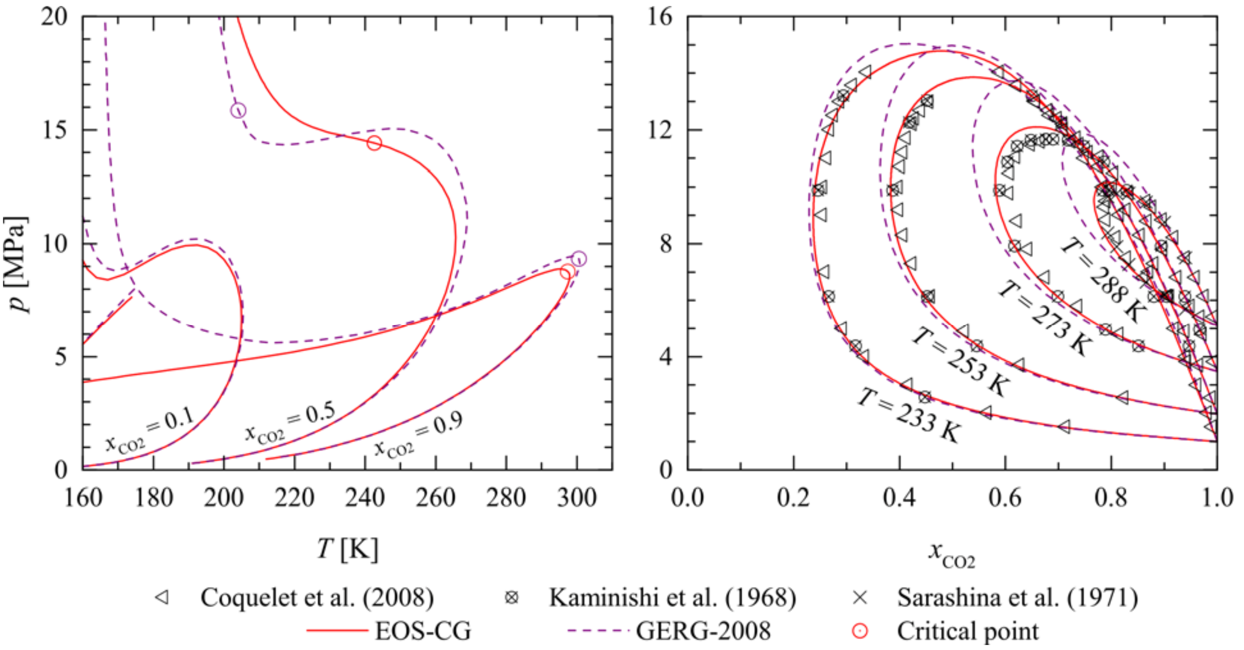


Figure 3.4: Description of the phase boundaries of the system carbon dioxide + argon by the GERG-2008 and the EOS-CG model.

The left diagram in Figure 3.4 depicts phase envelopes for three different compositions of the system carbon dioxide + argon as calculated with the EOS-CG mixture model and the GERG-2008 model. Along the dew line and at moderate pressures the models show close agreement. In contrast, the location of the maximum and critical pressure and the shape of the bubble line diverge strongly. With regard to the improved reproduction of the experimental data especially at higher temperatures and pressures this aspect is not surprising. However, a comparison of phase envelopes below temperatures around 216 K (depending on the composition) has only limited significance, because the system will probably form a solid phase that cannot be described by Helmholtz mixtures models alone.

The functional form of the model was also fitted to Joule-Thomson coefficient data. The only data available was measured by *Strakey et al. (1976)*. The authors claim an experimental uncertainty of 2.5 % in the gas phase and 1 % in the liquid phase. The reproduction of these data with the EOS-CG model is illustrated in Figure 3.5.

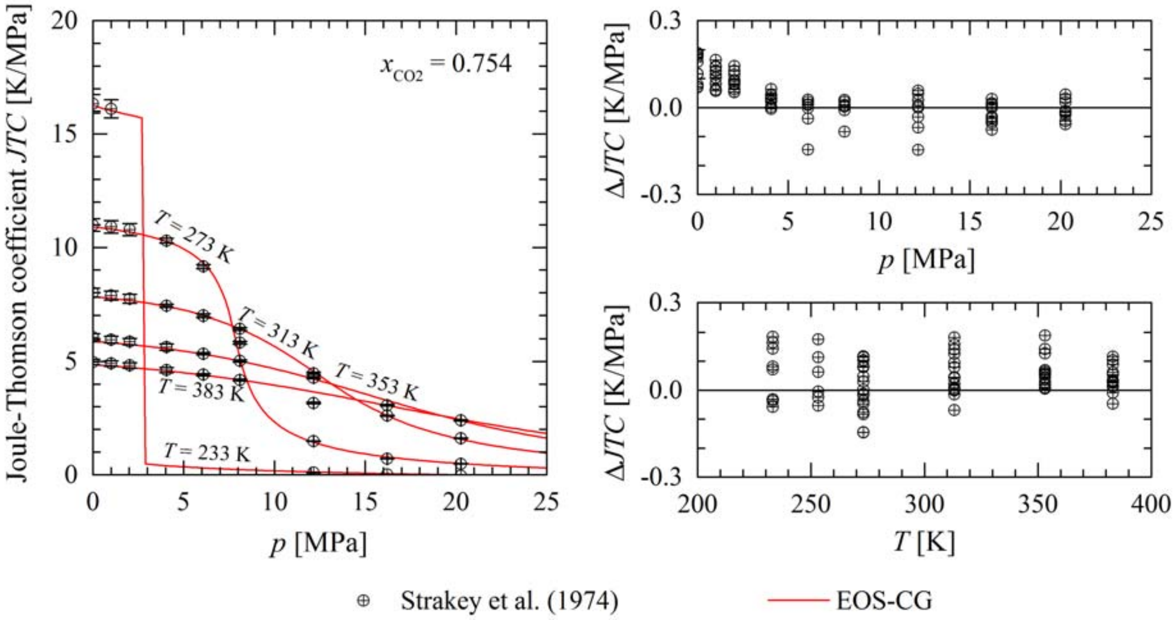


Figure 3.5: Absolute and relative deviations between experimental Joule-Thomson coefficient data and the EOS-CG mixture model.

The deviation plots (right side of figure 3.5) show that all data points are represented with maximum deviations of ±0.2 K/MPa, corresponding to less than ±2.5 %. The given uncertainty of 1 % in the liquid phase is not met by the model but was believed to be unrealistic by *Gernert (2013)* because the values of Joule-Thomson coefficients become very close to zero at high pressures. Thus, giving relative deviations is not meaningful in this region.

3.1.3 Carbon Dioxide + Oxygen and Carbon Dioxide + Carbon Monoxide

The very limited amount of experimental data for the binary systems carbon dioxide + oxygen and carbon dioxide + carbon monoxide did not enable the development of departure functions for these mixtures. Therefore, only the parameters of the reducing functions were adjusted.

For the mixture with oxygen the only available $p\rho T$ data were measured by *Mantovani et al. (2012)*. Like the measurements for carbon dioxide + argon presented in the same publication these data were not considered reliable and were therefore only partly included in the fit. In addition, *Muirbrook (1964)* measured some saturation densities for the 273 K isotherm. At lower pressures these values agree well with values calculated from the mixture model, but they show larger deviations closer to the critical pressure. However, due to the lack of comparative data these measurements will not be further discussed in this report.

Figure 3.6 illustrates phase boundaries calculated with the new EOS-CG model and the GERG-2008.

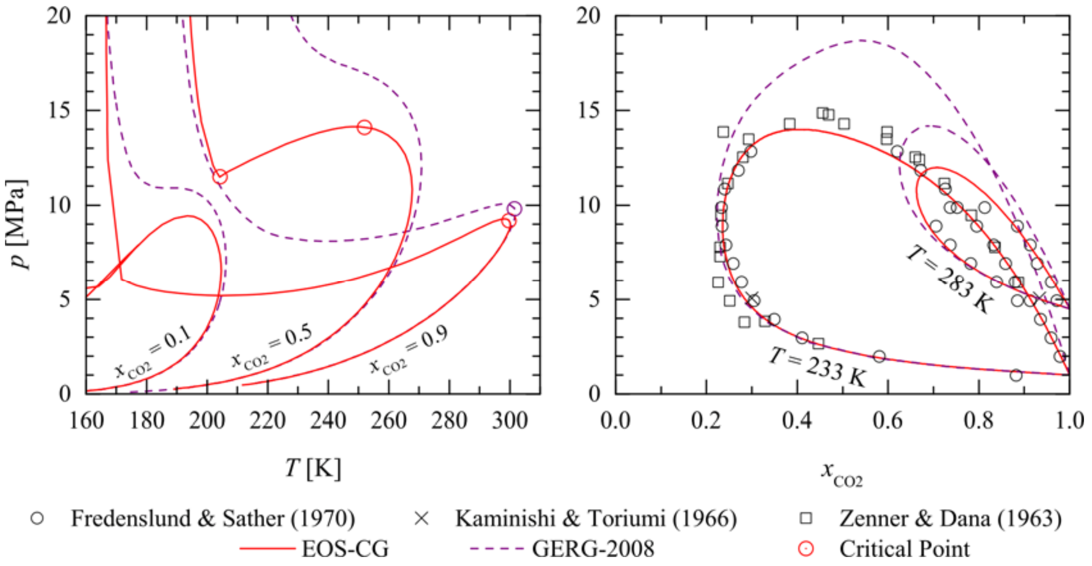


Figure 3.6: Description of the phase boundaries of the system carbon dioxide + oxygen by the GERG-2008 model and by the EOS-CG model.

Although the experimental VLE data scatter considerably, the description of the phase boundary was significantly improved compared to the GERG-2008 model. This improvement becomes particularly evident at the bubble line for higher oxygen contents and lower temperatures.

For the system carbon dioxide + carbon monoxide there are three $p\rho T$ and two VLE data sets available. Again, the available $p\rho T$ data cover such a limited area of the fluid phase that the uncertainty of the models can only be estimated. In the gas phase *Gernert (2013)* claims an uncertainty of ±1 % for EOS-CG, while liquid densities should be calculated within ± 2-3 %.
In comparison to the GERG-2008 the representation of VLE data achieved with the EOS-CG model is significantly better again. Nevertheless, it should be noted that the two data sets by *Christiansen et al. (1974)* and *Kaminishi et al. (1968)* diverge considerably (see Figure 3.7).

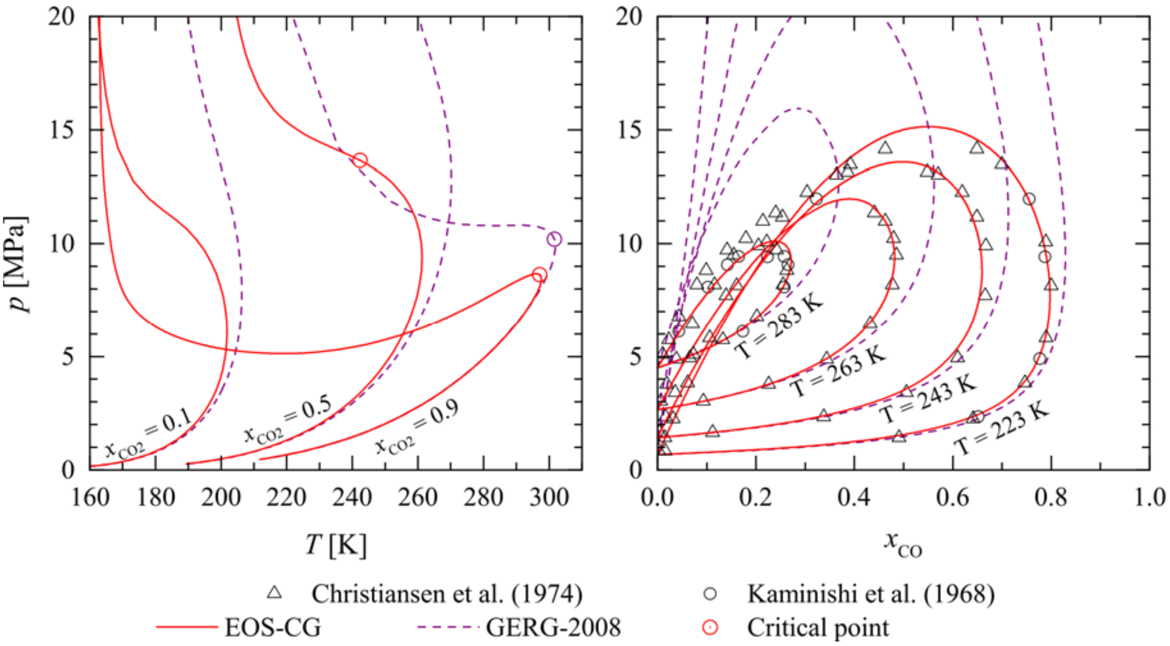


Figure 3.7: Description of the phase boundaries of the system carbon dioxide + carbon monoxide by the GERG-2008 and the EOS-CG model.

3.2 Binary Mixtures with Water

The EOS-CG mixture model includes binary mixtures of water with carbon dioxide, nitrogen, oxygen, argon and carbon monoxide. For all these systems the low solubility of the gases in water and the small water contents in saturated gases is characteristic. The difference between the critical values of water and the other components is large. In combination with the two characteristic features mentioned above, this leads to a wide *pTx* region where the system splits into two phases. This two-phase region is not limited by an upper pressure limit, but increases to “infinite” pressure. By contrast, the upper temperature limit corresponds approximately to the critical temperature of water and the lower limit to the formation temperature of ice or hydrates.

3.2.1 Water + Carbon Dioxide

Among all other binary mixtures included in the EOS-CG mixture model, the binary system water + carbon dioxide is probably the most complex one to describe. The unique characteristics of the system are discussed in several publications such as *Jäger et al. (2013)* or *Gernert (2013)* and will therefore not be repeated in this report. However, the complexity of the system required some compromises about fitting the experimental data. In the two-phase region it was not possible to fit the data over the whole temperature and pressure range. In the work of *Gernert (2013)* this problem is described as follows: “If the model was forced to follow the high-temperature, high-pressure data […] the phase compositions at lower temperatures were not represented well, and vice versa.”

In general, $p\rho T$ data for the system water + carbon dioxide are plentiful. There are almost 3000 available data points covering temperatures up to 1023 K and pressures up to 600 MPa. In the gas phase the most accurate densities are provided by *Patel and Eubank (1988)*. These measurements include CO_2 contents > 50 % and cover a temperature range between 323 K and 500 K at pressures up to 10 MPa. The new mixture model reproduces these data within ±0.2 % and with an AAD of 0.02 %. In addition, there are gas phase measurements by *Fenghour and Wakeham (1996)* and unpublished data by *McLinden (2011)* covering higher temperatures up to 700 K and pressures up to 35 MPa. The data are less accurate than the measurements of *Patel and Eubank (1988)* and are probably affected by some systematic errors. The EOS-CG model represents these data points with deviations up to ±2 %. The data situation in the liquid phase is questionable, too. The existing measurements diverge strongly (up to 1.5 %). For the development of the new mixture model the data set of *Hebach et al. (2004)* was considered the most reliable one. The data go well together with the measurements of *King et al. (1992)*. Both data sets are described within ±0.5 % over the whole pressure and temperature range and within ±0.2% up to 10 MPa. In the supercritical high-density region ($T > 650$ K and 30 MPa $< p <$ 600 MPa) the discrepancies between the different data sets are so significant that an accurate fit was impossible. The $p\rho T$ data situation is illustrated in the following two figures.

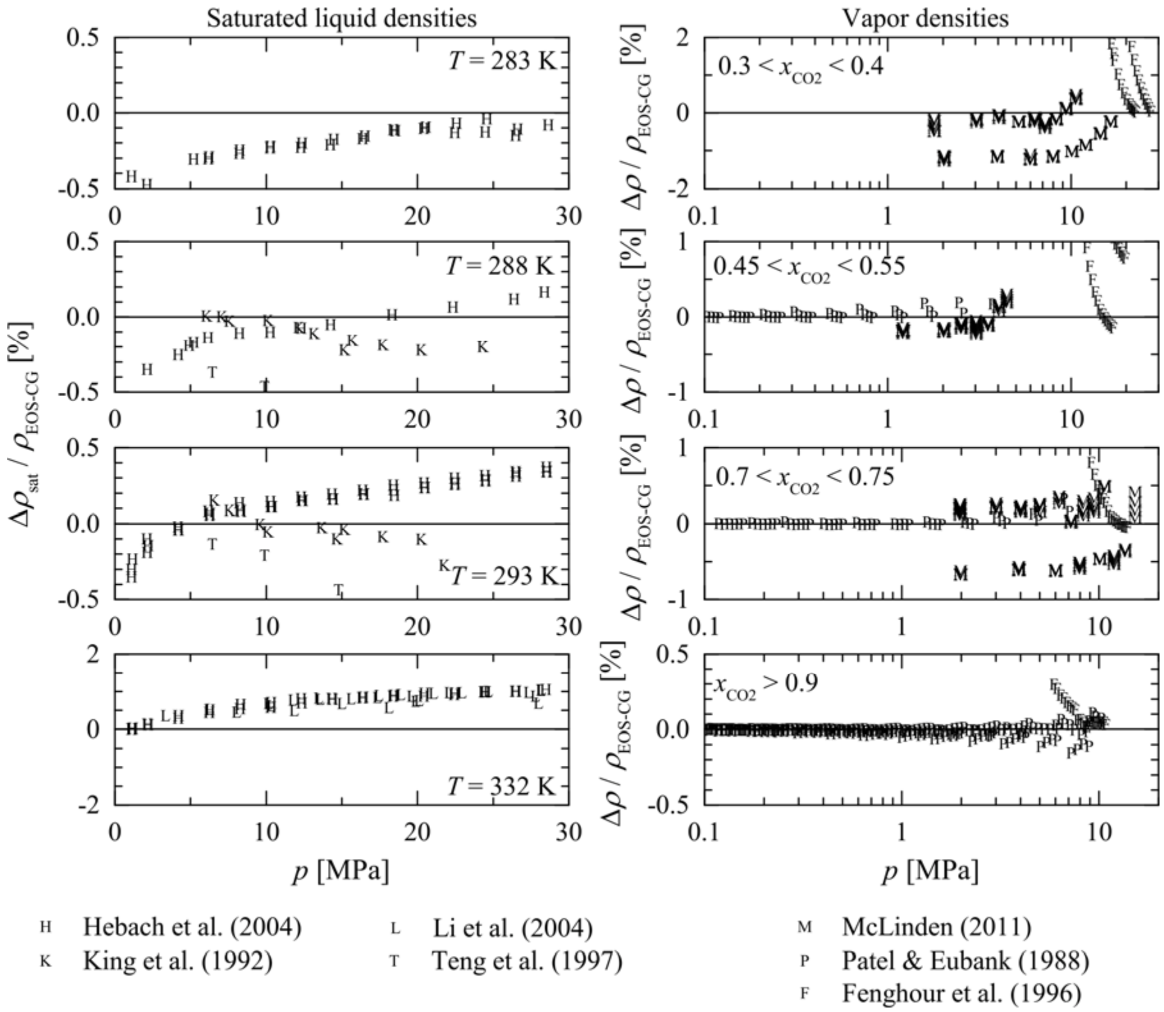


Figure 3.8: Deviations between selected experimental $p\rho T$ data and the new mixture model in the saturated liquid and vapor region for the system water + carbon dioxide.

Figure 3.8 shows some exemplary deviation plots for the saturated liquid and vapor region, whereas Figure 3.9 depicts deviations in the supercritical region as well as an absolute pressure over density plot along supercritical isotherms.

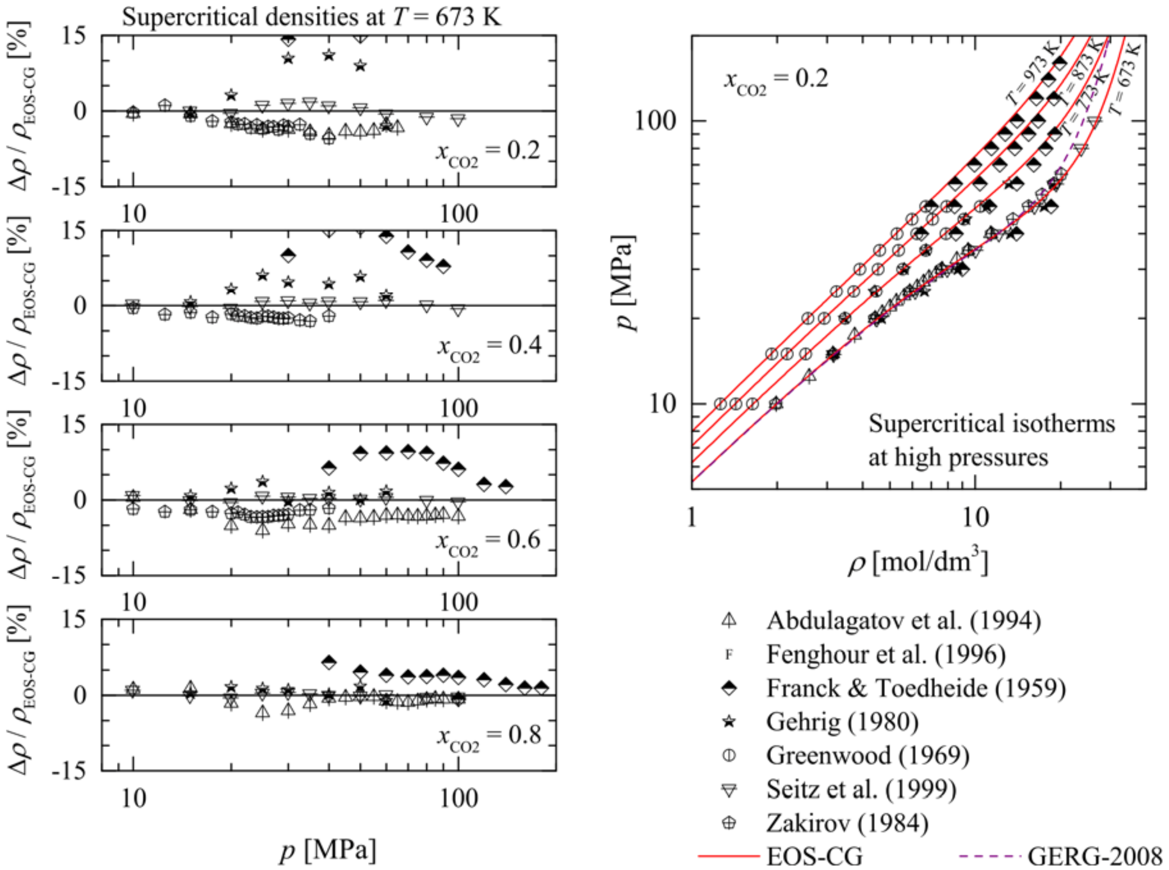


Figure 3.9: Left: Deviations between selected experimental $p\rho T$ data and the evaluated mixture models in the supercritical region for the system water + carbon dioxide. Right: Pressure over density along isotherms in the supercritical region including experimental data and different mixture models.

Although the amount of experimental values for the CO_2 solubility and saturated water content is comparably large, a majority of the data were only of limited importance in the fitting process. The reason for this is the low accuracy of some data sets and the fact that a large number of publications contains only information on one of the phases in equilibrium. The data cover the whole fluid range but the high-temperature and high-pressure VLE region is included only in the data sets of *Takenouchi and Kennedy (1964)* and *Tödheide and Franck (1963)*. These measurements show large differences in the phase compositions and critical pressures and were therefore found to be less accurate. In the low-temperature (VLE) region, accurate solubility data is given by *Anderson (2002)*, *Chapoy (2004)* and *Dalmolin et al. (2006)*. The new EOS-CG mixture model reproduces these data within maximum deviations of 0.2 mole-%. The agreement between experimental and calculated phase compositions is shown in Figure 3.10. The two absolute plots included in the figure also illustrate the representation of the data reached with the GERG-2008, with the cubic PSRK equation of state of *Holderbaum and Gmehling (1991)* and with the virial LKP equation of *Plöcker et al. (1978)*.

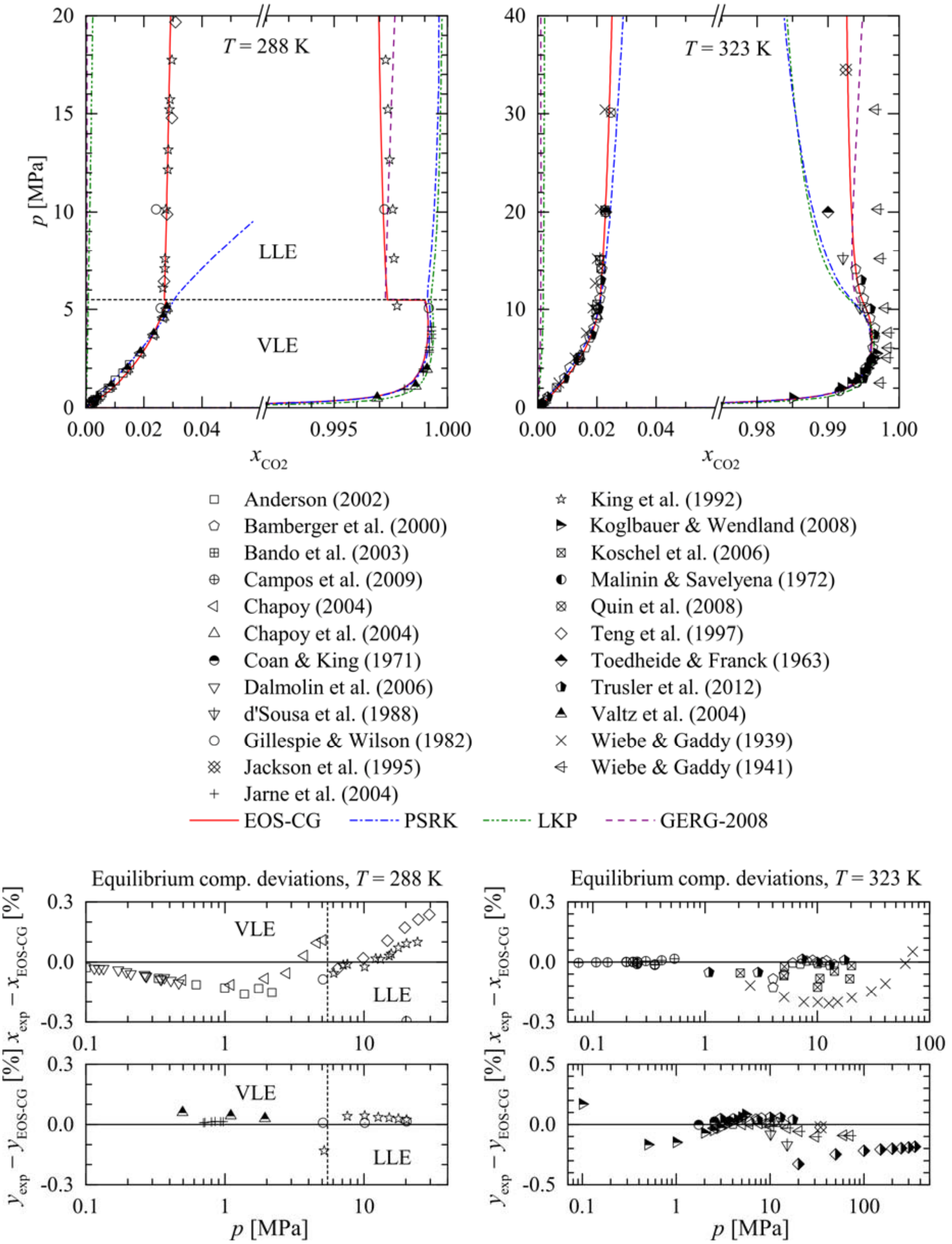


Figure 3.10: Experimental and calculated phase compositions for the system water + carbon dioxide at two different isotherms.

Based on the shown plots it becomes apparent that the EOS-CG mixture model represents the experimental data significantly better than all other models. However, there is still a tendency to overestimate the solubility at elevated temperatures.

In the liquid-liquid-equilibrium region the new mixture model shows close agreement with the data of *King et al. (1992)* and *Teng et al. (1997)*. The deviations for these data are within ±0.3 mole-%. At temperatures above 500 K and pressures above 20 MPa the model starts to diverge significantly from the experimental VLE data. *Gernert (2013)* describes the situation in this region as follows: “While the data sets by *Takenouchi and Kennedy (1964)* and *Tödheide and Franck (1963)* suggest a ‘closed’ VLE region above 540 K with a critical pressure below 140 MPa the model predicts an ‘open’ VLE region (no critical pressure) up to 600 K […].” This disagreement is illustrated in Figure 3.11.

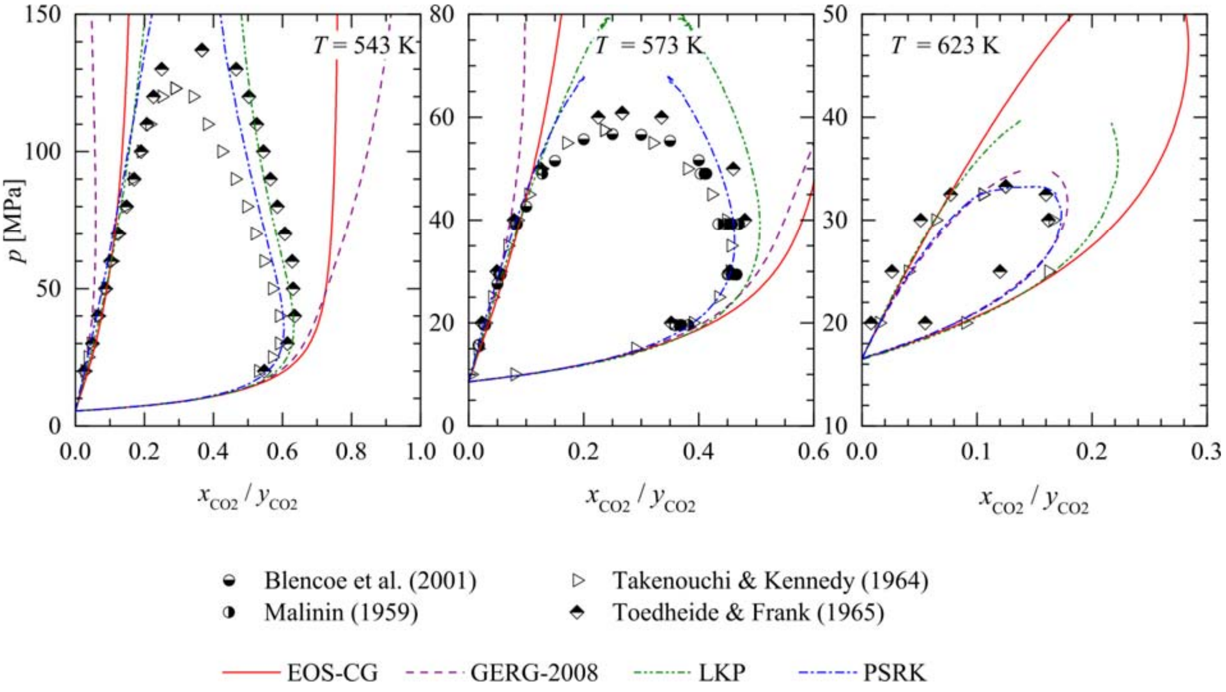


Figure 3.11: Experimental and calculated phase compositions at high temperatures for the system water + carbon dioxide at two different isotherms.

While the new mixture model mainly shows a better agreement with the data than the GERG-2008, the PSRK and LKP models describe the phase equilibrium better at high temperatures and pressures.

3.2.2 Water + Nitrogen

Beside of the system water + carbon dioxide the binary mixture of water with nitrogen is the best measured system within all water mixtures included in EOS-CG. Due to this good data situation it was not only possible to fit the reducing functions but also the specific binary departure function for the system.

In the gas phase, the most reliable densities were measured by *McLinden (2011)* covering temperatures between 500 K and 620 K and pressures up to 25 MPa. The EOS-CG mixture model generally reproduces these data within ±0.5 % and with an AAD of ±0.2 %. Deviation plots for these data are shown in Figure 3.12. Additionally, the figure includes other less accurate $p\rho T$ data measured in the vapor, liquid-like and supercritical region.

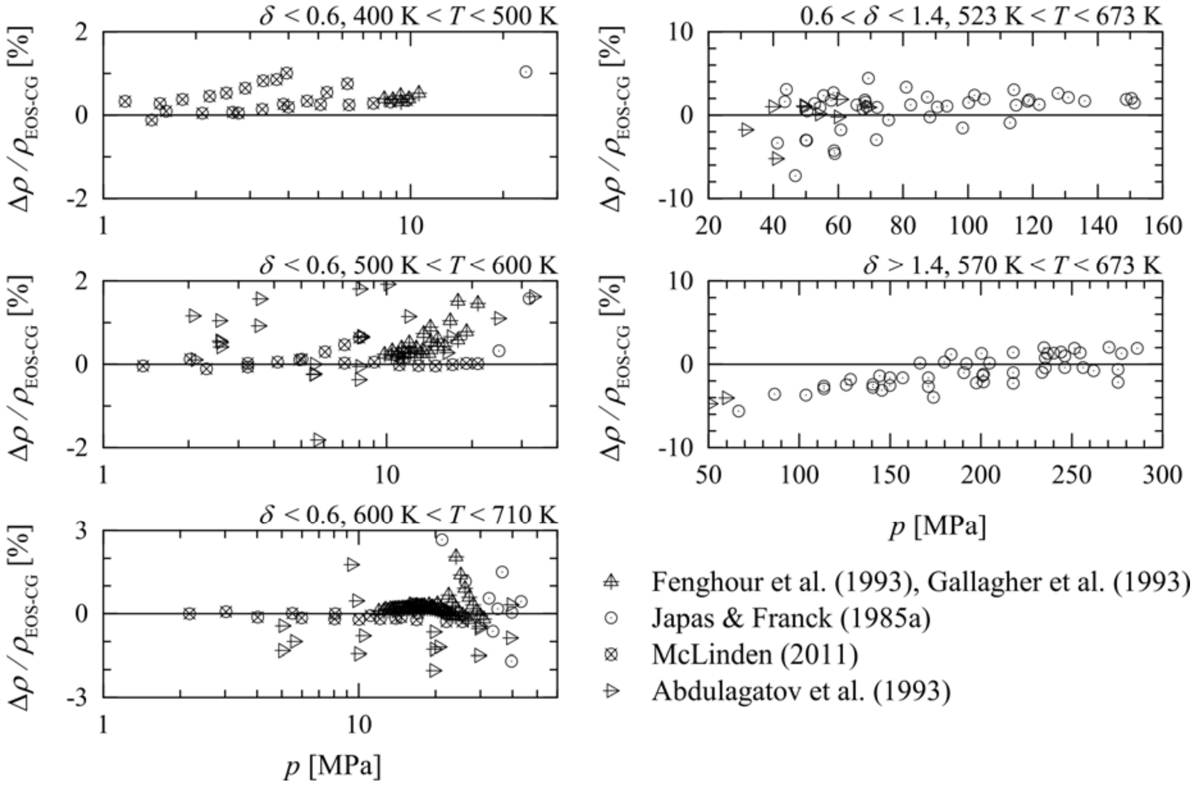


Figure 3.12: Deviations between experimental $p\rho T$ data and the new mixture model in the vapor, liquid-like, and supercritical region for the system water + nitrogen.

Although the data situation for water + nitrogen was found to be quite good, the number of complete *pTxy* data sets is limited. In Figure 3.13 the available data points are compared to values calculated with other mixture models. It can be seen that a considerable improvement is reached by employing the new EOS-CG model.

As typical for mixtures with water, the GERG-2008 and the LKP model significantly underestimate the solubility of nitrogen in water. The new mixture model gives a physically reasonable description of the temperature and pressure dependence of the solubility up to 573 K and 100 MPa and extrapolates well up to 500 MPa. The accurate solubility measurements of *Chapoy et al. (2004)*, *Smith et al. (1962)*, and *Kennan and Pollack (1990)* are reproduced with AAD values below 0.007 mole-%. The deviations increase for high-pressure values like the ones given by *Krichevsky and Kasarnovsky (1935)* (up to 0.12 mole-% at 100 MPa and 373 K).

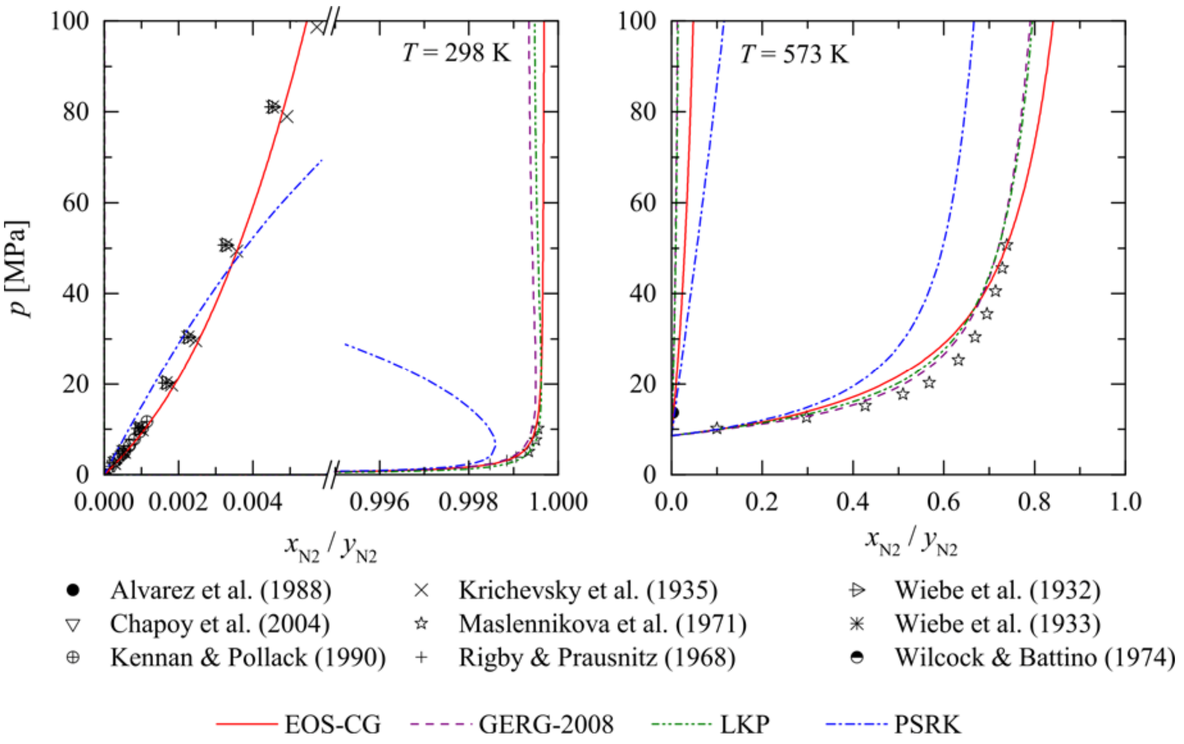


Figure 3.13: Experimental and calculated phase compositions at two isotherms for the system water + nitrogen.

3.2.3 Water + Oxygen and Water + Argon

Due to a quite similar data situation the two systems water + oxygen and water + argon can be discussed in one section. For both systems the number of publications providing experimental information is small. Therefore, it was not possible to fit all adjustable parameters of the functional form. For water + oxygen the departure function of the system water + nitrogen was used as a generalized departure function by fitting only the weighing parameter F_{ij}. The representation of the experimental data for water + argon could not be improved by means of such a generalized function. Thus, Gernert included only the parameters of the reducing functions in the fitting process.

The representation of the few available $p\rho T$ measurements will not be discussed in this report because most of the data cover the high-pressure, high-temperature region outside of the range of validity of the new mixture model. A short discussion and some deviation plots showing these data can be found in *Gernert (2013)*. Figure 3.14 depicts the description of phase boundaries for the system water + argon by means of the new mixture model and the GERG-2008 model.

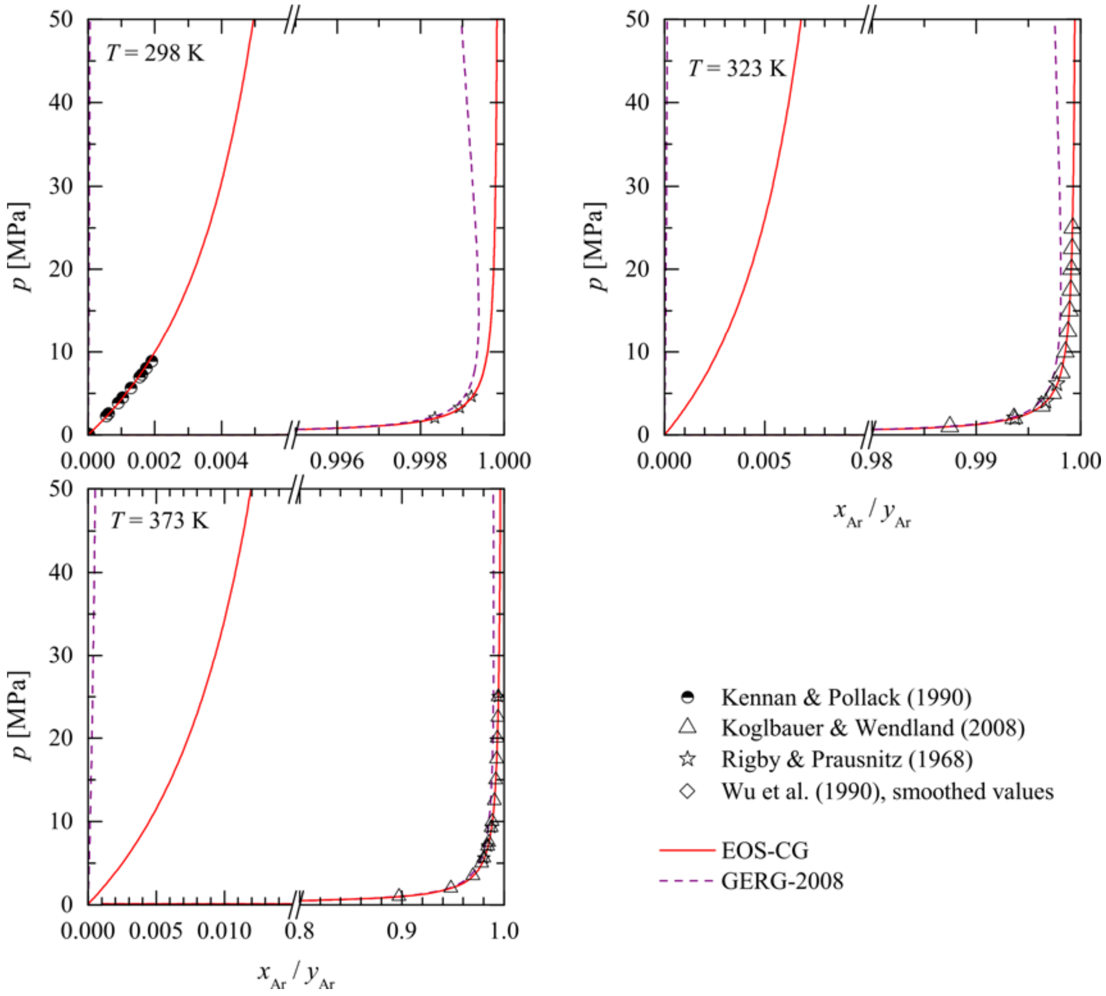


Figure 3.14: Experimental and calculated isothermal phase boundaries of the binary system water + argon.

Both the representation of the data and the extrapolation behavior were improved by the new model. The data sets by *Koglbauer and Wendland (2008)* and *Rigby and Prausnitz (1968)* are reproduced mainly within ±0.05 mole-%. Not shown in the plots are the accurate low temperature measurements of *Oellrich and Althaus (2001)* that are represented within ±0.002 mole-%.

For the system water + oxygen there are only a few phase boundary measurements given by *Wylie and Fisher (1996)*. Deviations between these data and values calculated from the new mixture model are within ±0.02 mole-%.

3.2.4 Water + Carbon Monoxide

Experimental data for the system water + carbon monoxide is quite limited. There are no $p\rho T$ measurements and only one $pTxy$ data set provided by *Gillespie and Wilson (1980)* that covers temperatures between 310 K and 588 K and pressures up to 14 MPa. Due to this poor data situation the departure function for the system water + nitrogen was used as a generalized departure function by adjusting the weighing factor F_{ij}. Furthermore, only three of the four parameters included in the reducing functions were adjusted to avoid overfitting the functional form.

The liquid phase data of *Gillespie and Wilson (1980)* are reproduced with a maximum deviation of ±0.03 mole-% and an AAD of 0.011 mole-% whereas the gas-phase data are described within deviations of ±2 mole-% and an AAD of 0.372 mole-%.

3.3 Other Binary Mixtures

Besides the binary mixtures with carbon dioxide and with water the EOS-CG mixture model includes six systems that are binary combinations of the main components of air, namely nitrogen, oxygen, and argon, and additionally carbon monoxide. In comparison to the systems with carbon dioxide and water the behavior of these mixtures is relatively simple. Therefore and due to the limited data situation no departure functions were fitted for these systems. The amount of experimental data for the binary mixtures of the air components is quite limited to measurements along the phase boundaries whereas homogenous data are comparably spare. The availability of data for binary mixtures with carbon monoxide is generally poor.

3.3.1 Nitrogen + Oxygen

After validating the representation of thermophysical properties of the system nitrogen + oxygen with the GERG-2008 model, *Gernert (2013)* decided to adopt the reducing parameters of this model without any readjustment. These parameters already yield the best agreement between experimental data and properties calculated from the mixture model. Furthermore, new data that would require further fitting efforts have not become available since the development of the GERG-2008 model.

Experimental $p\rho T$ data in the homogeneous gas, liquid and supercritical phase is given in five references of which only three include measurements above atmospheric pressure. Two of these references are unpublished data sets of the thermodynamics group at Ruhr-University Bochum measured by *Wöll (2003)* and *Schilling (2003)*, which cover parts of the supercritical gas region. The third reference by *Kuenen et al. (1922)* also includes measurements in the supercritical liquid-like region and near the critical point. Not surprisingly, these data are not as accurate as the measurements of the thermodynamics group in Bochum published more than 80 years later. In the gas region, the EOS-CG mixture model reproduces the experimental data within ±0.1 %, and within ±0.025 % for pressures below 7 MPa, respectively. The data of *Kuenen et al. (1922)* is described within an uncertainty of ±1 % (in pressure) near the critical point and within ±2 % (in density) in the liquid-like supercritical region. Deviation plots for the gas, liquid and critical region are given in Figure 3.15.

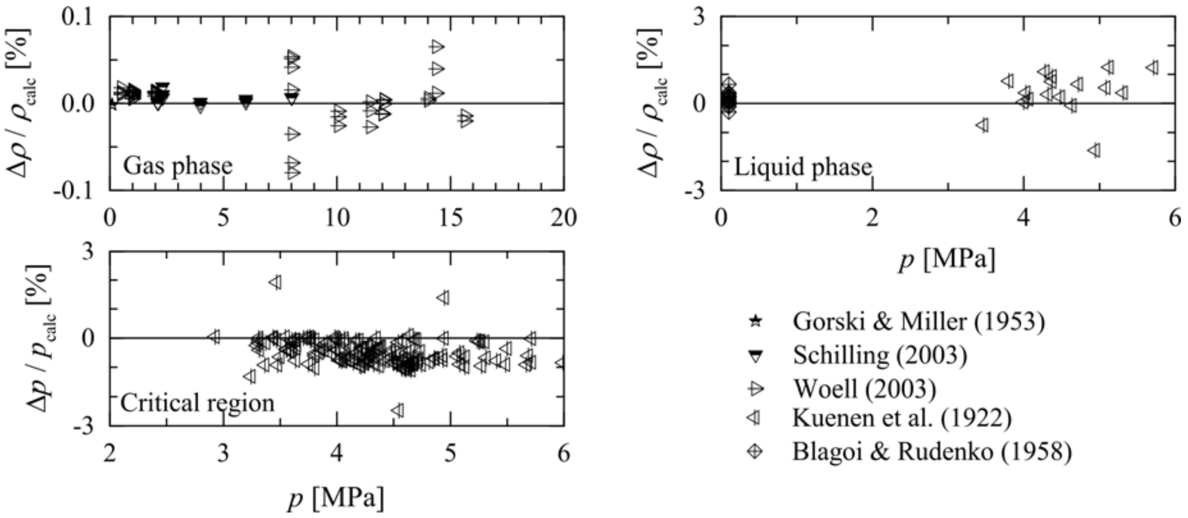


Figure 3.15: Deviations between experimental $p\rho T$ data in the gas, liquid and critical region and the new mixture model for the system nitrogen + oxygen.

The phase boundaries of the system were measured by a couple of authors but most of the data are older than 40 years. In general, the GERG-2008 model and the EOS-CG model, using the same mixting rules as GERG-2008, reproduce the data within their scatter and without any systematic offset. Figure 3.16 shows a selection of the available data including the most recent measurements by *Baba-Ahmed et al. (1999)*.

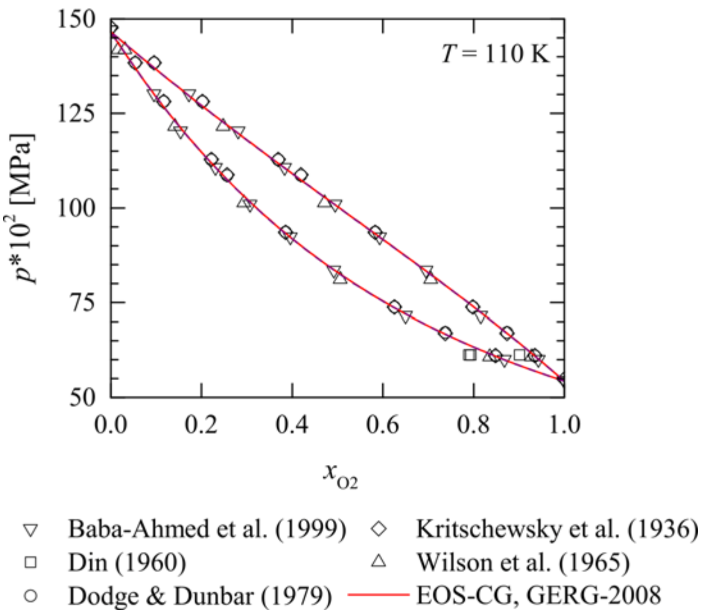


Figure 3.16: Experimental and calculated phase compositions at 110 K for the system nitrogen + oxygen.

Absolute deviations between measured and calculated dew and bubble point temperatures are for most of the data points below ±0.5 K whereas the corresponding AAD values for the data of *Hiza et al. (1990)* and *Baba-Ahmed et al. (1999)* are below 0.01 K.

3.3.2 Nitrogen + Argon

The parameters of the reducing functions for the system nitrogen + argon were not directly adopted for the EOS-CG mixture model but were used as starting values for some careful fitting calculations. The aim of this refitting was mainly to obtain a consistent transition from the mixture model to the pure fluid (reference) equations used in the EOS-CG model. However, *Gernert (2013)* found the prediction of $p\rho T$ data and phase boundaries to be basically identical for EOS-CG and GERG-2008.

In comparison to other binary mixtures discussed in this work the amount of available $p\rho T$ data for the system nitrogen + argon is quite large. There are more than 1000 data points from nine different publications covering temperatures between 70 K and 423 K and pressures up to 800 MPa. Unfortunately, none of these data sets can be considered very accurate. In the gas phase most of the data are reproduced within ±0.5 % with higher deviations near the critical point. In the critical region deviations are still within ±1 % except for the strongly scattered data of *Crain and Sonntag (1966)*. The majority of the liquid-like measurements are also described within ±0.5 % including the high-pressure data of *Maslennikova et al. (1979)*. Deviations plots including the most accurate experimental data are given in Figure 3.17.

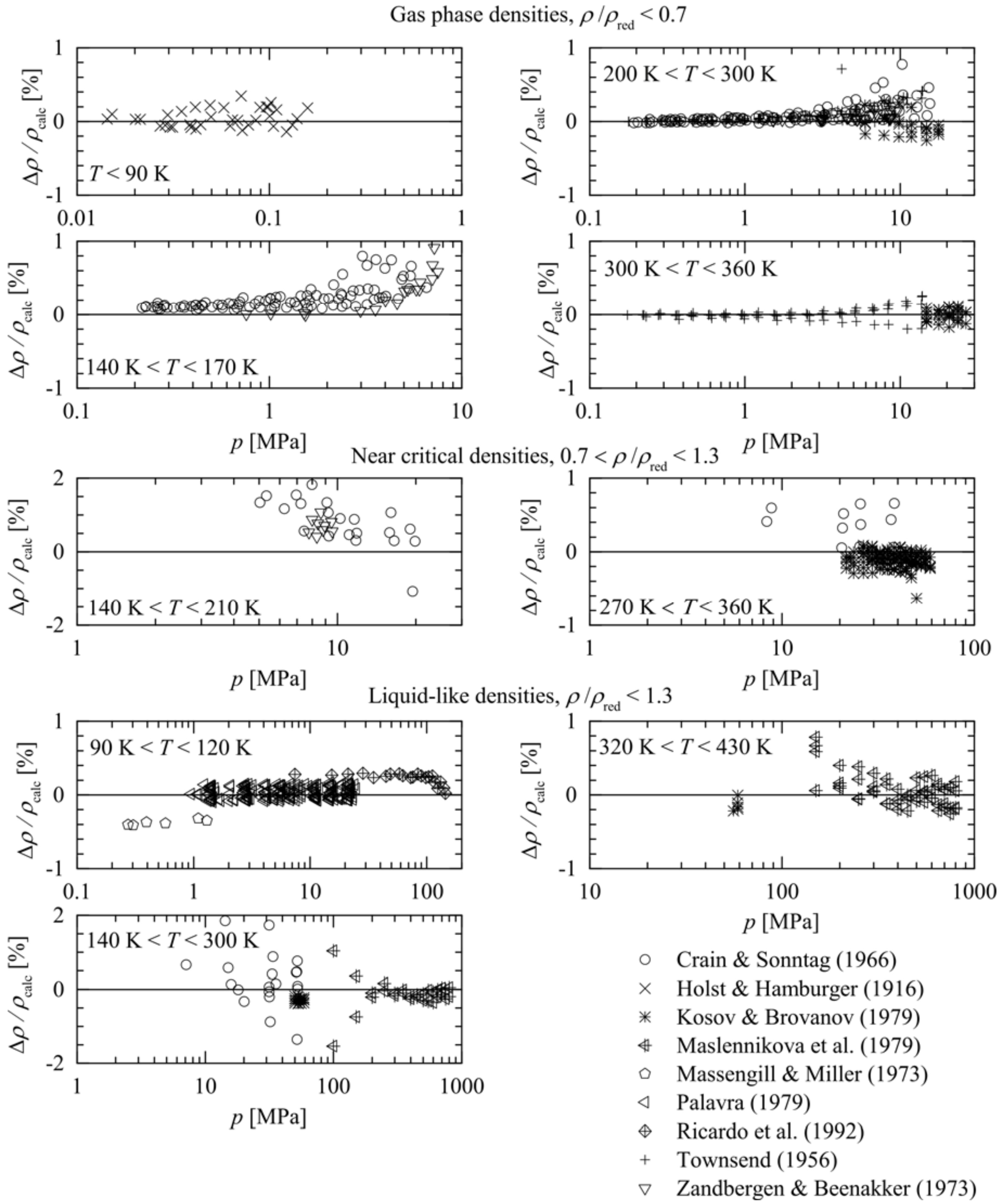


Figure 3.17: Deviations between experimental $p\rho T$ data and the new mixture model in the gas, supercritical, and liquid phase for the system nitrogen + argon.

Measurements for phase boundaries for nitrogen + argon are presented in 12 references including a total of 500 data points that cover nearly the whole two-phase region. The EOS-CG model mainly describes the data within the experimental scatter; results are almost identical with those of the GERG-2008 model. As an example Figure 3.18 shows two plots of isothermal phase boundaries at 100 K and 110 K. More plots are included in the appendix of the work of *Gernert (2013)*.

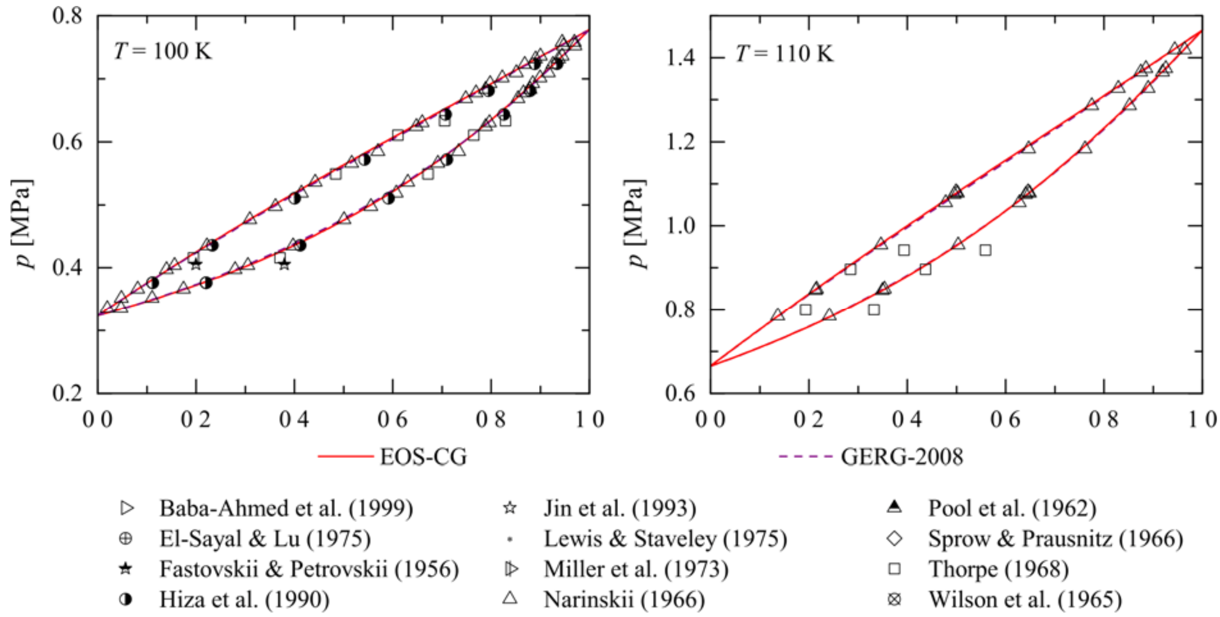


Figure 3.18: Experimental and calculated phase boundaries of the system nitrogen + argon.

3.3.3 Oxygen + Argon

The binary mixture of oxygen and argon is not as well measured as the two systems of dry air components discussed above. Only three data sets describe the $p\rho T$ relation. The earliest publication of *Masson and Dolley (1923)* just includes measurements of the equimolar gaseous mixture along one isotherm (298 K). The data are found to be less accurate and can only be reproduced with a constant offset of about -1.3 %. Liquid densities at low pressures are presented by *Blagoi and Rudenko (1958)* and *Saji and Okuda (1965)*. In general EOS-CG describes these data within ±0.5 % (see Figure 3.19).

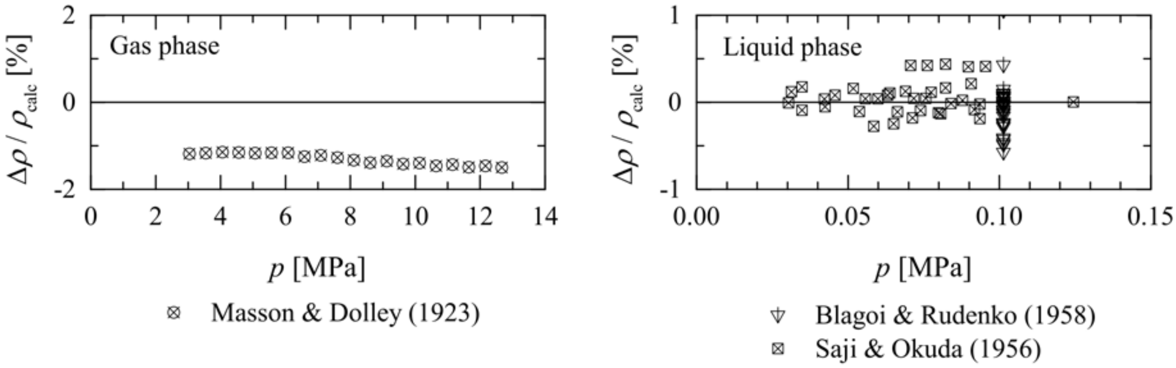


Figure 3.19: Deviations between experimental $p\rho T$ data and the new mixture model in the supercritical gas and liquid phase for the system oxygen + argon.

Experimental data for phase boundaries are given in 12 different references. The measurements of *Burn and Din (1962)*, *Clark et al. (1954)*, *Narinskii (1957)*, and *Pool et al. (1962)* are considered the most accurate data available. As Figure 3.20 illustrates, the representation of the available data is quite similar for the EOS-CG and the GERG-2008 mixture model.

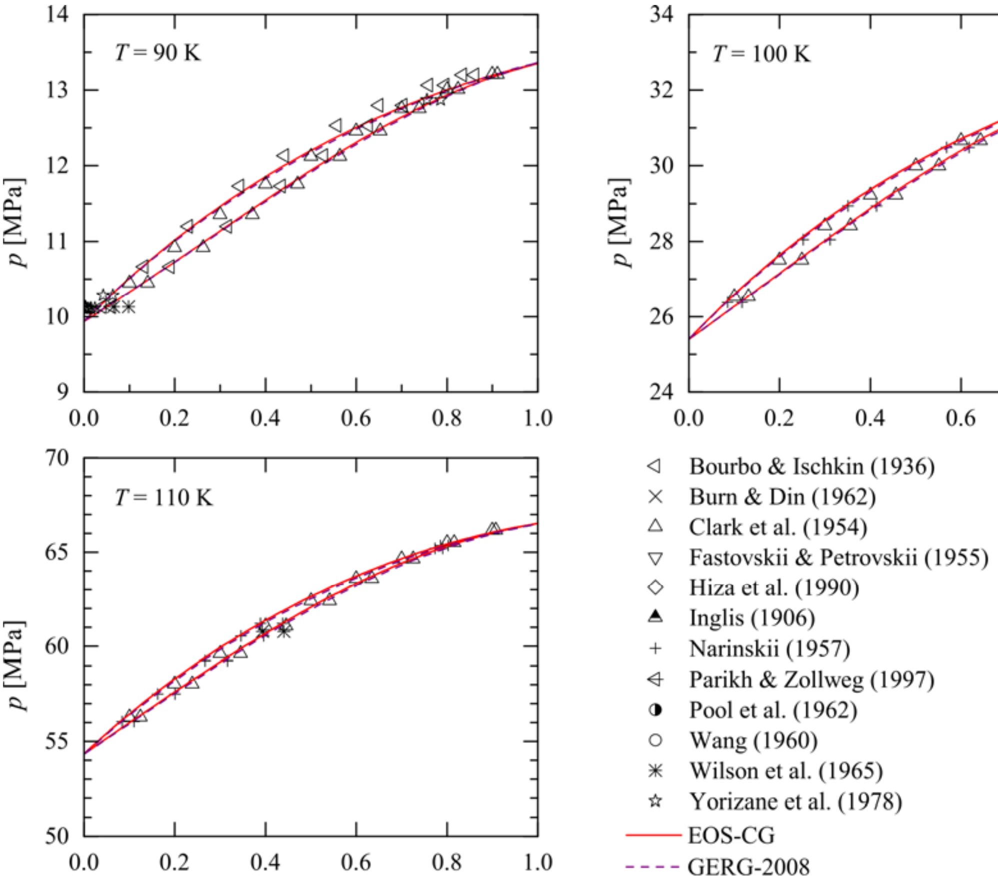


Figure 3.20: Experimental and calculated phase boundaries of the system oxygen + argon.

Vapor pressures calculated from both mixture models are slightly higher than the experimental values given in the references mentioned above. However, experimental values for bubble and dew point temperatures are still reproduced within $\pm 0.05\ \mathrm{K}$.

3.3.4 Nitrogen + Carbon Monoxide

For the system nitrogen + carbon monoxide two highly accurate $p\rho T$ data sets are available. The measurements of *Jaeschke and Humphreys (1991)* were performed with two different apparatus leading to estimated experimental uncertainties of 0.07 % and 0.08 %, respectively. The authors measured just one nitrogen-rich mixture ($x_{\mathrm{N2}} = 0.9669$) in a temperature range from 273 K to 353 K and pressures up to 30 MPa. The second data set presented by *Mondéjar et al. (2011)* includes two compositions ($x_{\mathrm{N2}} = 0.85$ and 0.95) and covers a broader temperature range from 250 K to 400 K. The experimental uncertainty of these data is estimated to be 0.10 %. The EOS-CG mixture model reproduces both data sets within $\pm 0.05\ \%$ and thus within their experimental uncertainties. Although the development of the reducing functions benefited from the high accuracy of these data, the small composition range made it difficult to shape the physical behavior of the model. In addition, no data was found for liquid-like densities.

In comparison to the $p\rho T$ data situation, the amount of publications presenting the phase boundaries is satisfying. There are eight available data sets covering a wide $p\rho Tx$ region. However, some of these data sets show a large scatter and are thus considered less accurate. The most accurate measurements are provided by *Gill and Morrison (1966)*, *Pool et al. (1962)*, and *Sprow and Prausnitz (1966)*. The representation of the experimental data for three isotherms is shown in Figure 3.21. Some additional plots are presented in *Gernert (2013)*.

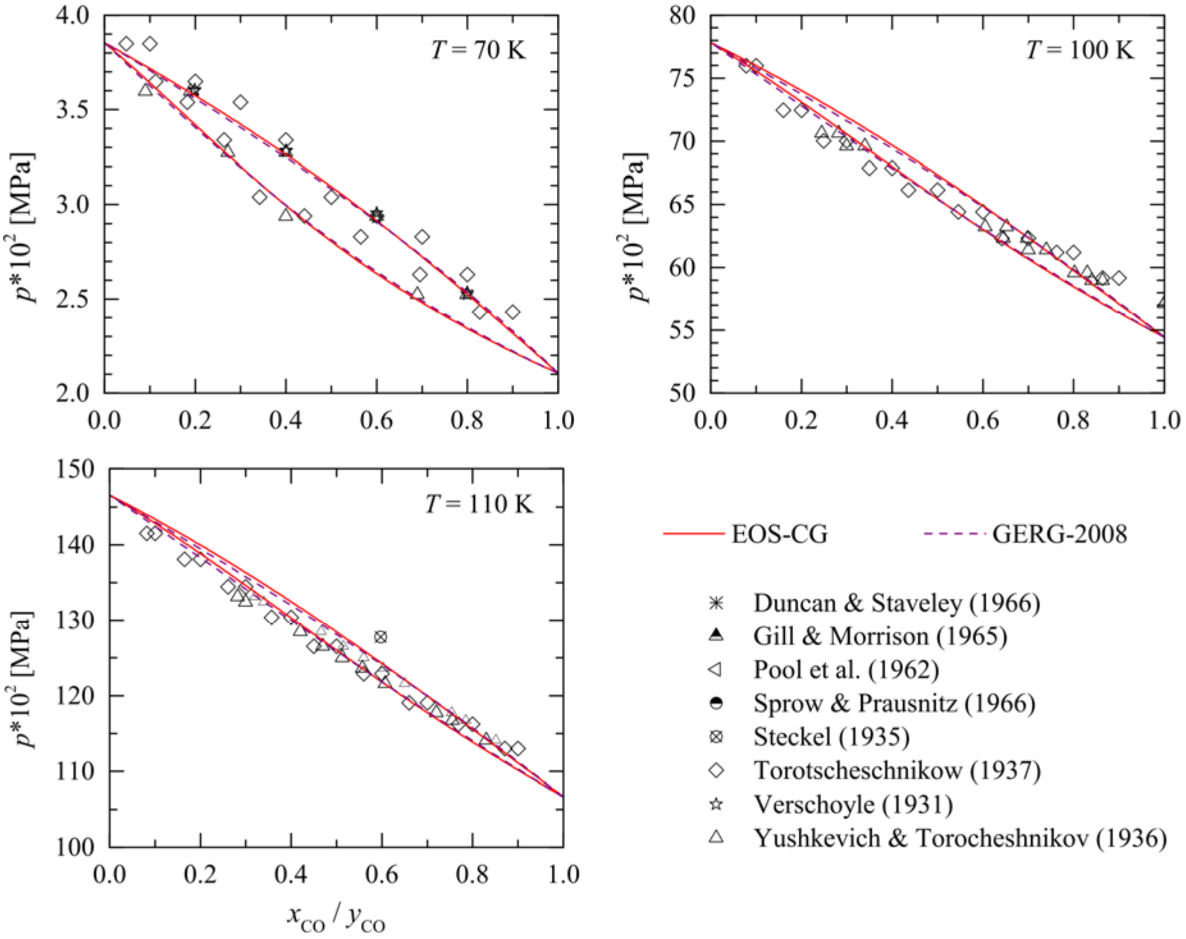


Figure 3.21: Experimental and calculated phase boundaries of the system nitrogen + carbon monoxide.

The prediction of phase boundaries by the EOS-CG model and the GERG-2008 model is almost identical. The most accurate experimental data for dew and bubble point temperatures are reproduced with absolute deviations below ±0.05 K.

3.3.5 Oxygen + Carbon Monoxide and Argon + Carbon Monoxide

The last two binary systems discussed in this report are oxygen + carbon monoxide and argon + carbon monoxide. For both systems there are little or no experimental data available.

For the system argon + carbon monoxide the data base includes two data sets by *Duncan and Staveley (1966)* and *Christiansen et al. (1973)* describing the phase boundaries at three different temperatures and some data points by *Pool et al. (1962)* for the excess volume at the triple point conditions of pure argon. Due to this poor data situation the adjusted parameters of the GERG-2008 model were adopted for the EOS-CG model without any new fitting. With these parameters the shape of the phase boundary data is reproduced correctly; the uncertainty of calculated densities is estimated to be 0.2 %.

No data was found for the system oxygen + carbon monoxide. The parameters of the reducing functions were therefore set to unity; the mixing rules of both GERG-2008 and EOS-CG are used purely on the basis of combination rules.

4 CONCLUSION AND OUTLOOK

This report presents a thorough validation of the current version of the reference model for thermodynamic properties of CO_2-rich mixtures, the EOS-CG model by *Gernert* (2013). The validation is based on detailed comparisons with selected experimental data and with other established models. Particular attention was paid to comparisons of the new mixture model with the GERG-2008 equation of state for natural gas mixtures developed by *Kunz and Wagner (2012)*, since the mathematical structure and some binary mixing parameters of this equation were adopted in the EOS-CG mixture model.

Based on the existing experimental data it can be noted that the new model represents the currently best fit to all reliable data points. For all binary mixtures both the representation of the data and the extrapolation behavior of EOS-CG are comparable or better the ones of the GERG-2008 model. Significant improvements were reached with regard to the description of properties of binary mixtures with water. However, future publications presenting new accurate data might require some further validations or careful refitting, in particular for binary systems where the current data situation is quite limited like, e.g., carbon dioxide + carbon monoxide, water + oxygen or water + carbon monoxide.

RUB is currently working on an extension of EOS-CG to methane and hydrogen to cover mixtures with the remaining secondary components. As a first step a complete database of experimental data for binary mixtures with methane is being developed. With regard to mixtures containing hydrogen current work by colleagues at the National Institute of Standards and Technology in Boulder and at the Washington State University is monitored to avoid duplications of work.

TABLE OF SYMBOLS

Latin Symbols

a	Molar Helmholtz free energy
F	Departure function parameter
K	Number of terms in the EOS
M	Number of measurements in a data sets
N	Number of components in a mixture
n	– Amount of substance, mole number
	– Coefficient of the Helmholtz equation of state
	– Iteration step
p	Pressure
R	Universal gas constant
T	Temperature
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
z	Arbitrary thermodynamic property

Greek Symbols

Δ	Finite change of a variable
α	Reduced Helmholtz free energy
β	– Binary reducing function parameter
	– Adjustable parameter in the binary departure function α_{ij}^{r}
δ	Reduced density
ε	Adjustable parameter in the binary departure function α_{ij}^{r}
γ	Adjustable parameter in the binary departure function α_{ij}^{r}
η	Adjustable parameter in the binary departure function α_{ij}^{r}
μ_{JT}	Joule-Thomson coefficient
ρ	Molar density
τ	Inverse reduced temperature, $\tau = T_{\mathrm{r}}/T$

Subscripts

c	Property at critical conditions
calc	Calculated property
exp	Experimental property
i,j,k,m	Component indices
N	Last component in the mixture
o	Pure fluid property
r	Reducing parameter
rel	Relative deviation
tot	Absolute deviation
tp	Property at the triple point

Superscripts

o	Ideal-gas property
r	Residual property

Abbreviations

AAD	Absolute average deviation
CCS	Carbon capture and storage
EOS	Equation of state
EOS-CG	Equation of state for combustion gases and combustion gas like mixtures
exp	Exponential term
LKP	Lee-Kesler-Ploecker equation
LLE	Liquid-liquid equilibrium
pol	Polynomial
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
spec	Special exponential term
SRK	Soave-Redlich-Kwong equation
VLE	Vapor-liquid equilibrium

REFERENCES

Abdulagatov, I. M.; Bazaev, A. R.; Ramazamova, A. E. (1993): *P-V-T-x Measurements of Aqueous Mixtures at Supercritical Conditions*. Int. J. Thermophys. 14 (1993), 231–250.

Abdulagatov, I. M.; Bazaev, A. R.; Ramazamova, A. E.; Gasanov, R.K (1994): *Experimental Study of the PVTX-Properties of the Binary System Carbon Dioxide-Water in the Supercritical Range*: Proceedings of the 12th International Conference on the Properties of Water and Steam. Orlando (1994), 558–563.

Abraham, W. H.; Bennett, C. O. (1960): *The Compressibility of Carbon Dioxide-Argon Mixtures*. AlChE J. 6 (1960), 257–261.

Al-Sahhaf, T. A.; Kidnay, A. J.; Sloan, E. D. (1983): *Liquid + Vapor Equilibria in the* N_2+CO_2+CH_4 *System*. Ind. Eng. Chem. Fundam. 22 (1983), 372–380.

Altunin, V. V.; Koposhilov, O. D. (1976): *Thermal Properties of Gaseous Mixtures of Carbon Dioxide-Argon at Elevated Temperatures*. Trudy Moskovskogo Energeticheskogo Instituta 313 (1976), 20–23.

Altunin, V. V.; Koposhilov, O. D. (1977): *An Experimental Investigation of the Thermal Properties of Gaseous Mixtures of Carbon Dioxide and Argon*. Teploenergetika 24 (1977), 66–70.

Alvarez, J.; Crovetto, R.; Fernández-Prini, R. (1988): *The Dissolution of* N_2 *and of* H_2 *in Water from Room Temperature to 640 K*. Ber. Bunsen Ges. Phys. Chem. 92 (1988), 935–940.

Anderson, G. K. (2002): *Solubility of Carbon Dioxide in Water under Incipient Clathrate Formation Conditions*. J. Chem. Eng. Data 47 (2002), 219–222.

Aursand, E.; Aashammer Gjennestad, M. (2013): *Implementing and testing a robust density-solver for the TREND equation of state*. Memo, SINTEF Energi AS, Trondheim, 2013.

Baba-Ahmed, A.; Guilbot, P.; Richon, D. (1999): *New Equipment Using a Static Analytic Method for the Study of Vapour-Liquid Equilibria at Temperatures Down to 77 K*. Fluid Phase Equilib. 166 (1999), 225–236.

Bailey, D. M.; Esper, G. J.; Holste, J. C.; Hall, K. R.; Eubank, P. T.; Marsh, K. N.; Rogers, W. J. (1989): *Properties of* CO_2 *Mixtures with* N_2 *and with* CH_4*. Research Report RR-122*. Gas Processors Association, Tulsa, 1989.

Bamberger, A.; Sieder, G.; Maurer, G. (2000): *High-Pressure (Vapor + Liquid) Equilibrium in Binary Mixtures of (Carbon Dioxide + Water or Acetic Acid) at Temperatures from 313 to 353 K*. J. Supercrit. Fluids 17 (2000), 97–110.

Bando, S.; Takemura, F.; Nishio, M.; Hihara, E.; Akai, M. (2003): *Solubility of* CO_2 *in Aqueous Solutions of NaCl at (30 to 60) °C and (10 to 20) MPa*. J. Chem. Eng. Data 48 (2003), 576–579.

Blagoi, Yu P.; Rudenko, N. C. (1958): *Density of Liquified Gas Solutions* N_2-O_2*,* Ar-O_2 *[in Russian]*. Izv. Vyssh. Ucheb. Zaved. Fiz. 1 (1958), 145–151.

Blencoe, J. G.; Naney, M. T.; Anovitz, L. M. (2001): *The* CO_2-H_2O *System: III. A New Experimental Method for Determining Liquid-Vapor Equilibria at High Subcritical Temperatures*. Am. Mineral. 86 (2001), 1100–1111.

Bourbo, P.; Ischkin, I. (1936): *Untersuchungen über das Gleichgewicht von Flüssigkeit und Dampf des Systems Argon-Sauerstoff*. Physica 3 (1936), 1067–1081.

Brown, T. S.; Niesen, V. G.; Sloan, E. D.; Kidnay, A. J. (1989a): *Vapor-Liquid Equilibria for the Binary Systems of Nitrogen, Carbon Dioxide and n-Butane at Temperatures from 220 to 344 K*. Fluid Phase Equilib. 53 (1989), 7–14.

Brugge, H. B.; Holste, J. C.; Hall, K. R.; Gammon, B. E.; Marsh, K. N. (1997): *Densities of Carbon Dioxide + Nitrogen from 225 K to 450 K at Pressures up to 70 MPa*. J. Chem. Eng. Data 42 (1997), 903–907.

Brugge, H. B.; Hwang, C. A.; Rogers, W. J.; Holste, J. C.; Hall, K. R.; Lemming, W. Esper, G. J.; Marsh, K. N.; Gammon, G. E. (1989): *Experimental Cross Virial Coefficients for Binary Mixtures of Carbon Dioxide with Nitrogen, Methane and Ethane at 300 and 320 K*. Physica A 156 (1989), 382–416.

Burn, I.; Din, F. (1962): *Liquid-Vapour Equilibrium of the System Argon +Oxygen at Pressures up to 10 Atmospheres*. Trans. Faraday Soc. 58 (1962), 1341–1356.

Campos, C.; Villardi, H.; Pessoa, F. Uller A. (2009): *Solubility of Carbon Dioxide in Water and Hexadecane: Experimental Measurement and Thermodynamic Modeling*. J. Chem. Eng. Data 54 (2009), 2881–2886.

Chapoy, A. (2004): *Phase Behaviour in Water/Hydrocarbon Mixtures Involved in Gas Production Systems*. Dissertation, Ecole de Mines, 2004.

Chapoy, A.; Mohammadi, A. H.; Chareton, A.; Tohidi, B.; Richon, D. (2004): *Measurement and Modeling of Gas Solubility and Literature Review of the Properties for the Carbon Dioxide-Water System*. Ind. Eng. Chem. Res. 43 (2004), 1794–1802.

Christiansen, L.J; Fredenslund, A.; Mollerup, J. (1973): *Vapour-Liquid Equilibrium of the CH_4-Ar, CH_4-CO, and Ar-CO Systems at Elevated Pressures*. Cryogenics 13 (1973), 405–413.

Christiansen, L. J.; Fredenslund, A.; Cardner, N. (1974): *Gas-Liquid Equilibria of the System CO_2-CO and CO_2-CH_4-CO Systems*. Adv. Cryog. Eng. 19 (1974), 309–319.

Clark, A. M.; Din, F.; Robb, J. (1954): *The Liquid-Vapour Equilibrium of the Binary System Argon/Oxygen*. Proc. R. Soc. London, Ser. A 221 (1954), 517–534.

Coan, C. R.; King, A. D. (1971): *Solubility of Water in Compressed Carbon Dioxide, Nitrous Oxide, and Ethane. Evidence for Hydration of Carbon Dioxide and Nitrous Oxide in the Gas Phase*. J. Am. Chem. Soc. 93 (1971), 1857–1862.

Coquelet, C.; Valtz, A.; Dieu, F.; Richon, D.; Arpentinier, P.; Lockwood, F. (2008): *Isothermal P, x, y data for the argon+carbon dioxide system at six temperatures from 233.32 to 299.21 K and pressures up to 14 MPa*. Fluid Phase Equilib. 273 (2008), 38–43.

Crain, R. W.; Sonntag, R. E. (1966): *The P-V-T Behavior of Nitrogen, Argon, and their Mixtures*. Adv. Cryog. Eng. 11 (1966), 379–391.

Dalmolin, I.; Skovroinski, E.; Biasi, A.; Corazza, M. L.; Dariva, C.; Oliveira, J. V. (2006): *Solubility of Carbon Dioxide in Binary and Ternary Mixtures with Ethanol and Water*. Fluid Phase Equilib. 245 (2006), 193–200.

Din, F. (1960): *The Liquid-Vapour Equilibrium of the System Nitrogen+Oxygen at Pressures up to 10 atm*. Trans. Faraday Soc. 56 (1960), 668–681.

Dodge, B. F.; Dunbar, A. F. (1927): *An Investigation of the Coexisting Liquid and Vapor Phases of Solutions of Oxygen and Nitrogen*. J. Am. Chem. Soc. 49 (1927), 591–610.

Duarte-Garza, H. A.; Holste, J. C.; Hall, K. R.; Marsh, K. N.; Gammon, B. E. (1995a): *Isochoric pVT and Phase Equilibrium Measurements for Carbon Dioxide + Nitrogen*. J. Chem. Eng. Data 40 (1995), 704–711.

Duncan, A. G.; Staveley, L. A. (1966): *Thermodynamic Functions of the Liquid Systems Argon + Carbon Monoxide, Oxygen + Nitrogen, and Carbon Monoxide + Nitrogen*. Trans. Faraday Soc. 62 (1966), 548–552.

D'Sousa, R.; Patrick, J. R.; Teja, A. S. (1988): *High Pressure Phase Equilibria in the Carbon Dioxide-n-Hexadecane and Carbon Dioxide-Water Systems*. Can. J. Chem. Eng. 66 (1988), 319–323.

El-Sayal, I. M.; Lu, B. C.-Y (1975): *Measurement of Total Pressures for Ethylene-Propane Mixtures*. Can. J. Chem. Eng. 53 (1975), 83–87.

Ely, J. F.; Haynes, W. M.; Bain, B. C. (1989): *Isochoric* (p,V_m,T) *Measurements on* CO_2 *and on* $(0.982\ CO_2+0.018\ N_2)$ *from 250 to 330 K at Pressures to 35 MPa*. J. Chem. Thermodyn. 21 (1989), 879–894.

Esper, G. J. (1987): *Direkte und indirekte p-v-T-Messungen an Fluiden.* Fortschritts-Berichte VDI, Reihe 3, Nr. 148, VDI, Düsseldorf, 1987.

Fastovskii, V.G; Petrovskii, Yu.V (1956): *Investigation of the Equilibrium Liquid and Vapor in the System Argon-Nitrogen II.* Zh. Fiz. Khim. 30 (1956), 76–78.

Fenghour, A.; Wakeham, W. A.; Ferguson, D.; Scott, A. C.; Watson, J. T. R. (1993): *Densities of (Water + Nitrogen) in the Temperature Range 533 K to 703 K and at Pressures up to 31 MPa*. J. Chem. Thermodyn. 25 (1993), 1151–1159.

Fenghour, A.; Wakeham, W. A. (1996): *Densities of (Water + Carbon Dioxide) in the Temperature Range 415 K to 700 K and Pressures up to 35 MPa*. J. Chem. Thermodyn. 28 (1996), 433–446.

Fredenslund, A.; Sather, G. A. (1970): *Gas-Liquid Equilibrium of the Oxygen-Carbon Dioxide System*. J. Chem. Eng. Data 15 (1970), 17–22.

Gallagher, J. S.; Sengers, H. L; Abdulagatov, I. M; Watson, J. T. R; Fenghour, A. (1993): *Thermodynamic Properties of Homogeneous Mixtures of Nitrogen and Water from 440 to 1000 K, up to 100 MPa and 0.8 Mole Fraction* N_2. NIST Technical Note 1404, NIST, Washington DC, 1993.

Gehrig, M. (1980): *Phasengleichgewichte und pVT-Daten ternärer Mischungen aus Wasser, Kohlendioxid und Natriumchlorid bis 3 kbar und 550 °C.* Hochschulsammlung Naturwissenschaft Chemie, Band 1, Hochschulverlag, Freiburg, 1980.

Gernert, J. G. (2013): *A New Helmholtz Energy Model for Humid Gases and CCS Mixtures*. PhD Thesis. Ruhr-Universität Bochum. Lehrstuhl für Thermodynamik, 2013.

Gill, E. K.; Morrison, J. A. (1966): *Thermodynamic Properties of Condensed CO*. J. Chem. Phys. 45 (1966), 1585–1590.

Gillespie, P. C; Wilson, G. M (1982): *Research Report RR-48. Vapor-Liquid and Liquid-Liquid Equilibria: Water-Methane, Water-Carbon Dioxide, Water-Hydrogen Sulfide, Water-nPentane, Water-Methane-nPentane*. Gas Processors Association, Tulsa OK, 1982.

Gorski, R. A.; Miller, J. G. (1953): *The Interaction Coefficients of Gas Mixtures*. J. Am. Chem. Soc. 75 (1953), 550–552.

Greenwood, H. J. (1969): *The Compressibility of Gaseous Mixtures of Carbon Dioxide and Water between 0 and 500 bars Pressure and 450° and 800° Centrigrade*. Am. J. Sci. 267-A (1969), 191–208.

Haney, R. E. D; Bliss, H. (1944): *Compressibilities of Nitrogen-Carbon Dioxide Mixtures*. Ind. Eng. Chem. 36 (1944), 985–989.

Hebach, A.; Oberhof, A.; Dahmen, N. (2004): *Density of Water + Carbon Dioxide at Elevated Pressures: Measurements and Correlation*. J. Chem. Eng. Data 49 (2004), 950–953.

Hiza, M. J.; Kidnay, A. J.; Haynes, W. M. (1990): *Liquid-Vapor Equilibria in Binary Systems Containing Nitrogen, Oxygen, and Argon between 63 and 100 K. Preliminary Unpublished Results [Source: Kunz et al. (2007)]*. National Institute of Standards and Technology, Boulder CO, 1990.

Holderbaum, T.; Gmehling, J. (1991): *PSRK: A Group-Contribution Equation of State Based on UNIFAC*. Fluid Phase Equilib. 70 (1991), 251–256.

Holst, G.; Hamburger, L. (1916): *Untersuchungen über das Gleichgewicht von Flüssigkeit und Dampf des Systems Argon-Stickstoff*. Z. Phys. Chem. 91 (1916), 513–547.

Inglis, J. K. H. (1906): *The Isothermal Distillation of Nitrogen and Oxygen and of Argon and Oxygen*. Philos. Mag. 11 (1906), 640–659.

Jackson, K.; Bowman, L. E.; Fulton, J. L. (1995): *Water Solubility Measurements in Supercritical Fluids and High-pressure Liquids Using Near-Infrared Spectroscopy*. Anal. Chem. 67 (1995), 2368–2372.

Jaeschke, M.; Humphreys, A. E. (1991): *The GERG Databank of High Accuracy Compressibility Factor Measurements. GERG Technical Monograph 4*. Fortschritts-Berichte VDI, Reihe 6, Nr. 251. VDI Verlag, Düsseldorf, 1991.

Jäger, A.; Vinš, V.; Gernert, J.; Span, R.; Hrubý, J. (2013): *Phase Equilibria with Hydrate Formation in* H_2O+CO_2 *Mixtures Modeled with Reference Equations of State*. Fluid Phase Equilib. 338 (2013), 100–113.

Japas, M. L.; Franck, E. U. (1985a): *High Pressure Phase Equilibria and PVT-Data of the Water-Nitrogen System to 673 K and 250 MPa*. Ber. Bunsen Ges. Phys. Chem. 89 (1985), 793–800.

Jarne, C.; Blanco, S. T.; Artal, M.; Rauzy, E.; Otin, S.; Velasco, I. (2004): *Dew Points of Binary Carbon Dioxide + Water and Ternary Carbon Dioxide + Water + Methanol Mixtures - Measurement and Modelling*. Fluid Phase Equilib. 216 (2004), 85–93.

Jin, Z. L.; Liu, K. Y.; Sheng, W. W. (1993): *Vapor-Liquid Equilibrium in Binary and Ternary Mixtures of Nitrogen, Argon, and Methane*. J. Chem. Eng. Data 38 (1993), 353–355.

Kaminishi, G.; Arai, Y.; Saito, S.; Maeda, S. (1968): *Vapor-Liquid Equilibria for Binary and Ternary Systems Containing Carbon Dioxide*. J. Chem. Eng. Jpn. 1 (1968), 109–116.

Kaminishi, G.; Toriumi, T. (1966): *Vapor-Liquid Phase Equilibrium in the* CO_2-H_2, CO_2-N_2 *and* CO_2-O_2 *Systems [in Japanese]*. Kogyo Kagaku Zasshi 69 (1966), 175–178.

Kennan, R. P.; Pollack, G. L. (1990): *Pressure Dependence of the Solubility of Nitrogen, Argon, Krypton, and Xenon in Water*. J. Chem. Phys. 93 (1990), 2724–2735.

King, M. B.; Mubarak, A.; Kim, J. D.; Bott, T. R. (1992): *The Mutual Solubilities of Water with Supercritical and Liquid Carbon Dioxide*. J. Supercrit. Fluids 5 (1992), 296–302.

Klimeck, R. (2000): *Entwicklung einer Fundamentalgleichung für Erdgase für das Gas- und Flüssigkeitsgebiet sowie das Phasengleichgewicht*. PhD Thesis, Ruhr-Universität Bochum, Fakultät für Maschinenbau, 2000.

Koglbauer, G.; Wendland, M. (2008): *Water Vapor Concentration Enhancement in Compressed Humid Nitrogen, Argon, and Carbon Dioxide Measured by Fourier Transform Infrared Spectroscopy*. J. Chem. Eng. Data 53 (2008), 77–82.

Koschel, D.; Coxam, J.; Rodier, L.; Majer, V. (2006): *Enthalpy and Solubility Data of CO_2 in Water and NaCl(aq) at Conditions of Interest for Geological Sequestration*. Fluid Phase Equilib. 247 (2006), 107–120.

Kosov, N. D.; Brovanov, I. S. (1975): *The Compressibility of Binary Mixtures of Helium, Nitrogen and Argon with Carbon Dioxide from $59x10^5$ to $590x10^5$ Pa*. Teploenergetika (Engl: Therm. Eng.) 22 (1975), 87–89.

Kosov, N. D.; Brovanov, I. S. (1979): *Compressibility of an Argon-Nitrogen Binary Mixture at Different Concentrations in the 59-590 bar Range*. Inz. Fiz. Zh. 36 (1979), 627-632 (413–417).

Krichevsky, I. R; Kasarnovsky, J. S (1935): *Thermodynamical Calculations of Solubilities of Nitrogen and Hydrogen in Water at High Pressures*. J. Am. Chem. Soc. 57 (1935), 2168–2171.

Kritschewsky, I. R.; Torotscheschnikow, N. S. (1936): *Thermodynamik des Flüssigkeitdampf-gleichgewichts im Stickstoff-Sauerstoff-System*. Z. Phys. Chem. Abt. A: 176 (1936), 338–346.

Kuenen, J. P.; Verschoyle, T.; van Urk, A. T. (1922): *Isotherms of Diatomic Substances and their Binary Mixtures. XX. The Critical Curve of Oxygen - Nitrogen Mixtures, the Critical Phenomena and some Isotherms of Two Mixtures of 50% and 75% by Volume of Oxygen in the Neighborhood of the Critical Region*. Proc. R. Acad. 22 (1922), 49–64.

Kunz, O.; Klimeck, R.; Wagner, W.; Jaeschke, M. (2007): *The GERG-2004 Wide-Range Equation of State for Natural Gases and Other Mixtures*. GERG Technical Monograph TM15. Fortschritts-Berichte VDI, Reihe 6, Nr. 557. VDI Verlag, Düsseldorf, 2007.

Kunz, O.; Wagner, W. (2012): *The GERG-2008 Wide-Range Equation of State for Natural Gases and Other Mixtures: An Expansion of GERG-2004*. J. Chem. Eng. Data 57 (2012), 3032–3091.

Lemmon, E. W.; Jacobsen, R. T. (1999): *A Generalized Model for the Thermodynamic Properties of Mixtures*. Int. J. Thermophys. 20 (1999), 825–835.

Lemmon, E. W.; Span, R. (2006): *Short Fundamental Equations of State for 20 Industrial Fluids*. J. Chem. Eng. Data 51 (2006), 785–850.

Lewis, K. L.; Staveley, L. A. K. (1975): *Excess Enthalpies of the Mixtures Nitrogen + Oxygen, Nitrogen + Argon, Argon + Ethane, and Methane + Carbon Tetrafluoride*. J. Chem. Thermodyn. 7 (1975), 855–864.

Li, Z.; Dong, M.; Li, S.; Dai, L. (2004): *Densities and Solubilities for Binary Systems of Carbon Dioxide + Water and Carbon Dioxide + Brine at 59 °C and Pressures to 29 MPa*. J. Chem. Eng. Data 49 (2004), 1026–1031.

Masson, I.; Dolley, L. G. F. (1923): *The Pressures of Gaseous Mixtures*. Proc. R. Soc. London, Ser. A 103 (1923), 524–538.

Malinin, S. D. (1959): *The System Water-Carbon Dioxide at High Temperatures and Pressures*. Geochemistry 3 (1959), 292–306.

Malinin, S. D.; Savelyeva, N. I. (1972): *The Solubility of CO_2 in NaCl and $CaCl_2$ Solutions at 25, 50 and 75° Under Elevated CO_2 Pressures*. Geochem. Int. 9 (1972), 410–418.

Maslennikova, V. Y.; Vdovina, N. A.; Tsiklis, D. S. (1971): *Solubility of Water in Compressed Nitrogen*. Zh. Fiz. Khim. 45 (1971), 1354.

Maslennikova, V. Y.; Egorov, A. N.; Tsiklis, D. S. (1979): *Compressibility of Homogeneous Gas Mixtures at High Pressures. The Nitrogen-Argon System*. Zh. Fiz. Khim. 53 (1979), 919–920.

Massengill, D. R.; Miller, R. C. (1973): *Temperature Dependence of Excess Volumes for Simple Liquid Mixtures: N_2+Ar, N_2+Ar+CH_4*. J. Chem. Thermodyn. 5 (1973), 207–217.

McLinden, M. O. (2011): *Experimental $p-\rho-T$ Data for Mixtures of Water with Nitrogen and Carbon Dioxide*, National Institute of Standards and Technology, Boulder CO, private communication, 2011.

Miller, R. C.; Kidnay, A. J.; Hiza, M. J. (1973): *Liquid-Vapor Equilibria at 112.00 K for Systems Containing Nitrogen, Argon, and Methane*. AlChE J. 19 (1973), 145–151.

Mondéjar, M. E.; Villamañán, M. A.; Span, R.; Chamorro, C. R. (2011): *(p, ρ, T) Behavior of Two Mixtures of Carbon Monoxide with Nitrogen in the Temperature Range from (250 to 400) K and Pressures up to 20 MPa*. J. Chem. Eng. Data 56 (2011), 3933–3939.

Mondéjar, M. E.; Villamañán, R. M.; Span, R.; Chamorro, C. R. (2012): *Accurate (p,ρ,T) Data for Two New (Carbon Dioxide+Nitrogen) Mixtures from (250 to 400) K at Pressures up to 20 MPa*. J. Chem. Thermodyn. 48 (2012), 254–259.

Muirbrook, N. K. (1964): *Experimental and Thermodynamic Study of the High-Pressure Vapor-Liquid Equilibria for the Nitrogen-Oxygen-Carbon Dioxide System*. PhD Thesis, Berkeley, 1964.

Narinskii, G. B. (1957): *Investigation of the Equilibrium of Liquid-Vapor in the System Oxygen-Argon [in Russian]*. Kislorod : naucnyj i proizvodstvenno-techniceskij zurna 10 (1957), 9–16.

Narinskii, G. B. (1966): *Liquid-Vapor Equilibrium in the Argon-Nitrogen System. I. Experimental Data and their Verification*. Russ. J. Phys. Chem. 40 (1966), 1093–1096.

NIST (2013): National Institue of Standards and Technology – *Reference Fluid Thermodynamic and Transport Properties Database (REFPROP)*: Version 9.1, 2013.

Oellrich, L. R.; Althaus, K. (2001): *GERG-Water Correlation*. GERG Technical Monograph TM14. Fortschritts-Berichte VDI, Reihe 3, Nr. 679. VDI Verlag, Düsseldorf, 2001.

Parikh, N. C.; Zollweg, J. A. (1997): *Vapor-Liquid Equilibrium in the Argon-Oxygen System. Proc. Energy Week*. Energy Week 7, 8th Annual. Houston (1997), 58–64.

Palavra, A. M. (1979): *Effect of Pressure and Temperature on Excess Properties in the System Argon-Nitrogen*. Master's Thesis, Universidade Tecnica De Lisboa, Instituto Superior Tecnico, 1979.

Patel, M. R.; Eubank, P. T. (1988): *Experimental Densities and Derived Thermodynamic Properties for Carbon Dioxide-Water Mixtures*. J. Chem. Eng. Data 33 (1988), 185–193.

Plöcker, U.; Knapp, H.; Prausnitz, J. (1978): *Calculation of High-Pressure Vapor-Liquid Equilibria from a Corresponding-States Correlation with Emphasis on Asymmetric Mixtures*. Ind. Eng. Chem. Proc. Des. Dev. 17 (1978), 324–332.

Pool, R. A. H.; Saville, G.; Herrington, T. M.; Staveley, L. A.; Shields, B. D. C. (1962): *Some Excess Thermodynamic Functions for the Liquid Systems Argon+Oxygen, Argon+Nitrogen, Nitrogen+Oxygen, Nitrogen+Carbon Monoxide, and Argon+Carbon Monoxide*. Trans. Faraday Soc. 58 (1962), 1692–1704.

Quin, J.; Rosenbauer, R. J.; Duan, Z. (2008): *Experimental Measurements of Vapor–Liquid Equilibria of the* $H_2O+CO_2+CH_4$ *Ternary System*. J. Chem. Eng. Data 53 (2008), 1246–1249.

Ricardo, A. A.; Barreiros, S. F.; da Ponte, M. N.; Albuquerque, G. M. N.; Calado, J. C. G. (1992): *(p,* V_m*, T) of (0.476 Ar + 0.524* N_2*) (l) and the Calculation of Thermodynamic Properties of Liquid Air*. J. Chem. Thermodyn. 24 (1992), 1281–1291.

Rigby, M.; Prausnitz, J. M. (1968): *Solubility of Water in Compressed Nitrogen, Argon, and Methane*. J. Phys. Chem. 72 (1968), 330–334.

Saji, Y.; Okuda, T. (1965): *A Certain Excess Property of the Liquid System Oxygen-Argon*. Adv. Cryog. Eng. 10 (1965), 209–223.

Sarashina, E.; Arai, Y.; Saito, S. (1971): *The P-V-T-X Relation for the Carbon Dioxide Argon System*. J. Chem. Eng. Jpn. 4 (1971), 379–381.

Shilling, W. G.; Partington, J. R. (1928): *Measurements of the Velocity of Sound in Air, Nitrogen, and Oxygen with Special Reference to the Coefficients of the Molecular Heats*. Philos. Mag. 6 (1928), 920–939.

Schmidt, R.; Wagner, W. (1985): *A New Form of the Equation of State for Pure Substances and its Application to Oxygen*. Fluid Phase Equilib. 19 (1985), 175–200.

Smith, N. O.; Kelemen, S.; Nagy, B. (1962): *Solubility of Natural Gases in Aqueous Salt Solutions-II. Nitrogen in Aqueous NaCl,* $CaCl_2$ Na_2S0_4 *and* $MgSO_4$ *at Room Temperatures and at Pressures Below 1000 psia*. Geochim. Cosmochim. Acta 26 (1962), 921–926.

Schönmann, W. (1971): *Messung der thermischen Eigenschaften und Aufstellung einer empirischen Zustandsgleichung gasförmiger Argon-Kohlendioxid-Gemische*. Dissertation, Universität Karlsruhe, Fakultät für Chemieingenieurwesen, 1971.

Seitz, J. C.; Blencoe, J. G. (1999): *The* CO_2*-*H_2O *system. I. Experimental Determination of Volumetric Properties at 400 Degrees C, 10-100 MPa*. Geochim. Cosmochim. Acta 63 (1999), 1559–1569.

Seitz, J. C.; Blencoe, J. G. (1996): *Volumetric Properties for* $\{(1-x)CO_2+xCH_4\}$, $\{(1-x)CO_2+xN_2\}$, *and* $\{(1-x)CH_4+xN_2\}$ *at the Pressures (19.94, 29.94, 39.94, 59.93, 79.93, and 99.93) MPa and the Temperature 673.15 K*. J. Chem. Thermodyn. 28 (1996), 1207–1213.

Seitz, J. C.; Blencoe, J. G.; Bodnar, R. J. (1996): *Volumetric Properties for* $\{(1-x)CO_2+xCH_4\}$, $\{(1-x)CO_2+xN_2\}$ *and* $\{(1-x)CH_4+xN_2\}$ *at the Pressures (9.94, 19.94, 29.94, 39.94, 59.93, 79.93, and 99.93) MPa and Temperatures (323.15, 373.15, 473.15, and 573.15) K*. J. Chem. Thermodyn. 28 (1996), 521–538.

Span, R.; Gernert, J.; Jäger, A.; Thol, M.; Wiens, T. (2012): *TREND. Thermodynamic Reference and Engineering Data* 1.0, Lehrstuhl für Thermodynamik, Ruhr-Universität Bochum, 2012.

Span, R.; Eckermann, T; Gernert, J.; Herrig, S; Jäger, A.; Thol, M. (2013): *TREND. Thermodynamic Reference and Engineering Data* 1.1, Lehrstuhl für Thermodynamik, Ruhr-Universität Bochum, 2013.

Span, R; Wagner, W. (1996): *A New Equation of State for Carbon Dioxide Covering the Fluid Region from the Triple-Point Temperature to 1100 K at Pressures up to 800 MPa*. J. Phys. Chem. Ref. Data 25 (1996), 1509.

Span, R.; Lemmon, E. W.; Jacobsen, R. T.; Wagner, W.; Yokozeki, A. (2000): *A Reference Equation of State for the Thermodynamic Properties of Nitrogen for Temperatures from 63.151 to 1000 K and Pressures to 2200 MPa*. J. Phys. Chem. Ref. Data 29 (2000), 1361.

Sprow, F. B.; Prausnitz, J. M. (1966): *Vapor-Liquid Equilibria for Five Cryogenic Mixtures*. AlChE J. 12 (1966), 780–784.

Steckel, F. (1935): *Dew and Boiling Curves of Nitrogen-Carbon Monoxide Mixtures up to 17 Atmospheres*. Physikalische Zeitschrift der Sowjetunion 8 (1935), 337–341.

Strakey, J. P.; Bennett, C. O.; Dodge, B. F. (1974): *Joule-Thomson Coefficients of Argon-Carbon Dioxide Mixtures*. AlChE J. 20 (1974), 803–814.

Takenouchi, S.; Kennedy, G. C. (1964): *The Binary System H_2O-CO_2 at High Pressures and Temperatures*. Am. J. Sci. 262 (1964), 1055–1074.

Tegeler, C.; Span, R.; Wagner, W. (1999): *A New Equation of State for Argon Covering the Fluid Region for Temperatures From the Melting Line to 700 K at Pressures up to 1000 MPa*. J. Phys. Chem. Ref. Data 28 (1999), 779–850.

Teng, H.; Yamasaki, A.; Chun, M. K.; Lee, H. (1997): *Solubility of Liquid CO_2 in Water at Temperatures from 278 K to 293 K and Pressures from 6.44 MPa to 29.49 MPa and Densities of the Corresponding Aqueous Solutions*. J. Chem. Thermodyn. 29 (1997), 1301–1310.

Thorpe, P. L. (1968): *Liquid-Vapour Equilibrium of the System Nitrogen+Argon at Pressures up to 10 atm*. Trans. Faraday Soc. 64 (1968), 2273–2280.

Tödheide, K.; Franck, E. U. (1959): *Thermische Eigenschaften überkritischer Mischungen von Kohlendioxyd und Wasser bis zu 750 °C und 2000 Atm*. Z. Phys. Chem. Neue Folgen 22 (1959), 232–245.

Torotscheschnikow, N. (1937): *Isotherms and Isobars of the Nitrogen-Carbon Monoxide System*. Tech. Phys. of the USSR 4 (1937), 365–369.

Townsend, P. W. (1956): *Pressure-Volume-Temperature Relationships of Binary Gaseous Mixtures*. Dissertation, Faculty of Pure Science, Columbia University, 1956.

Trappehl, G. (1987): *Experimentelle Untersuchung der Dampf-Flüssigkeits-Phasengleichgewichte und kalorischen Eigenschaften bei tiefen Temperaturen und hohen Drücken an Stoffgemischen bestehend aus N_2, CH_4, C_2H_6, C_3H_8 und CO_2*. Dissertation, Technische Universität Berlin, 1987.

Trusler, M. (2012): *pTxy Data for the System Carbon Dioxide + Water*. Imperial College of Science, Technology and Medicine, London, UK, private communication, 2012.

Valtz, A.; Chapoy, A.; Coquelet, C.; Paricaud, P.; Richon, D. (2004): *Vapour-Liquid Equilibria in the Carbon Dioxide-Water System, Measurement and Modelling from 278.2 to 318.2 K*. Fluid Phase Equilib. 226 (2004), 333–344.

Verschoyle, T. T. H. (1932): *The Ternary System Carbon Monoxide-Nitrogen-Hydrogen and the Component Binary Systems between Temperatures of - 185 degrees and - 215 degrees C., and between Pressures of 0 and 225 Atm.* Philos.Trans. Roy. Soc. A 230 (1932), 189–220.

Wang, D. I. J. (1960): *Vapor-Liquid Equilibrium Studies on the System Argon-Oxygen*. Adv. Cryog. Eng. 3 (1960), 294–304.

Wagner, W.; Pruß, A. (2002): *The IAPWS Formulation 1995 for the Thermodynamic Properties of Ordinary Water Substance for General and Scientific Use*. J. Phys. Chem. Ref. Data 31 (2002), 387.

Wiebe, R.; Gaddy, V. L. (1939): *The Solubility in Water of Carbon Dioxide at 50, 75 and 100°, at Pressures to 700 Atmospheres*. J. Am. Chem. Soc. 61 (1939), 315–318.

Wiebe, R.; Gaddy, V. L. (1941): *Vapor Phase Composition of Carbon Dioxide-Water Mixtures at Various Temperatures and at Pressures to 700 Atmospheres*. J. Am. Chem. Soc. 63 (1941), 475–477.

Wiebe, R.; Gaddy, V.L; Heinss, C. Jr (1932): *Solubility of Nitrogen in Water at 25 °C from 25 to 1000 Atmospheres*. Ind. Eng. Chem. 24 (1932), 927-927.

Wiebe, R.; Gaddy, V.L; Heinss, C. Jr (1933): *The Solubility of Nitrogen in Water at 50, 75 and 100° from 25 to 1000 Atmospheres*. J. Am. Chem. Soc. 55 (1933), 947–953.

Wilcock, R. J.; Battino, R. (1974): *Solubility of Oxygen-Nitrogen Mixture in Water*. Nature 252 (1974), 614–615.

Wilson, G. M.; Silverberg, P. M.; Zellner, M. G. (1965): *Argon-Oxygen-Nitrogen Three-Component System Experimental Vapor-Liquid Equilibrium Data*. Adv. Cryog. Eng. 10 (1965), 192–208.

Wöll, O. (2003): *Experimental pVT Data for the System Nitrogen - Oxygen [Source: Kunz et al. (2007)]*, Lehrstuhl für Thermodynamik, Ruhr-Universität Bochum, 2003.

Wu, G.; Heilig, M.; Lentz, H.; Franck, E. U. (1990): *High Pressure Phase Equilibria of the Water-Argon System*. Ber. Bunsen Ges. Phys. Chem. 94 (1990), 24–27.

Wylie, R. G.; Fisher, R. S. (1996): *Molecular Interaction of Water Vapor and Oxygen*. J. Chem. Eng. Data 41 (1996), 175–180.

Yorizane, M.; Yoshimura, S.; Masuoka, H.; Toyama, A.; Nakao, Y.; Funada, I. (1978): *Measurement and Estimation of Low Temperature Vapor-Liquid Equilibrium for the System Oxygen-Argon at High Oxygen Concentrations*. Chem. Eng. Sci. 33 (1978), 641–649.

Younglove, B. A.; Frederick, N. V.; McCarty, R. D. (1993): *Speed of Sound Data and Related Models for Mixtures of Natural Gas Constituents.* NIST Monograph, 178. National Institute of Standards and Technology, Gaithersburg MD, 1993.

Yushkevich, N. F.; Torocheshnikov, N. S. (1936): *Study of the Coexistence of Liquid and Vapor Phases of Solutions of Nitrogen and Carbon monoxide*. Zh. Khim. Prom. 13 (1936), 1273.

Zandbergen, P.; Beenakker, J. J. M. (1967): *Experimental Determination of the Volume Change on Mixing for Gaseous* N_2-H_2*,* Ar-H_2 *and* Ar-N_2 *between 170 And 292 °K up to 100 atm*. Physica 33 (1967), 343–365.

Zakirov, I. V. (1984): *The P-V-T Relations in the* H_2O-CO_2 *System at 300 and 400 °C up to 1000 bar*. Geochem. Int. 21 (1984), 13–20.

Zenner, G. H.; Dana, L. I. (1963): *Liquid-Vapor Equilibrium Compositions of Carbon Dioxide-Oxygen-Nitrogen Mixtures*. Chem. Eng. Prog. Symp. Ser. 59 (1963), 36–41.