Combination of Gibbs and Helmholtz Energy Equations of State in a Multiparameter Mixture Model Using the IAPWS Seawater Model as an Example

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Abstract
For carbon capture and storage (CCS) applications different sets of equations of state are used to describe the whole CCS-chain. While for the transport and pipeline sections highly accurate equations of state (EOS) explicit in the Helmholtz energy are used, properties under typical geological storage conditions are described by more simple, mostly cubic EOS, and brines are described by Gibbs energy models. Combining the transport and storage sections leads to inconsistent calculations. Since the used models are formulated in different independent variables (temperature and density versus temperature and pressure), mass and energy balances are challenging and equilibria in the injection region are difficult to model. To overcome these limitations, a predictive combination of the Gibbs energy-based IAPWS seawater model (IAPWS R13-08, 2008) with Helmholtz energy-based multi-parameter EOS is presented within this work. The Helmholtz energy model used in this work is based on the EOS-CG-2016 of Gernert and Span (J Chem Thermodyn 93:274–293, https://doi.org/10.1016/j.jct.2015.05.015, 2016). The results prove that a consistent combination of the two different models is possible. Furthermore, it is shown, that a more complex brine model needs to be combined with Helmholtz energy EOS for calculations at storage conditions.

Keywords Brines · CCS · Gibbs energy · Helmholtz energy · Seawater

List of Symbols

Abbreviations
CCS Carbon capture and storage

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1 Ruhr-Universität Bochum, Universitätsstr. 150, 44801 Bochum, Germany
EOS-CG  Equation of state for combustion gases  
EOS  Equation of state  
GERG  Groupe Européen de Recherches Gazières  
IAPWS  The International Association for the Properties of Water and Steam  
SMOW  Standard mean ocean water  

**Chemical Symbols**  
CO₂  Carbon dioxide  
N₂  Nitrogen  
O₂  Oxygen  
H₂O  Water  

**Greek Letters**  
α  Reduced Helmholtz energy  
β  Binary-specific reducing parameter  
δ  Reduced density  
γ  Binary-specific reducing parameter  
μ  Chemical potential  
π  Reduced pressure  
ρ  Density  
τ  Reciprocal temperature  
ξ  Mass fraction, reduced salinity  
Δ  Departure function  

**Superscript**  
^  Partial molar property  
*  Reducing property of saline part  
corr  Term of correction  
o  Ideal part  
r  Residual part, residual part of Helmholtz energy  
S  Property of saline part  
W  Property of water part  

**Latin Letters**  
a  Helmholtz energy  
c  Heat capacity  
g  Gibbs energy  
h  Enthalpy  
i  Index  
j  Index  
k  Index  
N  Number of components  
p  Pressure  
R  Gas constant  
s  Entropy  
T  Temperature
1 Introduction

In the past, fluid phases in carbon capture and storage (CCS) applications were modeled as pure carbon dioxide (CO$_2$). An improved, highly accurate description of properties of CO$_2$ containing significant amounts of impurities became possible with the GERG-2008 model of Kunz and Wagner [1], which was originally developed for natural gases. Previously, cubic models were used for mixtures containing significant amounts of impurities. The EOS-CG-2016 model of Gernert and Span [2] improved particularly the description of mixtures containing water. Recently, the EOS-CG-2016 [2] was extended to further components [3–6]. In these models, reference equations of state (EOS) in terms of the Helmholtz energy for each of the components of the mixture are combined using a Helmholtz energy-based mixture approach. The parameters of the mixture approach, which combines an extended corresponding states approach and an empirical departure function, are fitted to experimental data for phase equilibria, density, speed of sound, and other properties of the binary subsystems of the multicomponent mixture under consideration. However, storage of CO$_2$-rich CCS mixtures often takes place in saline aquifers. Therefore, models like EOS-CG-2016 [2] need to be linked to brine models to take the differences between thermodynamic properties of pure water and of brines into account. Salts dissolved in water have significant effects on thermodynamic properties, like changes of the freezing and boiling temperature. The salts also have a
strong impact on gas solubilities in the liquid water-rich brine phase. Experimental data show that this effect lead to lower gas solubilities (salting-out effect) in mixtures, which also effects the overall storage site conditions.

Up to now, transport and storage sections of the CCS-chain are calculated with different types of EOS. For the transport section, highly accurate EOS in terms of the Helmholtz energy are available. However, in industrial applications simpler models are still frequently used. The independent variables of these models are temperature and density. For the storage section with its brine phase, cubic models combined with electrolyte models explicit in the Gibbs energy are frequently used. The independent variables of the Gibbs energy are temperature and pressure. In terms of mixtures, both types of EOS depend on the composition as well. Designing an entire CCS-chain, the different property models with their significantly different accuracies lead to problems regarding the transition from the transport to the storage regime. For instance, when temperature, pressure and volume flow are given as boundary condition, the densities and, in consequence, the calculated mass flow will not be equal in both sections. Failure in mass balances will lead to problems with process monitoring, e.g., due to erroneous leak detections. Furthermore, a more accurate calculation of the densities of the coexisting phases at storage conditions will improve the prediction regarding storage capacity and phase distribution in storage sites.

Therefore, to overcome these difficulties, a consistent combination of a Helmholtz energy mixture model used for the transport section and a model explicit in the Gibbs energy that describes a brine, is presented here. This approach combines the different types of EOS in the Helmholtz energy framework and allows for the consistent calculation of properties of CO$_2$-rich mixtures in contact with brines. In this work, the brine part is implemented in form of the IAPWS seawater model [7]. Therefore, the salt composition has to match the one of ocean water. Different salinities can be considered, but not different salt compositions.

2 Theory

In this section, an overview of the Helmholtz energy multi-fluid approach is given together with a brief introduction to the Gibbs energy model for seawater [7]. Subsequently, an approach for a temperature, pressure, and density-based combination of the two types of models is presented. The IAPWS seawater model [7] is rewritten in a way that it can be used in combination with Helmholtz energy mixture models, for example the EOS-CG-2016 [2] for CO$_2$-rich mixtures.

2.1 The Helmholtz Energy Multi-fluid Approach

For approximately 150 pure fluids, multi-parameter EOS in terms of the Helmholtz energy are available. Multicomponent mixtures containing these fluids can be described with a weighted summation of binary interactions as shown by, e.g., Lemmon and Tillner-Roth [8] and Kunz and Wagner [1].
In general, the Helmholtz energy of a pure fluid or mixture is calculated considering two contributions

\[ a(T, \rho) = a^o(T, \rho) + a^r(T, \rho). \]  

The first part (superscript o) represents the hypothetical ideal gas state of the fluid, whereas the second part (superscript r) describes the residual behavior of the fluid. The independent variables of the Helmholtz energy are temperature \( T \) and density \( \rho \). In terms of mixtures the composition vector \( \vec{x} \) is a further independent variable, which is not shown here for simplicity. For convenience, the Helmholtz energy is reduced by the molar gas constant \( R \) and the thermodynamic temperature \( T \)

\[ a(\tau, \delta) = \frac{a(T, \rho)}{RT} = \alpha^o(\tau, \delta) + \alpha^r(\tau, \delta). \]  

The independent variables are reduced as well:

\[ \tau = \frac{T_r}{T} \quad \text{and} \quad \delta = \frac{\rho}{\rho_r}. \]  

The reducing functions for \( T_r \) and \( \rho_r \) are calculated with the following equations, where \( \beta \) and \( \gamma \) are the so called binary interaction parameters:

\[ T(\vec{x})_r = \sum_{i=1}^{N} x_i^2 T_{c,i} + \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} 2x_i x_j \beta_{T,ij} \gamma_{T,ij} \frac{x_i + x_j}{\beta_{T,ij}^2 x_i + x_j} \left( T_{c,i} T_{c,j} \right)^{0.5} \]  

\[ \frac{1}{\rho(\vec{x})_r} = \sum_{i=1}^{N} \frac{x_i^2}{\rho_{c,i}} + \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} 2x_i x_j \beta_{\rho,ij} \gamma_{\rho,ij} \frac{x_i + x_j}{\beta_{\rho,ij}^2 x_i + x_j} \frac{1}{\rho_{c,i}^{1/3}} + \frac{1}{\rho_{c,j}^{1/3}} \right)^3. \]  

The density \( \rho \) is divided by the reducing density \( \rho_r \), which is usually equal to the critical density for pure fluids \( \rho_c \) or a function of the composition and the critical densities of the pure fluids \( \rho_c(\vec{x}) \) in case of a mixture. The temperature is reduced by multiplying the inverse temperature with the reducing temperature \( T_r \), which is usually equal to the critical temperature for pure fluids \( T_c \) or a function of the composition and the critical temperatures of the pure fluids \( T_c(\vec{x}) \) in case of a mixture. The ideal part of the Helmholtz energy in a mixture of \( N \) components is a linear combination of the pure fluid contributions (marked by the subscript o) multiplied by the composition and an additional term representing the ideal entropy of mixing:

\[ \alpha^o(T, \rho, \vec{x}) = \sum_{i=1}^{N} x_i \left[ \alpha_{o,i}^o(\tau_{o,i}, \delta_{o,i}) + \ln x_i \right]. \]  

Temperature and density are reduced with the corresponding parameters of the pure fluids, \( T_{c,i} \) and \( \rho_{c,i} \). The residual part of the Helmholtz energy generally consists of two parts.
\[ \alpha^x(\tau, \delta, \bar{x}) = \sum_{i=1}^{N} x_i \alpha_{\nu i}^x(\tau, \delta) + \Delta \alpha^x(\tau, \delta, \bar{x}). \] (7)

In Eq. 7, the first contribution is a summation of the pure fluid properties at corresponding states weighted by the molar composition. Temperature and density are reduced with the reducing functions of the mixture \( T_i(\bar{x}) \) and \( \rho_i(\bar{x}) \). The second contribution is used to describe deviations from the corresponding states approach. Usually, this additional departure function \( \Delta \alpha^x \) is applied only if a comprehensive and accurate experimental database is available. For further information see, e.g., Thol and Bell [9].

Due to the fundamental nature of Helmholtz energy EOS, all thermodynamic properties can be calculated by combinations of the derivatives of the Helmholtz energy with respect to the independent variables \( T \) and \( \rho \). This ensures a consistent calculation of thermodynamic properties that are all derived from a single equation. In Table 1, selected thermodynamic properties and their relations to the reduced Helmholtz energy are listed. The subscript \( \tau \) indicates a derivative with respect to the reduced temperature \( \tau \) at constant reduced density and composition \( \bar{x} \), whereas the subscript \( \delta \) stands for a derivative with respect to the reduced density at constant \( \tau \) and \( \bar{x} \). A more detailed overview is given in Kunz and Wagner [1] as well as in Gernert and Span [2].

| Property               | Definition                                                                 | Formulation in terms of the reduced Helmholtz energy\( \alpha(\tau, \delta, \bar{x}) \). |
|------------------------|-----------------------------------------------------------------------------|----------------------------------------------------------------------------------------|
| Pressure               | \( p = -(\frac{\partial a}{\partial v})_{T, \bar{x}} \)                  | \( \frac{p}{\rho R T} = 1 + \delta \alpha^p \)                                        |
| Entropy                | \( s = -(\frac{\partial a}{\partial T})_{v, \bar{x}} \)                  | \( \frac{s}{R} = \tau (a^o + a^x) - a^0 - a^x \)                                      |
| Internal energy        | \( u = a + Ts \)                                                          | \( \frac{u}{R T} = \tau (a^o + a^x) \)                                                |
| Enthalpy               | \( h = u + pv \)                                                          | \( \frac{h}{R T} = 1 + \tau (a^o + a^x) + \delta \alpha^p \)                         |
| Isochoric heat capacity| \( c_v = (\frac{\partial h}{\partial T})_{v, \bar{x}} \)                | \( \frac{c_v}{R} = -\tau^2 (a^o + a^x) \)                                            |
| Isobaric heat capacity | \( c_p = (\frac{\partial h}{\partial T})_{\rho, \bar{x}} \)             | \( \frac{c_p}{R} = -\tau^2 (a^o + a^x) \)                                            |
| Gibbs energy           | \( g = h - Ts \)                                                          | \( \frac{g}{R T} = 1 + a^0 + a^x + \delta \alpha^p \)                                 |

\[ 2 \alpha_x = (\frac{\partial a}{\partial \bar{x}})_{\delta, \bar{x}} \cdot \alpha^x = (\frac{\partial a}{\partial \delta})_{T, \bar{x}} \cdot \alpha_{\nu x} = (\frac{\partial^2 a}{\partial \bar{x}^2})_{\delta, \bar{x}} \cdot \alpha^x = (\frac{\partial^2 a}{\partial \delta^2})_{T, \bar{x}} \cdot \alpha^x = (\frac{\partial^2 a}{\partial \bar{x} \partial \delta})_{\tau, \bar{x}} \cdot \alpha^x = (\frac{\partial^2 a}{\partial \delta \partial \delta})_{T, \bar{x}} \cdot \alpha^x = (\frac{\partial^2 a}{\partial \bar{x} \partial \delta \partial \delta})_{\bar{x}} \cdot \alpha^x = (\frac{\partial^2 a}{\partial \delta \partial \delta \partial \delta})_{T, \bar{x}} \cdot \alpha^x. \]
2.2 The IAPWS Seawater EOS

The IAPWS seawater EOS [7] which is chosen here to demonstrate the combination of Helmholtz and Gibbs energy models, is explicit in the Gibbs energy. It is used to consider brines with a seawater-like composition in Helmholtz energy-based multi-fluid mixture models. The seawater model adds a saline contribution to the Gibbs energy of the pure water calculated with the IAPWS-95 EOS [10]. The saline contribution depends on the absolute salinity \( S_A \) of the seawater, temperature \( T \), and pressure \( p \). The absolute salinity is defined as the mass fraction of salt in the seawater.

\[
g(T, p, S_A) = g^W(T, p) + g^S(T, p, S_A)
\]  

(15)

The superscript \( W \) indicates the part of the specific Gibbs energy derived from the IAPWS-95 EOS [10] according to Eq. 14. The saline contribution is marked with the superscript \( S \). The density for the evaluation of the water part is related to the pressure and temperature of the pure water in the seawater and has to be determined iteratively, c.f. Feistel [11]. Different validity regions depending on temperature, pressure and salinity are given in the IAPWS release [7] and are briefly summarized in Table 2. A more detailed description for the combination of the pure water and the saline part is given in the IAPWS release [7] and by Feistel [11].

The IAPWS-95 standard for pure water [10] is formulated in terms of the Helmholtz energy with the independent variables temperature and density. In consequence, the properties for the seawater equation must be derived from the Gibbs energy as described in the IAPWS release [7] for the independent variables temperature and density. These derivatives are quite different from the derivatives of the Helmholtz energy explicit EOS with respect to \( \frac{\partial g}{\partial \rho} \) and \( \frac{\partial g}{\partial T} \), as described by Span [12]. The Gibbs energy of the saline part of the seawater EOS is calculated with a polynomial-like correlation as function of temperature \( T \), pressure \( p \), and absolute salinity \( S_A \)

\[
g^S(T, p, S_A) = g^* \sum_{k=0}^{5} \sum_{j=0}^{6} \left( g_{1jk} \xi^2 \ln \xi + \sum_{i=2}^{7} g_{ijk} \xi^i \right) T^j P^k.
\]  

(16)

According to the IAPWS release [7], temperature and pressure are reduced in a different way than in Helmholtz energy EOS. The value for \( g^* \) and the functions for the reduced salinity \( \xi \), reduced temperature \( r_T \), and reduced pressure \( r_p \) are given in Eqs. 17–20. The parameters of the relations are used as listed in the corresponding IAPWS guideline [7].

| Table 2 | Regions of validity for the IAPWS seawater EOS [7, 11] |
|-------------------|-------------------|-------------------|-------------------|
| Salinity/kg · kg\(^{-1}\) | Temperature/K | Pressure/Pa |
| 1 | 0 ≤ \( S_A \) ≤ 0.042 | \( T_{\text{freeze}} \leq T \leq 313 \) | 10 1325 ≤ \( p \) ≤ 10\(^8\) |
| 2 | 0 ≤ \( S_A \) ≤ 0.05 | \( T_{\text{freeze}} \leq T \leq 313 \) | \( p_v \leq p \leq 10 1325 \) |
| 3 | 0 ≤ \( S_A \) ≤ 0.12 | \( T_{\text{freeze}} \leq T \leq 353 \) | \( p = 10 1325 \) |
The value of $S_A = 0.03516504 \text{ kg} \cdot \text{kg}^{-1}$ in Eq. 18 is the normal salinity of standard mean ocean water (SMOW). As both parts of the seawater EOS are polynomial expressions, the derivatives can be derived separately. In Table 3, the required combinations of the Gibbs energy and their derivatives with respect to the independent variables for the calculation of common thermodynamic properties are shown. Non-linear combinations of derivatives have to be derived carefully to ensure the correct calculation of the property. A simple addition of the properties from the water and saline part would lead to wrong results.

Although Feistel [13] published an extension of the seawater EOS for a better representation of density data at higher temperatures from Millero and Huang [14], this extension is not yet included in the IAPWS standard. For this reason, the extension term is not subject of the work presented here. For the sake of completeness, it has to be mentioned, that this additional extension term cancels out at $T = 273.15 \text{ K}$ or $p = 0.101325 \text{ MPa}$. Therefore, it has no influence on the data shown in this work, as they either refer to ambient pressure or to a temperature of $T = 273.15 \text{ K}$.

### 2.3 Combination of Gibbs Energy and Helmholtz Energy Equations

In a system containing a brine instead of water, in particular the chemical potential of water changes. In phase equilibrium calculations (VLE), it can be assumed that

$$g^* = J \cdot \text{kg}^{-1},$$

$$\xi = \sqrt{S_A/S^*} \quad \text{with} \quad S^* = 0.03516504 \text{ kg} \cdot \text{kg}^{-1} \cdot \frac{40}{35},$$

$$\tau_S = \frac{T - T_0}{T^*} \quad \text{with} \quad T_0 = 273.15 \text{ K}, \quad T^* = 40 \text{ K},$$

$$\pi = \frac{p - p_0}{p^*} \quad \text{with} \quad p_0 = 101325 \text{ Pa}, \quad p^* = 10^8 \text{ Pa}.$$
the salt is contained only in the water-rich liquid phase. No phase equilibrium condition has to be formulated for the salt. For a salt mixture equal to the salt in standard mean ocean water (SMOW), the water EOS [10] in a multi-parameter mixture model can be replaced by the seawater formulation of IAPWS [7] to describe the corresponding change in chemical potential of water as a function of temperature, pressure, and salinity. Therefore, it has to be considered that the IAPWS seawater EOS [7] allows for a variable mass of salt dissolved in the water but the ratio between the different ions must always be the same. With the assumption that the salt ions interact primarily with water molecules in the water-rich liquid phase, the same purely predictive approach can be used to calculate properties of the homogeneous water-rich phase. For a consistent temperature and pressure dependent combination of Gibbs energy and Helmholtz energy EOS, the independent variables temperature $T$, pressure $p$, density $\rho$, and composition $\bar{x}$ must be handled in a consistent way. This is important to ensure the evaluation of both types of equations at the same state point due to the direct link between density and pressure, see the derivatives given in Eqs. 8 and 21. To combine Gibbs excess energy models with the departure function of Helmholtz energy models or cubic EOS approaches from Jäger et al. [15] as well as Kontogeorgis and Coutsikos [16] are available. Jäger et al. [15] have recently shown how Helmholtz energy multi-parameter models can be combined with a theoretically based departure function based on Gibbs energy models. This approach does not consider salt or pressure dependencies, which only allows for VLE-calculations of salt free mixtures up to moderate pressures. For the transformation of the Gibbs energy to the Helmholtz energy and vise versa, a Legendre transformation [17] can be used.

For pure or pseudo-pure fluids, i.e. water and salt, this transformation seems to be trivial. Methods like the Legendre transformation [17] can be applied and the IAPWS guideline [18] describes how to determine the equivalence between Helmholtz and Gibbs energy derivatives with the different independent variables. As shown in Table 4, the common distinction between ideal part $\alpha^0$ and residual part $\alpha^r$

| Helmholtz energy derivative | Combination of Gibbs energy derivatives |
|-----------------------------|----------------------------------------|
| $\alpha^r + \alpha^t$       | $\equiv \frac{(g - pg_p)(RT)^{-1}}{(RT)^{-1}pg_p - 1}$ (28) |
| $\delta\alpha^t_\delta$     | $\equiv \frac{(RT)^{-1}pg_p - 1}{RT}$ (29) |
| $\tau (a^r_t + a^t_t)$      | $\equiv \frac{(RT)^{-1} (g - Tg_T pg_p)}{pg_p}$ (30) |
| $\tau^2 (a^o_t + a^r_t)$    | $\equiv \frac{T(\frac{g^2_{TP} - g_{TT} - g_{PP}}{g_p})}{pg_p} (RT)^{-1}$ (31) |
| $\delta^2\alpha^o_{\delta\delta}$ | $\equiv \frac{g^2_{PP} - 2pg_p}{RT} + 1$ (32) |
| $\tau\delta\alpha^r_{\tau\delta}$ | $\equiv \frac{g^2_{TP}g^2_p}{R^2g^2_{PP} + ppg_p} RT$ (33) |
is no longer feasible when transforming a Gibbs energy EOS to a Helmholtz energy EOS. This is not a limiting issue for the determination of the overall reduced Helmholtz energy or its derivatives because the necessary derivatives for property calculations can be determined without limitations regarding the thermodynamic properties shown in Table 1. However, losing the explicit separation between ideal and residual part of the combined Helmholtz energy leads to a loss of thermodynamic information. I.e., the separation between ideal and residual part is no longer possible for derivatives containing the ideal as well as the residual part (e.g., Eqs. 28, 30, or 31). Some thermodynamic properties like fugacity, the fugacity coefficient \(f_i = \frac{x_i \rho RT \exp(\frac{\partial \alpha}{\partial n_i})}{T V n_i}\), or the isentropic exponent of the ideal gas need an explicit separation between ideal and residual part of the Helmholtz energy. For this reason, they can only be calculated, if assumptions for this separation are made.

In case of the combination of the IAPWS seawater EOS [7] with Helmholtz energy mixture models for CCS applications including water, the combination of the different EOS models is even more challenging. When applying this approach to a mixture, i.e. water, salt, and impurities, the procedure is not as straightforward as for pure substances because mixing effects have to be taken into account for a correct description of the overall reduced Helmholtz energy of the mixture including seawater. The description of a binary mixture is based on combining results of the respective pure fluid EOS evaluated at “corresponding states”, i.e. if the mixture is evaluated at liquid-like states, the respective pure substance of the mixture needs to be evaluated at liquid-like states as well. This is enabled through the use of reduced input variables in combination with binary specific reducing functions. A thorough description is given by Lemmon and Tillner-Roth [8] as well as Kunz and Wagner [1] and is not subject of this article. Consequently, the corresponding reduced variables of pure water in seawater differ from the ones where water needs to be evaluated in mixtures with CCS-components. However, the salt does not effect the reducing parameters \(T\) and \(\rho\) as the salinity is considered in a separate part and not in the Helmholtz part of the mixture.

A flowchart for the combination of the different models is shown in Fig. 1.

Box 1 represents the evaluation of a Helmholtz energy mixture model containing water and other fluids relevant in CCS applications, as described in Sect. 2.1 and Eq. 34. Depending on the considered components, the reducing functions for temperature and density are applied and departure functions are used if available. The calculated properties correspond to the property of the real mixtures of real fluids.

The calculation of the Gibbs energy of the IAPWS seawater EOS [7] is shown in Box 2. The seawater EOS has to be evaluated at the same absolute temperature and pressure as the Helmholtz energy mixture of Box 1, see Eq. 35. Furthermore, the absolute salinity has to be considered to represent the salt dissolved in the water. In contrast to the calculations described in Sect. 2.2 and the IAPWS release [7], the water part in the seawater is evaluated at different reduced variables than the in the IAPWS release [7].

Box 3 considers, that the seawater EOS is formulated in the Gibbs energy. For the combination with Helmholtz energy mixture models, the Gibbs energy and its derivatives must be converted to derivatives based on the independent variables.
of the Helmholtz energy framework. This is done according to the relationships described in Table 4.

The term of correction (Box 4) considers the fact that the component water is present in both models. This term of correction is necessary to ensure the correct calculation of the water part in the mixture. Both models contain a water part, but it is evaluated at different reduced variables. The pure water part of the brine (Box 3) is not calculated according to the corresponding states approach for mixtures as it is in the Helmholtz multi-fluid mixture approach for CCS mixtures (Box 1). As a consequence, the water part from the brine model needs to be canceled out for a correct calculation according to the Helmholtz multi-fluid mixture approach. A mathematical description is shown in Eq. 37. This procedure also needs to be carried out for all derivatives of the Helmholtz energy.

Finally, in Box 5 and Eq. 38, the combination of all terms is shown. Some properties like the speed of sound are a non-linear combination of derivatives in terms of the Gibbs energy (see Table 3). These properties require a complete conversion of the Gibbs energy derivatives to the Helmholtz energy mixture derivative including the water part of the brine because a separation into an ideal and residual part is not possible. Only converting the salt-related part to derivatives based on the independent variables of the Helmholtz energy framework would lead to wrong results for these properties. Furthermore, the procedure of combining the derivatives transferred from one EOS to another has always to be based on a set of equal derivatives and not on the actual thermodynamic property. Simply adding the values of non-linear properties would lead to incorrect results.

\[
\alpha_{\text{mix}}(\tau, \delta, \bar{x}) = \alpha^o + \alpha^r = \sum_{i=1}^{N} x_i \left[ \alpha_{0,i}^o(\tau, \delta) + \ln x_i + \alpha_{0,i}^r(\tau, \delta) \right] + \Delta \alpha^r(\tau, \delta, \bar{x})
\]

(34)
If two or more phases are in equilibrium, a method to fulfill the condition of mechanical, thermal, and chemical equilibrium is necessary. In this work, the equality of the chemical potentials of all substances in all phases is used. The method is thoroughly described by Jäger et al. [19], Gernert et al. [20], and Hielscher et al. [21] and is not subject of this work. For phase equilibrium calculations, derivatives with respect to the composition are needed. In this work, the concept of partial molar properties is used to determine the partial molar Gibbs energy $\hat{g}$, which is equal to the chemical potential of a component in the mixture

$$\alpha_{\text{seaw}}(\tau, \delta, \bar{x}) = a_w^0 + a_w^\tau + \alpha_{\text{Saline}}(T, p, S_A) \quad (35)$$

$$\alpha_{\text{Saline}} = g_{\text{Saline}} - \rho_{\text{Saline}} \quad (36)$$

$$\alpha^{\text{corr}} = \chi_{\text{seaw}} \left[ \alpha_{o,w}(\tau_{o,w}, \delta_{o,w}) + \alpha_{o,w}^f(\tau_{o,w}, \delta_{o,w}) \right] \quad (37)$$

$$\alpha_{\text{seamix}}(\tau, \delta, \bar{x}) = \alpha(\tau, \delta, \bar{x}) + \alpha_{\text{seaw}}(\tau_{o,w}, \delta_{o,w}, S_A) - \alpha^{\text{corr}} \quad (38)$$

The implementation has been validated with a CO$_2$+H$_2$O mixture. For the water part, the seawater routines were used and the salinity was set to zero. The properties of seawater were tested against the values given in the IAPWS seawater release [7]. The phase compositions of the stable phases were in agreement with the results of a pure mixture calculated with the EOS-CG-2016 model of Gernert and Span [2]. Phase equilibrium compositions were determined with relative deviations in the order of magnitude of $10^{-6}$ compared to calculations with equal fugacity coefficients as criteria for the chemical equilibrium.

3 Results

The approach described in Sect. 2.3 is implemented in TREND 5.0 [22] to enable the calculation of CCS mixtures in contact with brines. To the authors best knowledge, no experimental data other than solubility data for CCS mixtures in contact with seawater-like brines are available in the literature. Values calculated with the presented approach are compared to these experimental data. For this purpose, the different salinity scales were converted to absolute salinity with the procedures described by Feistel [11]. Components relevant for CCS applications like carbon dioxide (CO$_2$), nitrogen (N$_2$), oxygen (O$_2$) and water (H$_2$O) are named CCS fluids in the following. For the description of CCS fluids, the EOS-CG-2016 of Gernert and Span [2] is chosen, since it is the most accurate model available in literature to describe the thermodynamic properties of CCS fluids in contact with pure water. The pure components are described with the reference EOS.
of Span and Wagner [23], Span et al. [24], and Schmidt and Wagner [25] for CO₂, N₂, and O₂, respectively. In the following, the term “pure mixture” is used to emphasize that the mixture does not contain salt. In general, other models in terms of the Helmholtz energy can also be used to describe the interaction of gaseous components with seawater-like brines, when a consistent combination of the models and especially the water part (related to the IAPWS-95 [10]) is ensured.

In the next sections, comparisons between the predictions of the model and experimental solubility data of CO₂, O₂, and N₂ in seawater are presented. The results refer to ambient temperature and pressure conditions because the solubility data were mainly measured at ambient conditions.

### 3.1 CO₂-Brine Interaction

In most cases, CCS-relevant mixtures are CO₂-rich mixtures. However, only a very limited number of experimental data is available for the solubility of CO₂ in seawater. The solubility data refer to different temperatures and salinities, mostly at atmospheric pressure. Few data were measured at elevated pressures with artificial seawater and salinities differing from standard salinity.

Figure 2 shows the solubility of CO₂ in seawater at ambient pressure (p = 0.10 1325 MPa) for two different temperatures. The salinity on the x-axis varies from pure water (Sₐ = 0 kg · kg⁻¹) up to Sₐ = 0.08 kg · kg⁻¹, while the mole fraction of CO₂ in the liquid brine phase at equilibrium conditions is shown on the y-axis. The solid curves indicate a large offset of the present model from the experimental data. A more detailed analysis shows that the offset mainly results from the solubility of CO₂ in pure water, calculated with the EOS-CG-2016 [2]. This results from the fact that solubility data at low pressures were not considered for the development of the
EOS-CG-2016 [2]; the model was adjusted only to phase equilibria at higher pressures and concentrations. This offset caused by the EOS-CG-2016 [2] was manually corrected by the difference of calculated solubilities at $S_A = 0 \text{ kg} \cdot \text{kg}^{-1}$ and the corresponding experimental state point. The course of the corrected CO$_2$ concentrations (dashed curves in Fig. 2) shows that our predictive model describes the salting-out effect correctly.

The reduction of the gas solubility resulting from the seasalt dissolved in the water is represented well. Only the slightly different slopes of experimental data and calculated values indicate a small overestimation of the salting-out effect regarding the experimental data of Murray and Riley [26] at $T = 274$ K. Since no other data are available for comparison, it is impossible to tell whether this discrepancy at the lowest investigated temperature results from the model or from the experimental data. Experiments of Li and Tsui [27] are well represented. At this point, it should be noted that the presented model does not contain any adjusted parameters; the description of the salting-out effect is purely predictive.

### 3.2 N$_2$-Brine Interaction

As nitrogen is the main component of air, it is a common impurity in particular of CO$_2$-rich mixtures resulting from oxyfuel capture-processes. For this reason, N$_2$-brine interactions are analyzed here by comparing calculated values for the solubility of nitrogen in seawater with experimental data of Douglas [28] and Murray and Riley [29]. Figure 3 illustrates that the offset resulting from the system N$_2$+H$_2$O caused by the EOS-CG-2016 [2] at zero salinity is smaller than for CO$_2$+H$_2$O.

The reduction of the gas solubility can be described well for a predictive model. As already noted for the CO$_2$-brine interaction, the difference of the calculated reduction of solubility from the experimental data for temperatures close

![Fig. 3 N$_2$ solubility in seawater as function of salinity](image)
to the freezing point of pure water is bigger than for temperatures of approximately 303 K.

### 3.3 O$_2$-Brine Interaction

As CCS is usually linked to combustion processes, oxygen is another possible component of mixtures with brines. Figure 4 illustrates the solubility of O$_2$ in brines. The offset is again related to the EOS-CG-2016 model [2] for the binary system H$_2$O+O$_2$ at zero salinity. The solubility of O$_2$ in pure water calculated with the EOS-CG-2016 [2] exhibits only a small offset at $T = 293$ K. The predicted decrease of solubility with increasing salinity follows the experimental data by Green [30]. In addition to the original experimental data, Green [30] calculated so called “smoothed values”. While the experimental data are shown with solid circles, the “smoothed values” are indicated by open circles in the same color. Further experimental data by Murray and Riley [31] are displayed as squares. At $T = 274$ K EOS-CG-2016 [2] significantly underestimates the solubility of oxygen in water. For a better comparison between the salting-out effect calculated with the combined model and the experimental data, the dashed black line indicates the predicted solubility corrected manually for the offset at zero salinity. At $T = 274$ K, the predicted salting-out effect agrees well with the data by Murray and Riley [31], while the smoothed data by Green [30] suggest a slightly larger salting-out effect. The difference in the slope of the experimental data appears to be quite significant for $T = 274$ K. This might be related to the fact, that slight temperature differences near the freezing point of pure water have a large effect on the solubility. The new model slightly overestimates the salting-out effect for $T = 293$ K.

![Fig. 4 O$_2$ solubility in seawater as a function of salinity](image-url)
3.4 High-Pressure and High-Salinity Data

As the IAPWS seawater standard [7] is limited to salinities of $S_A \leq 0.042 \text{ kg} \cdot \text{kg}^{-1}$ for pressures higher than $p = 0.101325 \text{ MPa}$, the present predictive approach is also limited to either low salinities or ambient pressure. To prove a reliable extrapolation behavior, a comparison between artificial seawater data of Stewart and Munjal [32] and values calculated with the present approach is shown in Fig. 5. In contrast to natural seawater, this sample was prepared synthetically in a way that the salt composition matches the one of standard ocean water, while salinities are varied. The data of Stewart and Munjal [32] cover pressures up to $p = 3.5 \text{ MPa}$ at salinities up to three times higher than standard salinity.

Again, a difference between the solubilities calculated with the EOS-CG-2016 model [2] and the experimental data can be recognized for pure $\text{H}_2\text{O}+\text{CO}_2$ ($S_A = 0 \text{ kg} \cdot \text{kg}^{-1}$, black curve). The green curve and the green circles depict the calculated values for the solubility of $\text{CO}_2$ in seawater with a salinity of $S_A = 0.03442 \text{ kg} \cdot \text{kg}^{-1}$ and the corresponding experimental data, respectively. The deviation between the experimental data and the calculated values are also shown in the lower part of Fig. 5. Deviations at $S_A = 0 \text{ kg} \cdot \text{kg}^{-1}$ and $S_A = 0.03442 \text{ kg} \cdot \text{kg}^{-1}$

![Fig. 5 CO₂ solubility in seawater as a function of pressure at $T = 273.15 \text{ K}$](image_url)
show a similar trend while deviations at $S_A = 0.03 \text{ kg} \cdot \text{kg}^{-1}$ are larger than at $S_A = 0 \text{ kg} \cdot \text{kg}^{-1}$. However, at least 2/3 of the deviation is due to the misprediction of the CO$_2$ solubility in pure H$_2$O. Again, the salting-out effect is described reasonably well. The salting-out effect of data with salt contents higher than the standard salinity (red circles) is significantly over-predicted by the present approach (red curve). Due to the offset of the H$_2$O+CO$_2$ model [2], the present model was expected to overestimate the mass fraction of CO$_2$ dissolved in the brine with regard to the experimental data, like the data shown in black and green. However, the mass fraction of CO$_2$ is underestimated instead. The seawater model [7] does not reflect the influence of salt on the chemical potential of water correctly at this high salinity - the effect is significantly overestimated. This behavior was expected because for those applications, the seawater EOS [7] is applied out of its range of validity. A detailed description of the ranges of validity is given in the IAPWS release [7].

### 3.5 Consistent calculations for brine mixtures

In most reservoir simulation tools, calculations of thermodynamic properties of CO$_2$-rich mixtures containing brines are carried out with cubic EOS for the CCS-components and with Gibbs energy models for the brine. Models for the combination of activity and fugacity coefficient are for example published by Sun and Duan [33], Duan and Mao [34], and Geng and Duan [35]. Furthermore, models based on association theories can be used, which refer to simpler models based on the Helmholtz energy. They are either based on cubic models (c.f. Wu and Prausnitz [36]) or based on potential models (e.g. Harvey and Prausnitz [37]). Properties at transport conditions are modeled with accurate EOS in terms of the Helmholtz energy. In consequence, transport and storage sections of the CCS-process are described with different thermodynamic models. This leads to inconsistencies in mass and energy balances at the interface between the different process segments in the CCS chain.

The model presented in this work combines EOS explicit in Helmholtz energy and Gibbs energy in a consistent way. Therefore, it enables the use of the same EOS for transport and storage sections. In this way, inconsistencies at the interface between both sections are avoided. In Fig. 6, speed of sounds for a saturated seawater-N$_2$ mixture and density calculations for a saturated and predicted liquid phase densities are shown as a function of salinity. The speed of sounds are shown in the upper part of Fig. 6, while the densities are depicted in the lower part. The interaction between H$_2$O and CO$_2$ as well as H$_2$O and N$_2$ is calculated using the EOS-CG-2016 [2] in terms of Helmholtz energy. To consider the salinity, the IAPWS seawater model [7] is combined with the Helmholtz multi-fluid model with the approach presented in this work. As an increase of salinity is related to the salting-out effect of the gaseous components in the liquid phase and since the density of seawater is increasing with salinity, an increase of density was to be expected.

The combination of the Gibbs energy-based seawater model and Helmholtz energy-based mixture model allows for a consistent calculation of all thermodynamic properties of mixtures covered by EOS-CG-2016 [2] with seawater at different salinities.
4 Conclusion and Outlook

In this work, a combination of the IAPWS seawater model [7] explicit in the Gibbs energy with a Helmholtz multi-fluid model, i.e. with the EOS-CG-2016 of Gernert and Span [2] is presented as example for the potential of mixed Helmholtz/Gibbs approaches. The presented model is implemented in the thermodynamic reference and engineering database TREND 5.0 [22]. Calculations for this combined model are performed consistent to the Helmholtz multi-fluid approach, with the Helmholtz energy as the potential chosen for the actual calculation of properties. The approach ensures consistent calculations in the entire fluid region including phase equilibria. The required Helmholtz energy derivatives are obtained from the seawater model by a combination of Gibbs energy derivatives. Within this work, no interaction parameters were modified or added to the existing models. Results presented for equilibria with brines are purely predictive. In order to assess the accuracy of the model, it is compared to solubility

Fig. 6 Predicted speed of sound in the N$_2$ saturated liquid seawater phase at equilibrium conditions at $p = 0.10$ 1325 MPa and density of the CO$_2$ saturated liquid seawater phase at equilibrium conditions at $p = 0.10$ 1325 MPa for two temperatures
data of mixtures of seawater and the CCS-components CO₂, N₂, and O₂. The results prove that the combination and integration of the two different EOS is possible and that it leads to reasonable results for phase equilibrium calculations. The salting-out effect is describe qualitatively correct and quantitatively reasonable. A more accurate result would require the adjustment of parameters. However, systematic offsets between experimental data for gas solubilities and calculated values were found at zero salinity. This deviation is caused by the EOS-CG-2016 model [2]. While phase equilibria at higher temperature and pressure were considered, solubility data were not considered during the development of the EOS-CG-2016 model [2]. Therefore, the fitting procedures for multi-parameter Helmholtz energy mixture models should be modified in the future.

There are still improvements needed for a more accurate calculation of thermodynamic properties of CCS-relevant mixtures with brines. In particular varying salt compositions and a broader temperature, pressure, and salinity range need to be considered. Therefore, a more complex and more capable electrolyte model, based on Pitzers approach [38] will be combined with the most accurate Helmholtz energy models in future work. One advantage of a model based on Pitzers approach [38] is that it has adjustable parameters, which can be modified for an accurate description of brine mixtures up to high salinities. Furthermore, extensions considering ion-ion interactions, as well as interaction parameter for neutral species in brines are available in the literature for this kind of models. However, the approach described in the present article paves the way for a combination of multi-parameter Helmholtz energy models with temperature and pressure dependent Gibbs energy-based models and shows the potential of the resulting combined model.

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