8 Conclusions and Perspective

Technological and scientific progress imposes high requirements on the availability and accuracy of thermophysical property data of fluid and solid phases. While the fluid phases of many mixtures can be described accurately, the accurate and consistent description of solid phases that are relevant for power and process engineering applications has been neglected for many years.

In this work, the solid phase of carbon dioxide as well as the gas hydrates formed by the guests carbon dioxide, nitrogen, oxygen, argon, carbon monoxide, methane, ethane, and propane have been modeled consistently to the best available Helmholtz energy models for fluid phases of these substances (i.e. EOS-CG by Gernert (2013) and the GERG-2008 equation of state by Kunz and Wagner (2012)) for the first time. Hydrate models for binary mixtures of water with one of the mentioned guest molecules have been established. Mixed hydrates have not been considered in this work. The equation for solid water by Feistel and Wagner (2006) was used in this work to model solid water consistently to all other modeled phases. The substances considered in this work cover the main components of carbon capture and storage, natural gas, and energy storage applications as discussed in chapter 2.

The hydrate model proposed in this work represents a considerable improvement of the hydrate model by Ballard and Sloan Jr. (2002b). On the one hand, it could be shown that the use of the most accurate equations of state for other phases than hydrate improves the hydrate model, because the hydrate model directly depends on the fugacities coming from the fluid or pure solid phase models. On the other hand, a physically reasonable bulk modulus was used for hydrates in this work, whereas Ballard and Sloan Jr. (2002b) mainly treated the bulk modulus as an adjustable parameter to better represent high pressure three-phase hydrate formation data. When comparing the hydrate model proposed in this dissertation to the model suggested by Ballard and Sloan Jr. (2002b), the average deviations of the experimental three-phase hydrate formation data from the calculated ones were improved for most three-phase lines of the hydrate formers.

It was shown that the mixing rules of the GERG-2008 equation of state for mixtures of hydrocarbons with water need to be improved. While methane hydrates and propane hydrates can nevertheless be described with good accuracy, there are shortcomings for ethane hydrates. This result was however expected, as the focus of the GERG-2008 equation of state was set on typical natural gas mixtures in which water is only a minor component.
The enthalpies of formation calculated with the new hydrate model proposed in this work are in good agreement with literature data. The scatter in literature data on enthalpies of formation is quite large and the quality of the data cannot be assessed easily. As the best equations available for all phases present have been used for the evaluation of the enthalpy of formation, it can however be assumed that the calculated enthalpies of formation along the three phase lines reported in this work are more accurate than most of the data reported in literature. Furthermore, enthalpies of formation for argon and carbon monoxide hydrates are reported for the first time.

A well-known problem when fitting the potential parameters and the reference state parameters of van der Waals and Platteeuw (1959)-type hydrate models to three-phase hydrate formation data only is that the optimized parameters become indistinct (see Ballard and Sloan Jr. (2002b)). Ballard and Sloan Jr. (2002b) have been the first to incorporate hydrate composition data (i.e. hydration numbers and cage occupancies) in hydrate fitting by restricting the values of the Kihara potential parameters with these data. If enough accurate cage occupancy data along the three-phase line had been available, the Kihara potential parameters could have been fitted to these data independently of the reference state parameters in this work. Unfortunately, there was not enough data available to do so. However, all available hydrate composition data were implemented in the fitting procedure in this work and are reasonably represented.

Phase equilibrium algorithms and phase stability algorithms that are able to predict phase equilibria of up to three phases in equilibrium have been developed in this work. These algorithms have been implemented in the thermophysical property software TREND by Span et al. (2015). Thermophysical properties of fluid and solid phases can be calculated at any given combination of temperature and pressure, pressure and enthalpy, and pressure and entropy. Furthermore, the freezing temperature for a specified mixture at given pressure (i.e. the temperature at which a solid phase starts to form) can be calculated. Most of the equations of state utilized for fluid and pure solid phases in this dissertation are internationally accepted reference equations of state. In this work, a first step towards a consistent reference model for CCS-relevant hydrate formers was taken. However, some improvements of the hydrate models, phase equilibrium calculation methods, and the fluid phase equations of state can be recommended for future work:

- The GERG-2008 mixing rules for the binary mixtures methane + water, ethane + water, and propane + water need to be improved. Especially the solubility of the hydrocarbons in liquid water needs to be corrected. Also, the mixing rules of the CCS-relevant components with water by Gernert (2013) could be revisited as soon as new data will become available. Furthermore, three-phase equilibria should be considered in the fitting procedure of the fluid phase equations, as the correct
description of three-phase equilibria without hydrate formation (i.e. vapor-liquid-liquid and vapor-liquid-solid water) is a prerequisite for a good hydrate model.

– It is common practice to inject hydrate inhibitors into pipelines to prevent hydrate formation, see for example Sum et al. (2009). Glycols or alcohols are typically used for hydrate inhibition, so that mixing rules for mixtures of these substances with the hydrate forming components are needed in order to model this with Helmholtz equations of state. The calculation of phase equilibria with hydrate inhibitors in a given mixture can already be accomplished with the algorithms developed in this dissertation but these components are not considered in the fluid models yet.

– Aside from glycols and alcohols, electrolytes can be added for hydrate inhibition. Furthermore, considering electrolytes is important for modeling hydrates in seawater. A good starting point for this could be the model for sea water by Feistel (2003).

– The hydrate model presented in this work needs to be extended to mixed hydrates. For this purpose, a mixture model for the lattice parameter of hydrates at reference conditions needs to be developed. The mixture model of Ballard and Sloan Jr. (2002b) could be a good starting point. The phase equilibrium algorithms presented in this work will need to be modified to consider different guest molecules in the hydrate phase. Furthermore, phase equilibrium algorithms for four phases of a multicomponent mixture in equilibrium will be needed.

– As discussed in this work, some hydrate formers double occupy the large cavities of the hydrate unit cell at elevated pressures. The hydrate model needs to be modified to account for this double occupancy. Among other works (e.g. Martín and Peters (2009b)), Klauda and Sandler (2003) provided a modification of the van der Waals-Platteeuw hydrate model that considers double occupancy of large sII cavities by nitrogen. Thus, the method of Klauda and Sandler (2003) could be a good starting point for considering double occupancy of nitrogen, argon, and oxygen molecules in sII hydrate.

– In general, the data situation for all hydrate formers needs to be improved. Especially experimental data on cage occupancies, hydration numbers, and enthalpies of formation show large deviations from each other. As the model for the potential of the guest molecules in the cavity is known to strongly influence the predicted hydrate structure in case of mixed hydrates, more experimental cage occupancy data of good quality are needed to establish a sound model for mixed hydrates. The same holds true for the lattice parameter of mixed hydrates. Although some data exist for the lattice parameter of mixed hydrates, more high quality data would be highly welcome.