

GHGT-11

Accurate thermodynamic-property models for CO₂-rich mixtures

Roland Span*, Johannes Gernert, Andreas Jäger

Thermodynamics, Ruhr-Universität Bochum, D-44780 Bochum, Germany

Abstract

Carbon capture and storage (CCS) technologies result in demands on thermodynamic-property models that were previously unknown in energy technologies. This article summarises recent developments allowing for an accurate description of thermodynamic properties of mixtures that are typical for oxyfuel processes and for compression and transport of separated CO₂. It addresses homogeneous fluid state as well as phase equilibria of fluid and solid phases. However, phase equilibria with scrubbing agents, as they are common for post combustion processes, are out of the scope of this article.

© 2013 The Authors. Published by Elsevier Ltd.
Selection and/or peer-review under responsibility of GHGT

Keywords: Fundamental equations of state, CO₂-rich mixtures, phase equilibria, dry ice, CO₂ hydrates

1. Introduction

Carbon capture and storage (CCS) technologies result in demands on thermodynamic-property models that were previously unknown in energy technologies. On one hand complex mixtures with scrubbing agents have to be described particularly for post-combustion capture technologies. Like most processes in chemical engineering, the corresponding apparatuses are operated at or close to ambient pressure. Vapour/liquid phase equilibria need to be calculated to assess the selectivity of separation processes, enthalpies are required for energy balances. These tasks can be addressed on a reasonable level of accuracy by property models well known in process engineering. Problems result from the fact that the detailed composition of scrubbing agents is usually considered a company secret and that degradation of the scrubbing agents has to be considered, including the formation of solid phases. This effect is

* Corresponding author. Tel.: +49-234-32-23033; fax: +49-234-32-14163.
E-mail address: roland.span@thermo.rub.de.

understood in principle but cannot be described easily by common property models. Improving capabilities and accuracy of the used thermodynamic property models requires additional experimental data. However, fundamental research and company interests are in conflict in this area quite often.

On the other hand, CO₂-rich mixtures have to be considered at high pressure in some capture processes, e.g., in oxyfuel gas-turbines. CO₂-rich mixtures have to be compressed to typical pipeline pressures, to be dried, to be transported and finally to be stored. These steps involve apparatus design and energy balances which are typical for energy technologies. However, while high demands on accuracy of such calculations can usually be met by ideal gas models in energy technologies (accept for the properties of water and steam, where appropriate international standards are available), CCS technologies result in high demands on the accuracy of thermodynamic property data for highly non-ideal gaseous, supercritical and liquid mixtures. Certain low temperature transportation schemes and rapid expansion processes as a result of rupture or instationary operation of pipelines result in the formation of complex phase equilibria involving multiple fluid phases, water ice, dry ice, and hydrates. Internationally, a number of ongoing experimental and theoretical projects address these issues. This is the kind of requirements the current article deals with.

Current work focuses on the accurate description of mixtures of CO₂ (carbon dioxide), H₂O (water), N₂ (nitrogen), O₂ (oxygen), Ar (argon), and CO (carbon monoxide) as main components of typical CO₂-rich mixtures in CCS processes. The most accurate currently available thermodynamic model for mixtures of these components is the GERG-2008 by Kunz and Wagner [1]. Originally developed for natural gas mixtures, this model accurately describes mixtures of up to 21 components, including all of the six substances mentioned above. While gas phase and supercritical states are generally described with high accuracy, the GERG-2008 model shows some shortcomings regarding the description of phase equilibria and of gas solubilities. This point is addressed by a still ongoing project named EOS-CG (Equation Of State for Combustion Gases and combustion gas like mixtures). Preliminary results of this project [2] show that significant improvements for phase-equilibrium calculations and for properties of liquid phases are possible. However, CCS processes require data not only for fluid phase states, but also for phase equilibria involving ice, dry ice and CO₂ hydrates. Accurate models describing these states in a way that is consistent to advanced fluid models like GERG-2008 or EOS-CG became available recently.

The intention of this article is to summarise the current status of the development of accurate property models for the CO₂-rich mixtures relevant for CCS processes. Examples for the performance of state of the art property models will be given as well as an outlook regarding necessary next steps.

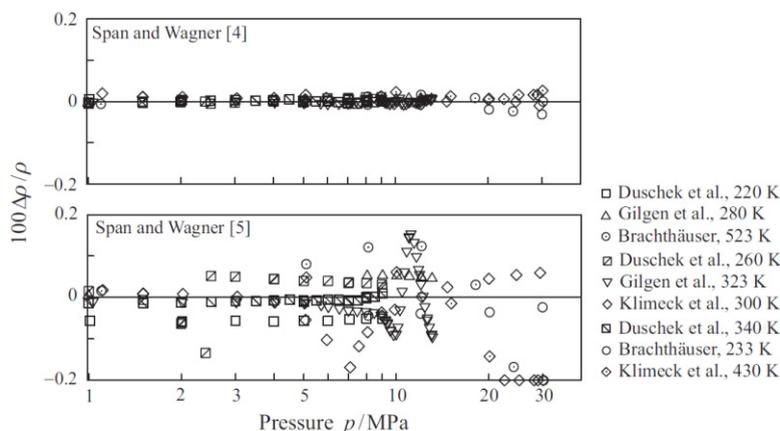


Fig. 1. Deviations between highly accurate experimental data for the density of pure CO₂ and values calculated from the reference equation of state for CO₂ [4], upper plot, and from an advanced technical equation of state for CO₂ [5], lower plot.

2. Properties of pure CO₂

In early studies CO₂ separated from power processes was assumed to be technically pure. Properties of pure CO₂ can be calculated with almost arbitrary accuracy from multiparameter equations of state in form of the reduced Helmholtz energy as a function of reduced temperature and density. Such fundamental equations of state allow for a consistent description of all thermodynamic properties of a pure fluid by just combining derivatives of the function; for an overview see, e.g., Span [3]. So called “reference equations of state” describe all experimental data available for thermodynamic properties of a certain fluid within their experimental uncertainty. For CO₂ both a reference equation of state [4] and a recent equation of state for typical technical applications [5], which causes somewhat less numerical efforts, are available. As an example for the accuracy of these equations of state, Fig. 1 shows percentage deviations between highly accurate results for the density of CO₂ and corresponding values calculated from the respective equation of state. The plotted data cover states from the liquid close to the triple point temperature to far supercritical temperatures.

3. Properties of relevant fluid mixtures

In the mid 90’s Lemmon and Tillner-Roth [6] independently of each other developed an approach, which in principle allows for a highly accurate description of thermodynamic properties of mixtures, provided a sufficient amount of accurate experimental data is available for the corresponding mixture. Following this approach, the reduced Helmholtz energy α of the mixture is written as

$$\alpha(\delta_m, \tau_m, \mathbf{x}) = \frac{a(\rho, T, \mathbf{x})}{RT} = \sum_{i=1}^N x_i \left[\alpha_{oi}^0(\rho, T) + \ln x_i \right] + \sum_{i=1}^N x_i \alpha_{oi}^r(\delta_m, \tau_m) + \sum_{i=1}^{N-1} \sum_{j=i+1}^N x_i x_j F_{ij} \alpha_{ij}^r(\delta_m, \tau_m) \quad (1)$$

$$\text{With } \tau_m = \frac{T_r(\mathbf{x})}{T}, \quad T_r(\mathbf{x}) = \sum_{i=1}^N \sum_{j=1}^N x_i x_j \beta_{T,ij} \gamma_{T,ij} \frac{x_i + x_j}{\beta_{T,ij}^2 x_i + x_j} T_{c,i} T_{c,j}^{0.5} \quad (2)$$

$$\text{and } \delta_m = \frac{\rho}{\rho_r(\mathbf{x})}, \quad \frac{1}{\rho_r(\mathbf{x})} = \sum_{i=1}^N \sum_{j=1}^N x_i x_j \beta_{\rho,ij} \gamma_{\rho,ij} \frac{x_i + x_j}{\beta_{\rho,ij}^2 x_i + x_j} \frac{1}{8} \left(\frac{1}{\rho_{c,i}^{1/3}} + \frac{1}{\rho_{c,j}^{1/3}} \right)^3 \quad (3)$$

the first two summations in Eq. (1) define an extended corresponding states approach for a mixture with N components, whereby a is the molar Helmholtz energy, ρ the molar density, T the thermodynamic temperature, R the molar gas constant, \mathbf{x} the vector of mole fractions describing the composition of the mixture, $x_{i/j}$ the mole fraction of the $i^{\text{th}} / j^{\text{th}}$ component, δ_m the reduced density of the mixture, τ_m the inversely reduced temperature of the mixture, α_{oi}^0 the reduced ideal-gas contribution to the reduced Helmholtz energy of the pure fluid i , α_{oi}^r the reduced residual (real-gas) contribution to the reduced Helmholtz energy of the pure fluid i . In Eq. (2) T_r is the reducing temperature of the mixture, $T_{c,ij}$ is the critical temperature of component i/j , and $\beta_{T,ij}$ and $\gamma_{T,ij}$ are adjustable parameters for the binary (sub-) system of the components i,j . In Eq. (3) ρ_r is the reducing temperature of the mixture, $\rho_{c,ij}$ is the critical density of component i/j , and $\beta_{\rho,ij}$ and $\gamma_{\rho,ij}$ are adjustable parameters for the binary (sub-) system of the components i,j . With just these two sums Eq. (1) defines a fundamental equation for the mixture (Helmholtz energy as a function of temperature and density) with up to four adjustable parameters for each binary (sub-) system of the mixture, which allows for an accuracy comparable to the accuracy of other extended corresponding states approaches.

The third sum in Eq. (1) defines a departure function, which allows for a correction of the (small) systematic errors made by the corresponding states approach, provided a sufficient amount of accurate data is available for the corresponding binary (sub-) system to fit more than the up to four adjustable parameters of the reducing functions, Eq. (1) and Eq. (2). In the third sum F_{ij} is an adjustable parameter for the binary (sub-) system of the components i,j . a_{ij} is the departure function in form of the reduced Helmholtz energy, for which, e.g., Kunz and Wagner [1] propose the general form

$$\alpha_{ij}(\delta_m, \tau_m) = \sum_{k=1}^{K_{Pol,ij}} n_k \delta_m^{d_k} \tau_m^{t_k} + \sum_{k=K_{Pol,ij}+1}^{K_{Pol,ij}+K_{Exp,ij}} n_k \delta_m^{d_k} \tau_m^{t_k} \exp \left[-\eta_k \delta_m - \varepsilon_k \delta_m^2 - \beta_k \delta_m - \gamma_k \right]. \quad (4)$$

The form of the departure function is similar to the form known for empirical, Helmholtz-energy based equations of state for pure fluids, but typical departure functions have only four to six terms. In Eq. (4) n_k , d_k , t_k , η_k , ε_k , β_k , and γ_k are adjustable parameters, which are characteristic for a certain binary (sub-) system (binary specific departure function) or for a group of binary (sub-) systems (for example mixtures of higher alkanes [1], generalized departure function).

The mixture model defined by Eqs. (1-4) seems rather complex, but in fact it has a number of advantages both with regard to fitting and using the model:

- Eq. (1) defines a fundamental equation of state for the mixture, which is explicit in the reduced Helmholtz energy. Consistent values for all kinds of (thermal and caloric) thermodynamic properties can be calculated from Eq. (1) in the same way as for pure fluids [3]. Only for phase equilibrium calculations more advanced routines are required.
- Eqs. (1-4) contain only binary parameters. Multi-component mixtures are described by their binary sub-systems; adjustable parameters are fitted only to data for binary mixtures. Ideally data for these binary mixtures should cover the whole composition range, even if only CO₂ rich multi-component mixtures are considered later on. Otherwise problems may occur particularly when calculating phase equilibria (in a CO₂-rich CO₂/H₂O mixture the liquid phase formed at or close to ambient pressure contains mostly H₂O for example).

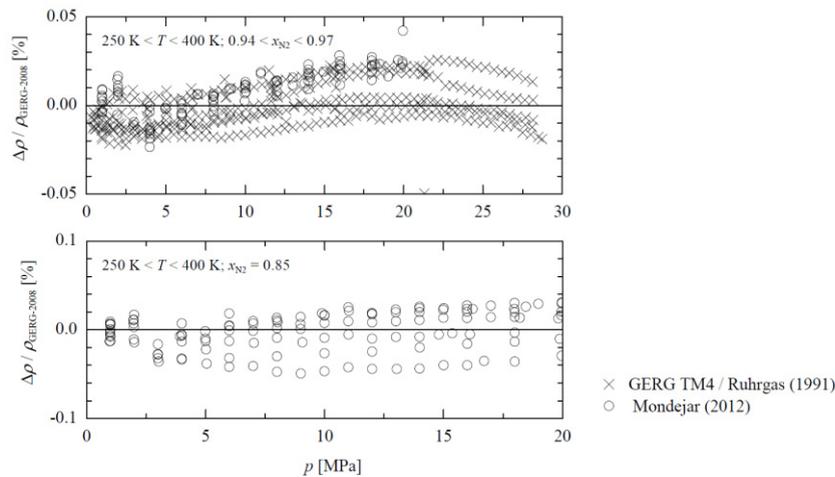


Fig. 2. Deviations between highly accurate experimental data for the density of N₂/CO mixtures and values calculated from the GERG-2008 model [1].

- Eq. (1) allows for combining binary sub-systems described on different levels of accuracy. In case no or only very few data are available for a binary system, the adjustable parameters in Eqs. (2) and (3) can be considered equal to one – Eqs. (2) and (3) turn into purely predictive combination rules this way. If more data are available, up to four parameters in the reducing functions can be fitted. And in case sufficiently accurate data are available for a sub-system, either a generalized departure function (in this case only F_{ij} is used as binary specific parameter) or even a binary specific departure function can be used.

The GERG-2008 model [1] makes use of the last feature to accurately describe mixtures of up to 21 components – the resulting 210 binary sub-systems can only be handled because less well investigated or less relevant sub-systems can be dealt with on a lower level of accuracy. With respect to mixtures relevant for CCS this leaves some room for improvements, because different sub-systems and concentration ranges are relevant in natural gas and in CCS applications. This is the approach EOS-CG [2] is based on – it aims at an improved description of binary systems particularly relevant for CCS, while compatibility to GERG-2008 is maintained to allow for a description of mixtures containing other components as well. In the following sections the performance of the two models will briefly be discussed for homogeneous gaseous and supercritical states, for phase equilibria with fluid phases, and for liquid states.

3.1. Gaseous and supercritical states

The GERG-2008 model [1] describes gaseous and supercritical states with high accuracy. For some of the binary sub-systems formed by mixtures of CO₂, H₂O, N₂, O₂, Ar, and CO highly accurate gas-phase data are available; these data are represented well by GERG-2008. As an example, Fig. 2 shows the representation of accurate density data for the system N₂/CO. For sub systems for which only few or less accurate data are available a sound assessment of the accuracy of property models becomes difficult. However, in general it can be stated that there is little room left for improvements regarding the description of gaseous and supercritical states, unless new experimental results for thermodynamic property data become available.

3.2. Phase equilibria

With regard to vapour-liquid phase equilibria (VLE) of the binary mixtures relevant for CCS the GERG-2008 model [1] describes the saturated gas phase quite well in most cases. However, in the (H₂O-

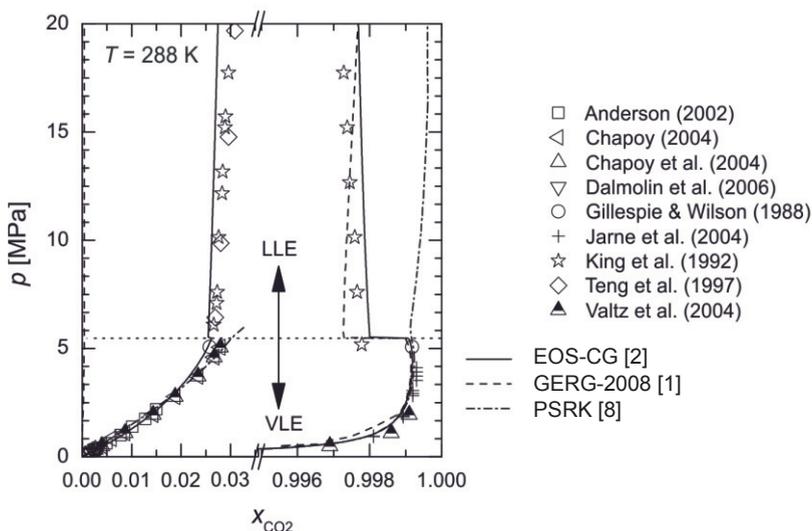


Fig. 3. Example for the description of phase equilibria in the binary system CO₂/H₂O.

rich) liquid phase gas solubilities are drastically underestimated. This becomes particularly obvious for the system that is most relevant for phase equilibria in CCS processes, for the system $\text{CO}_2/\text{H}_2\text{O}$. GERG-2008 is also able to describe the liquid-liquid equilibrium (LLE) in the system $\text{CO}_2/\text{H}_2\text{O}$ reasonably well. However, neither the software distributed by the authors of GERG-2008 nor REFPROP 9.0 [7], which contains an implementation of the GERG-2008 model, fully support this feature of the model. Compared to GERG-2008, EOS-CG improves mainly the description of the H_2O -rich liquid phase, where the CO_2 concentration is predicted quite accurately by EOS-CG. Just like GERG-2008 it predicts the formation of a CO_2 -rich liquid phase at high pressures, the change from VLE to LLE, and the composition of the CO_2 -rich liquid phase well. Most “engineering equations of state”, like the predictive Soave-Redlich-Kwong equation (PSRK) by Holderbaum and Gmehling [8], are not able to properly predict the change from VLE to LLE. Figure 3 illustrates the described features of the different models.

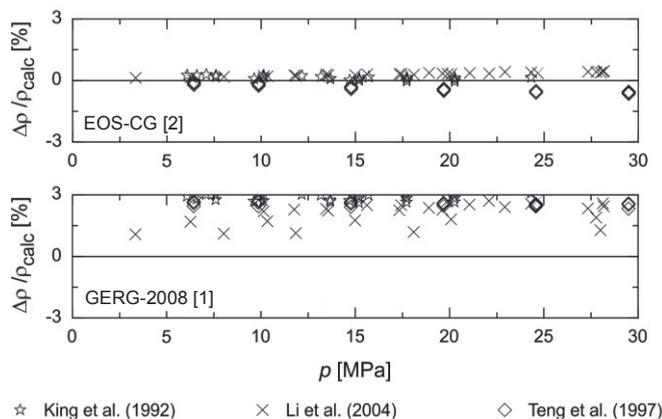


Fig. 4. Deviation between experimental data and density values calculated from EOS-CG [2] and GERG-2008 [1] in the H_2O -rich liquid phase of the binary system $\text{CO}_2/\text{H}_2\text{O}$.

3.3. Liquid states

The description of thermodynamic properties in the homogeneous or saturated liquid phase is related to the description of the liquid phase in phase equilibrium calculations. For CCS processes the most relevant liquid phases are CO_2 -rich and H_2O -rich liquid phases. While the GERG-2008 model performs quite well for CO_2 -rich liquid phases, it underestimates the density of the H_2O -rich liquid phase systematically, see Fig. 4. EOS-CG describes density data for the H_2O -rich liquid phase without significant systematic deviations. However, highly accurate data for thermodynamic properties at liquid states of the relevant systems are rare. While most properties can be determined at liquid states with higher accuracy than at gaseous or supercritical states for pure fluids, it is difficult to determine the exact composition of the liquid in the measuring cell for the mixtures considered here. Possible shifts in composition result in total experimental uncertainties exceeding those that can be achieved in the gaseous phase – an accuracy as it was demonstrated in Fig. 2 for gas-phase data cannot be achieved in the liquid phase, unless data from experimental apparatuses like the one currently under development for liquefied natural gas become available [9]. For properties at liquid states the application of most engineering-type equations of state results in uncertainties by far exceeding the systematic deviations shown for GERG-2008.

4. Phase equilibria with solid phases

At low temperatures, which become relevant, e.g., for ship transport of CO₂ or for expansion processes in pipelines, valves, and leaks, the system CO₂/H₂O forms not only phase equilibria with vapour and liquid phases (VLE and LLE), but also with solid phases (SLE and SVE). The relevant solid phases are ice (solid H₂O), dry ice (solid CO₂), and CO₂ hydrates. Simple models for the description of certain properties of the relevant phases are readily available; for sublimation and melting pressures of CO₂ see, e.g., [4]. However, to enable a consistent description of fluid and solid phases (allowing for example for flash calculations into two phase regions and for calculation of thermodynamic properties of the two phase system) fundamental equations of state for the solid phases are required. For the solid phases in the system CO₂/H₂O such fundamental equations recently became available. Together with a fundamental equation of state for the fluid phases, such as GERG-2008 or EOS-CG, these models allow for a consistent description of all relevant phase equilibria and of thermodynamic properties of the resulting two phase systems.

Figure 5 shows the three-phase lines separating the different two phase areas of the system CO₂/H₂O from each other. The lines were calculated by intersection of chemical potential surfaces of the different phases. Chemical potentials of the solid phases were calculated using the solid phase models briefly described in the following sections. Chemical potentials of the fluid phases were calculated with GERG-2008 [1] and EOS-CG [2], respectively. The phases indicated in Fig. 5 by abbreviations are V – Vapour phase, Lw – H₂O-rich liquid phase, Lc – CO₂-rich liquid phase, H – CO₂ hydrate, Iw – solid H₂O (ice), and Ic – solid CO₂ (dry ice).

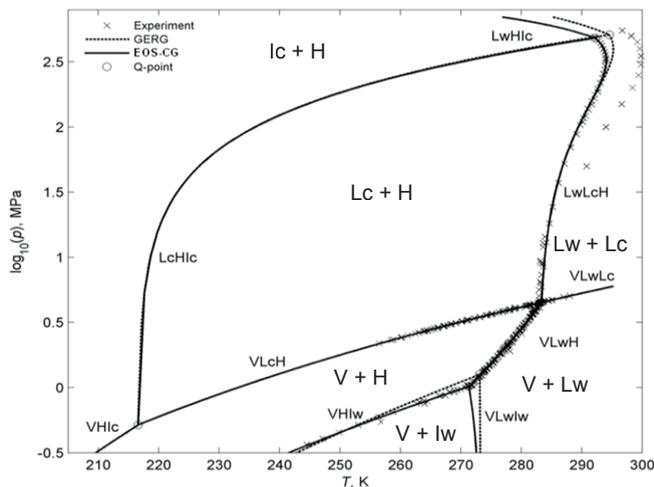


Fig. 5. Three-phase lines calculated by intersection of the chemical potential surfaces calculated from GERG-2008 [1] and EOS-CG [2] with the chemical potentials calculated from the discussed solid phase models.

4.1. Ice (solid H₂O)

Properties of ice can be described accurately using the standard established by the International Association for the Properties of Water and Steam (IAPWS). This fundamental equation by Feistel and

Wagner [10,11] is explicit in the reduced Gibbs energy as a function of temperature and pressure and can be used to calculate chemical potentials of the pure water ice phase. Suitable assumptions for the reference states of enthalpy and entropy, which have to be consistent with the different models used to calculate properties at fluid states, are discussed by Jäger et al. [12].

4.2. Dry ice (solid CO_2)

Properties of dry ice can be described accurately using either the equation by Jäger and Span [13] or the equation by Trusler [14]. Both equations are formulated in terms of the reduced Gibbs energy as a function of temperature and pressure and allow for calculation of chemical potentials of the pure dry ice phase. Suitable assumptions for the reference states of enthalpy and entropy, which have to be consistent with the different models used to calculate properties at fluid states, are discussed by Jäger et al. [12].

4.3. CO_2 hydrates

Properties of CO_2 hydrates can be calculated using the recent model by Jäger et al. [12]. This model describes the chemical potentials of the hydrate phase, which contains H_2O and CO_2 , and of its constituents. Thus, with appropriate reference states it can be used phase equilibrium calculations by intersection of chemical potential surfaces with surfaces calculated from fluid models. Several other models are available for the description of CO_2 hydrates. The main advantage of the model by Jäger et al. is that it was designed in a way, that it is consistent to fluid phase properties calculated with state of the art models like GERG-2008 or EOS-CG. Jäger et al. show that EOS-CG is slightly superior with regard to the description of the fluid phases of the system $\text{CO}_2/\text{H}_2\text{O}$. Using the GERG-2008 model, small but systematic deviations occur for three of the four three-phase lines separating fluid and solid states, see Fig. 5. These deviations cannot be explained by deficiencies of the hydrate model, which does not show significant systematic deviations in combination with EOS-CG.

5. Future steps

Over the last few years a number of property models became available, which enable an accurate description of mixtures containing the main components relevant for CCS processes, namely CO_2 , H_2O , N_2 , O_2 , Ar, and CO. For the first time, not only the fluid phases of a mixture but also relevant solid phases are described by accurate fundamental equations of state. This approach allows for consistent calculations including thermodynamic properties of two phase systems containing fluid and solid phases. Software that fully exploits the potential of the combined model is being developed.

An important next step will be the publication of a complete parameter set for EOS-CG in the Ph.D. thesis of J. Gernert in spring 2013 and subsequently in a scientific journal. However, this parameter set will not yet be the “final” parameter set, because a number of experimental projects aiming at an improved description of thermodynamic properties of mixtures relevant for CCS processes is going on. Thus, it is already obvious that work on EOS-CG has to continue to make use of these data, which will allow for an improved description of several of the important binary sub-systems. Further work on EOS-CG also has to take additional components into account. It became clear, that components like SO_2 (sulphur dioxide), NO_2 (nitrogen dioxide), H_2 (hydrogen), and H_2S (hydrogen sulphide) need to be considered as well. With regard to the description of solid phases the competing formation of N_2 and possibly also CH_4 hydrates needs to be considered to be able to accurately predict hydrate formation in multi-component mixtures.

A challenge for effective further experimental work is that several groups in the world address this point independently of each other. There is a certain risk that this approach will result in duplication of work for some of the relevant systems, while other systems are not considered at all. As part of the new European project IMPACTS an international workshop is planned for end of January 2013, which aims at an improved alignment of experimental work.

Some of the systems relevant for CCS processes can hardly be handled in existing highly accurate measurement equipment for reasons of corrosivity and toxicity. To generate data for these systems new approaches like molecular simulation based on accurately adjusted force fields or quantum chemical ab initio calculations of virial coefficients are considered useful supplements to experimental work.

References

- [1] Kunz O, Wagner W. The GERG-2008 wide-range equation of state for natural-gases and other mixtures: An expansion of GERG-2004. *J. Chem. Eng. Data* 2012, in Press [dx.doi.org/10.1021/je300655b].
- [2] Gernert J, Span R. EOS-CG: *An accurate property model for application in CCS processes*. Proc. Asian Thermophys. Prop. Conf., Beijing; 2010.
- [3] Span R. *Multiparameter equations of state – an accurate source of thermodynamic property data*. Springer, Berlin; 2000.
- [4] Span R, Wagner W. 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*, 1996; **25**: 1509–1596.
- [5] Span R, Wagner W. Equations of state for technical applications. III. Results for polar fluids. *Int. J. Thermophys.*, 2003; **24**, 111–162.
- [6] Lemmon EW, Tillner-Roth R. A Helmholtz energy equation of state for calculating the thermodynamic properties of fluid mixtures. *Fluid Phase Equilibria*, 1999; **165**: 1–21.
- [7] Lemmon EW, Huber ML, McLinden MO. *REFPROP, NIST Standard Reference Database 23 Version 9.0*, 2010.
- [8] Holderbaum T, Gmehling J. *PSRK: A Group Contribution Equation of State Based on UNIFAC*. *Fluid Phase Equilibria*, 1991; **70**: 251–265.
- [9] Richter M, Kleinrahm R, Span R, Schley P. A new apparatus for the accurate measurement of LNG densities. *gwf international*, 2010: 66–69.
- [10] Feistel R, Wagner W. A new equation of state for H₂O ice Ih. *J. Phys. Chem. Ref. Data*, 2006; **35**: 1021–1047.
- [11] Feistel R. *Revised Release on the Equation of State 2006 for H₂O Ice Ih*. <http://www.iapws.org/relguide/Ice-Rev2009.pdf>.
- [12] Jäger A, Vinš V, Gernert J, Hrubý J, Span R. Phase equilibria with hydrate formation in H₂O + CO₂ mixtures modeled with reference equations of state. Submitted to *Fluid Phase Equilibria*, 2012.
- [13] Jäger A, Span R. Equation of State for Solid Carbon Dioxide Based on the Gibbs Free Energy. *J. Chem. Eng. Data*, 2012; **57**: 590–597.
- [14] Trusler JPM. Equation of State for Solid Phase I of Carbon Dioxide Valid for Temperatures up to 800 K and Pressures up to 12 GPa. *J. Phys. Chem. Ref. Data*, 2011; **40**: 2689.