8 Conclusions and Recommendations

Within the scope of the present work, new empirical Helmholtz-explicit equations of state (EOS) for pure fluids and fluid mixtures were developed by non-linear fitting to mostly experimental data. The focus of these developments was on two main objectives: (1) a new reference EOS for pure heavy water and (2) an EOS for multi-component CO\textsubscript{2}-rich mixtures relevant to Carbon Capture and Storage (CCS). The work on CCS mixtures not only required the development of various mixture formulations but also the fitting of two additional pure-fluid EOS for chlorine and monoethanolamine (MEA).

The new EOS for heavy water will replace the previous standard formulation of the International Association for the Properties of Water and Steam (IAPWS) developed by Hill et al.\textsuperscript{1} in 1982. The new EOS enables calculations of all thermodynamic properties over the whole fluid surface from the melting-pressure curve up to a temperature of 825 K and at pressures up to 1200 MPa. The development of the EOS was based on a comprehensive evaluation of the available experimental data, including the most recent studies. It was shown that the EOS describes the most accurate experimental results and almost all other available data within their uncertainties. Based on these comparisons with experimental data, detailed uncertainty estimates for calculated values of the most important thermodynamic properties were presented, namely thermal saturation data, density, speed of sound, and isobaric heat capacity. The most accurate experimental data were published for homogeneous liquid densities at atmospheric pressure from the triple-point to the normal-boiling-point temperature; the EOS represents these data within their uncertainty of 0.01 %. Compared to the previous EOS of Hill et al., the new EOS allows for a significantly more accurate representation of sound speeds in the liquid phase (matching the most accurate data within their expanded uncertainty between 0.015 % and 0.02 %), liquid densities at pressures above 100 MPa, second and third virial coefficients, and also the available experimental data in the critical region and the metastable subcooled liquid. In fact, the description of the metastable subcooled liquid was carefully fitted, although the official range of validity of the EOS was limited to temperatures above the melting-pressure curve. Considering the entire fluid surface, it was shown that the EOS not only matches the experimental data, but also enables a correct representation of the physical behavior of the fluid including various specific characteristics of (heavy) water. Furthermore, the EOS has a more compact and numerically well-behaved functional form than its predecessor, and can be reasonably extrapolated to extreme values of temperature and pressure. For an explicit definition of the range of validity, auxiliary equations for the melting-pressure curves of the ice structures Ih, III, V, and VI, as well as the sublimation-pressure curve of ice Ih were developed that border the fluid region of heavy water described by the new reference EOS.
During the fitting process, some gaps in the available experimental database were revealed. If a further improved EOS were to be developed, accurate $pvT$ data at pressures above 100 MPa and speed-of-sound data at pressures higher than 60 MPa would be extremely valuable. Between temperatures of 300 K and 350 K, the experimental database on vapor pressures was found to be less accurate than for lower and higher temperatures. New accurate data would improve the description of vapor-liquid equilibria, which would also benefit from accurate saturated-density data that are so far not available in the literature. In general, the homogeneous vapor phase is experimentally less investigated; densities are only available at temperatures above 423 K and no data have been published for vapor-phase sound speeds. Based on a thorough literature research, no reliable experimental data are available for metastable superheated-liquid and subcooled-vapor states, although these state regions are of significant relevance for energy applications. Since a further improvement of the present EOS through a refit is not planned or expected to become necessary in the next years, new data would primarily be used to improve uncertainty estimates for calculated properties. The new EOS for heavy water was recently published by Herrig et al.\textsuperscript{57} and adopted as the new IAPWS standard at the 2018 IAPWS annual meeting in Prague. The IAPWS Release is expected to be available by the end of 2018 or early in 2019.

The second aim of this work, the multi-component mixture EOS for CCS applications, is considered as an expansion of the EOS-CG developed by Gernert\textsuperscript{17} and published by Gernert and Span\textsuperscript{2} that allows for a reliable description of mixtures containing the major components typically found in CCS processes (carbon dioxide, water, nitrogen, oxygen, argon, and carbon monoxide). Within the present work, that EOS was improved and extended to additional components typically present as minor impurities in CCS mixtures. The mathematical structure of the extended EOS consequently follows the one of EOS-CG, which was also adopted from the GERG-2008\textsuperscript{35,36} model for natural gas mixtures. This framework of mixture modelling is based on the “extended corresponding states principle” and allows the description of multi-component mixtures by combining formulations for every possible binary combination of the components. Depending on the amount of experimental or, if available, also molecular-simulation data, these binary formulations can differ in their mathematical complexity and thus in their accuracy. The description of a binary mixture is essentially based on combining results of the respective pure-fluid EOS evaluated at “corresponding states”. This is enabled through the use of reduced input variables. If experimental data are scarce, the corresponding reducing functions for density and temperature are adjusted following simple combining rules. A more accurate description results from fitting the parameters of these reducing functions to experimental data. If comprehensive data are available that cover a wider range of the fluid surface, a binary specific departure function can be fitted. This function is a correction of the extended corresponding states principle and allows the most accurate description of a binary mixture.
In the present work, new formulations for 59 binary mixtures were developed. Out of these formulations, four contain a new binary specific departure function, and 13 are based on adjusted reducing functions without a departure function. The remaining systems were described by simple combing rules because the available database does not allow for fitting the parameters of the reducing functions. Together with 13 binary formulations adopted from EOS-CG and 19 formulations adopted from GERG-2008, the new binary models allow for a description of CCS mixtures with up to 14 components and thus 91 binary mixtures. The complete multi-component mixture model considers the presence of carbon dioxide, water, nitrogen, oxygen, argon, carbon monoxide, hydrogen, methane, hydrogen sulfide, monoethanolamine, diethanolamine, hydrogen chloride, and chlorine. Binary specific departure functions were developed for the systems CO$_2$ + Ar, CO$_2$ + CO, H$_2$O + CH$_4$, and H$_2$O + H$_2$S that replace previous formulations from EOS-CG and GERG-2008. Reducing parameters were adjusted for a number of binary systems with SO$_2$, namely SO$_2$ plus CO$_2$, N$_2$, O$_2$, CH$_4$, Cl$_2$, HCl, H$_2$O, MEA and DEA (diethanolamine). Additional reducing parameters were fitted for MEA + DEA, MEA + H$_2$O, DEA + H$_2$O, and Cl$_2$ + HCl.

All new binary models were carefully validated through detailed comparisons with the available experimental data. Results for systems also considered in EOS-CG or GERG-2008 were additionally compared with values calculated from those models. Furthermore, results calculated from SRK,$^{15}$ LKP,$^{19}$ PSRK,$^{41}$ and PC(P)-SAFT$^{34-46}$ were considered for selected systems. The validation based on experimental data was mostly focused on vapor-liquid-equilibrium (VLE) data, which are the most important data for fitting and, in many cases, are the only data available. Overall, the new binary formulations provide a very accurate description of the available VLE data. Uncertainties in calculated VLE data were estimated for most binary formulations. These uncertainties vary considerably depending on the binary system and its phase-equilibrium behavior but mostly depending on the accuracy of the data used for fitting. The most accurate new formulations (for CO$_2$ + Ar and CO$_2$ + CO) predict phase-boundaries mostly within uncertainties of about 1 mol% or smaller. For less well investigated systems such as MEA + DEA or Cl$_2$ + HCl, the uncertainties of calculated values might increase up to about 5 mol%. Estimated uncertainties in other calculated properties were given when comparative experimental data were available. Comparisons with the best data sets available, for example gas-phase densities for CO$_2$ + Ar (with experimental uncertainties between 0.033 % and 0.043 %), showed that these data can be represented within their experimental uncertainties.

The mathematical structure of the mixture model requires reliable pure-fluid EOS for every component. To implement the binary formulations discussed above, new Helmholtz-energy explicit EOS for pure chlorine and monoethanolamine (MEA) were developed.

The new EOS for chlorine replaces the current standard EOS of the International Union of Pure and Applied Chemistry (IUPAC) presented by Angus et al.$^{152}$ in 1985. The functional
form of that EOS is not suitable for the use in multi-component mixture models. The EOS developed in this work is valid from the triple point \( (T_{\text{tp,Cl}_2} = 172.17 \text{ K}) \) up to \( 440 \text{ K} \) and at pressures up to \( 20 \text{ MPa} \). Because it was exclusively developed for the application in the extended EOS for CCS mixtures, its extrapolation behavior beyond the experimentally investigated state regions was carefully constrained. The EOS consequently yields qualitatively reasonable results for state points outside its range of validity, which is important when evaluating it in mixture calculations. Due to its high toxicity, the quantity and quality of the experimental database for chlorine is much more limited than, for example, for heavy water. Nevertheless, sufficiently accurate data were available to fit the new EOS. These data are mostly represented within their experimental uncertainties.

Prior to the present work, no reliable EOS for MEA was available in the literature, which is not surprising with regard to the extremely limited experimental database. Nevertheless, a pure-fluid EOS was urgently needed due to the importance of MEA as a solvent in the CO\(_2\)-capturing process. The proposed EOS was fitted to the scarce data found in the literature, which only include measurements at saturation and in the liquid phase at atmospheric pressure. The limited data for homogeneous densities, vapor pressures, sound speeds, and isochoric heat capacities are accurately represented. The EOS is valid from the triple point \( (T_{\text{tp,MEA}} = 283.7 \text{ K}) \) to at least \( 675 \text{ K} \) and \( 9 \text{ MPa} \); thus, to slightly above its critical point \( (T_{\text{c,MEA}} = 671.4 \text{ K} \text{ and } p_{\text{c,MEA}} = 8.125 \text{ MPa}) \). Its extrapolation behavior was continuously validated to allow for reasonable results of mixture calculations as shown for the binary systems MEA + DEA, MEA + H\(_2\)O, DEA + H\(_2\)O, and SO\(_2\) + MEA.

The present extended version of the multi-component mixture model, also including the new pure-fluid EOS for chlorine and MEA, presents a significant improvement in the description of the thermodynamic properties of CCS mixtures. The importance of an EOS for these mixtures was underlined in this thesis by showing the impact of impurities on phase-equilibria and homogeneous densities based on comparisons with the respective properties of pure CO\(_2\). For a more detailed impression of this impact and more importantly for a comprehensive validation of the multi-component mixture model, accurate experimental data for typical CCS mixtures with various components are mandatory and should be the focus of further research. Future measurement campaigns should also address the comparably large number of systems that are so scarcely covered by experimental data that no EOS parameters could be fitted in this work. In addition to extensive experimental work, a further improvement of the CCS-mixture model requires the development of new approaches to describe binary systems that will most likely never be covered by experimental data. Aside from this, the most important next step is a modification of the functional form that allows for the descriptions of chemically reactive systems, which are so far not considered but expected to be highly relevant to CCS. Finally, several other fluids such as ammonia, nitrogen oxides, methanol, or glycols are possible components of CCS-mixtures and should be considered for a further expansion of the multi-component EOS.