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Non-iterative phase-equilibrium model of the H₂O-CO₂-NaCl-system for large-scale numerical simulations

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Abstract

This article features a simple method for describing the phase equilibrium of the ternary water-salt-carbon dioxide system. At first, an iterative solution is shown using well known equations of state and solubility correlations to predict the compositions of liquid and gas phases in a saline aquifer. By virtue of several assumptions, iterations can be avoided entirely in order to use the method for demanding large-scale numerical simulations. Subsequently, the iterative method as well as the simplification are evaluated against experimental data. Both solutions provide adequate accuracy for engineering problems such as subsurface carbon dioxide storage.

Keywords: phase equilibrium, CO₂-H₂O-NaCl -system, saline aquifer, CO₂ storage, OpenGeoSys

1. Motivation

Numerical simulations of subsurface processes require the knowledge of many material properties and constitutive laws. Exact measurements on the laboratory and the field scale are essential in order to define material laws accurately. On the other hand, complex numerical simulations of multiple coupled processes such as thermo-hydro-mechanical-chemical (THMC) coupled problems are extremely costly and expensive in terms of computing time. In a typical computational setting using the finite element methods, the constitutive equations have to be integrated in each global iteration

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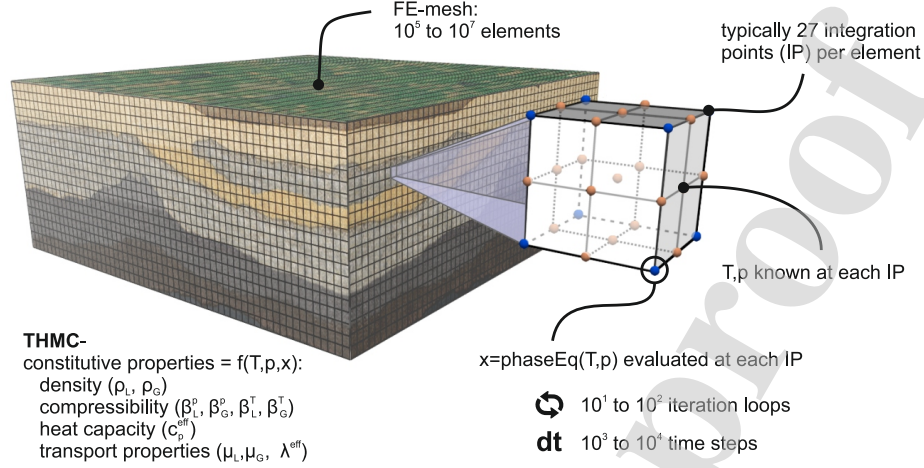


Figure 1: Complexity of a typical THMC-simulation: Constitutive fluid properties are functions of phase composition x and other state variables. <https://www.overleaf.com/project/5ebd3931fc05f40001c18676> This composition is calculated by a phase equilibrium model which has to be evaluated at each integration point of every domain element, once for each iteration step in every time step. For large-scale models, this can easily lead to several trillions (10^{12}) of individual evaluations. An iterative EOS evaluation enters this estimation as yet another multiplier increasing the order of magnitude of evaluations further. Therefore, implementing fast and robust methods for phase equilibrium calculation is essential.

in each integration point. Large-scale simulations, e. g. considering CO_2 -storage applications, can easily consist of millions of finite elements [27, 43], each containing multiple of those integration points (cf. Figure 1). Complex equations of state (EOS) can thus contribute a significant share of the overall computational effort of large-scale non-linear simulations. Thus, reducing the effort for solving constitutive relations is crucial. Choosing constitutive material laws is therefore always a trade-off between high accuracy of material properties and moderate computational effort. Describing the phase equilibrium (or vapour-liquid equilibrium, VLE) between saltwater below a CO_2 atmosphere is a non-trivial task. Depending on temperature, water evaporates into the gas phase until an equilibrium is reached, changing the composition of the water phase in favour of the salt component. From the gas phase, CO_2 will dissolve in the brine depending on salinity and gas phase pressure. All phase transitions and transfers are associated with a change of both phase compositions, such that the methods finding the VLE usually have to be conducted repeatedly in an iterative manner until their convergence. VLE-models for scientific use usually consist of hundreds

of empirical parameters and do not have a closed-form solution.

Supported by sophisticated EOS, those models allow to determine the phase equilibrium of certain substances up to very high accuracies [1, 40, 24, 25]. However, due to multiply nested iteration loops, the resulting computing time of accurate VLE-models is potentially compromising an efficient application in numerical modelling of large-scale domains. Furthermore, the reliable and fail-safe implementation into the actual simulation tools is laborious.

On this account, the method presented in this work is developed in order to find a fast, robust, and easy-to-use constitutive description of the distributions of water, salt, and carbon dioxide components among a liquid and a gas phase in a porous medium depending on temperature and pressure conditions.

It is based on well-known equations of state for gas mixtures and for saltwater [34, 38], as well as semi-empirical correlations for CO₂-salinity or fugacity coefficients. For best results, these equations still need to be solved iteratively, but the required computing time is low since the method converges very fast. However, by assuming several brine properties to be constant, iterations can be avoided entirely with the method presented herein while the produced results are still acceptable for typical subsurface engineering applications when compared to more sophisticated methods.

The reason why the simple methods of this work are cheaper to compute, easier to implement and yet comparatively accurate lies in the fact that they are restricted to the liquid region of the salt water phase, i. e., the valid temperature range is below the boiling temperature of salt water for all pressures. Furthermore, it is assumed that the initial salt mass concentration is not affected by water evaporation. This rather strong assumption is supportable at high gas pressures (usually in the range of several MPa). Thereby, the method is appropriate for pressure and temperature conditions as expected in natural saline aquifer systems. Covering the entire pressure-temperature-plane of such a ternary system is incredibly more difficult and remains the domain of the sophisticated VLE-models.

The intended use for this constitutive model was to describe the phase equilibrium between CO₂ and salt water for numerical investigations of underground carbon dioxide capture and storage (CCS) scenarios. Therefore, it was implemented into the open-source scientific FEM-simulator

OpenGeoSys [18, 4], which has been applied to several CCS-related studies [3, 5, 14, 19, 22, 32, 33, 37].

This paper is organized as follows: At first, the assumptions under which the methods are developed are pointed out, followed by a detailed description of both iterative and non-iterative methods, including the applied simplifications. The last part of the work contains a number of comparisons to experimental data and to other VLE-models in order to verify and validate the presented methods.

2. Assumptions and notation

The phase equilibrium model at hand was designed and tested to be valid over the liquid phase pressure range $10 \text{ MPa} \leq p_L \leq 26 \text{ MPa}$ and a temperature range $290 \text{ K} \leq T \leq 410 \text{ K}$, at a constant salt mass concentration of $\rho_L^N = 250 \text{ kg m}^{-3}$ in the liquid phase. Note that this initial salt mass concentration can be considered constant since the water content in the gas phase due to evaporation is assumed to be small. Comparisons to experimental data shown in Section 5 support this assumption.

However, the presented method can be used to evaluate phase equilibria at other pressure and temperature conditions or different salinities, as long as it is assured that phase boundaries are not intersected. In other words, the constitutive model is restricted to conditions where a liquid salt water phase and a gas phase coexist.

All phase properties in the subsequent parts of the text are described using the following notation: Liquid and gas phase properties are referred to by L or G, respectively. The chemical substances residing in those phases are referred to as components water (W), CO_2 (C), and NaCl (N). To specify a certain property, its phase is indicated as subscript while the component is indicated by a superscript. For example, ρ_L^W defines the partial density of the water component in the liquid phase. Properties without a superscript component correspond to an entire phase (e. g. p_G represents the gas phase pressure).

3. A method for phase equilibria at given salinity

This method uses well-known equations of state and property correlations to find the contribution of W, C, and N components among liquid and fluid phases at certain conditions in terms of liquid phase pressure p_L , gas phase pressure p_G , and temperature T . It is assumed that the initial salt mass concentration in the aqueous phase, ρ_L^N , is known.

3.1. The gas phase

The binary composition of the gas phase is calculated using Dalton's law, assuming that the mole fraction of a gas component equals the ratio of that component's partial pressure and the phase pressure. By this way, the mole fractions of carbon dioxide and water vapour can be found via

$$x_{n,G}^W = \frac{p_G^W}{p_G} \quad (1)$$

and

$$x_{n,G}^C = 1 - x_{n,G}^W \quad (2)$$

The partial pressure of water vapour, p_G^W , is assumed to be equal to the vapour pressure of pure water, corrected for salt content and for curved menisci as present in porous media. Pure water vapour pressure $p_{\text{vap},L}^W$ is found by a correlation presented in Wagner and Pruss [42], given by

$$\ln \frac{p_{\text{vap},L}^W}{p_{\text{cr}}^W} = \frac{T_{\text{cr}}^W}{T} \sum_{i=1}^6 a_i \theta^{t_i} \quad (3)$$

with critical temperature $T_{\text{cr}}^W = 647.096$ K, critical pressure $p_{\text{cr}}^W = 22.064$ MPa, with parameters $a_1 = -7.85951783$, $a_2 = 1.84408259$, $a_3 = -11.7866497$, $a_4 = 22.6807411$, $a_5 = -15.9618719$, $a_6 = 1.80122502$, $t_1 = 1.0$, $t_2 = 1.5$, $t_3 = 3.0$, $t_4 = 3.5$, $t_5 = 4.0$, and $t_6 = 7.5$, and with reduced temperature

$$\theta = 1 - \frac{T}{T_{\text{cr}}^W} \quad (4)$$

The pure water vapour pressure is corrected for salinity using a correlation presented by Nayar et al [28]. This correlation was established using measurements of brine with salt mass concentrations up to $\rho_L^N = 160 \text{ kg m}^{-3}$. However, it is assumed that the correlation can be extrapolated for slightly larger salinities S . It is given by ²

$$p_{\text{vap,L}} = \exp(c_1 \tilde{S} + c_2 \tilde{S}^2) p_{\text{vap,L}}^W \quad (5)$$

with $\tilde{S} = SS_0^{-1}$, $S_0 = 1 \text{ g kg}^{-1}$, and parameters $c_1 = -4.5818 \cdot 10^{-4}$ and $c_2 = -2.0443 \cdot 10^{-6}$. If salinity is unknown, it has to be evaluated from salt mass concentration using the methods of section 3.2. The brine vapour pressure $p_{\text{vap,L}}$ is valid for a free, planar liquid-vapour interface, it can be adjusted to curved interfaces as they exist in porous media with small pores using the Kelvin-equation [21]. Thereby, the partial pressure of water component in the gas phase is found by

$$p_G^W = p_{\text{vap,L}} \exp\left(\frac{p_{\text{cap}} M_L}{\rho_L R T}\right) \quad (6)$$

where M_L and ρ_L are molar mass (22) and density of the brine, $R = 8.3144598 \text{ J mol}^{-1} \text{ K}^{-1}$ is the universal gas constant, and capillary pressure p_{cap} as the pressure difference between gas and liquid phase is used to describe the curvature of the brine water surface. Brine density has to be found iteratively performing the steps described in Section 3.2.

With $x_{n,G}^W$ and $x_{n,G}^C$ the gas phase composition is known, and the density of that binary mixture can be computed directly using real-gas equations of state such as that presented by Peng and Robinson [34]. This cubic EOS, written in terms of compressibility factor Z , reads

$$Z^3 - (1 - B) Z^2 + (A - 3B^2 - 2B) Z - (AB - B^2 - B^3) = 0 \quad (7)$$

²In (5), the normalized salinity was introduced for the sake of unit consistency.

114 with

$$115 \quad A = \frac{a_m p_G}{R^2 T^2}, \quad B = \frac{b_m p_G}{RT}, \quad \text{and} \quad Z = \frac{M_G p_G}{\rho_G RT} \quad (8)$$

116 where a_m and b_m are parameters of the mixture, composed of substance-specific parameters a^ζ and
117 b^ζ which can be obtained from critical properties of the substance ζ by

$$118 \quad a^\zeta = a_c^\zeta \left[1 + m^\zeta \left(1 - \sqrt{T/T_{cr}^\zeta} \right) \right] \quad (9)$$

119 with

$$120 \quad a_c^\zeta = 0.45723553 \frac{R^2 T_{cr}^{\zeta 2}}{p_{cr}^\zeta} \quad \text{and} \quad b^\zeta = 0.077796074 \frac{RT_{cr}^\zeta}{p_{cr}^\zeta} \quad (10)$$

121 and with

$$122 \quad m^\zeta = 0.37464 + 1.54226\omega^\zeta - 0.26992\omega^{\zeta 2} \quad (11)$$

123 where $p_{cr}^\zeta, T_{cr}^\zeta$ are critical pressure and temperature and ω^ζ is the acentric factor of the substance
124 molecule ($\omega^W = 0.344$ and $\omega^C = 0.239$). The individual parameters a and b are averaged using the
125 binary mixing rules

$$126 \quad a_m = \sum_{\zeta} \sum_{\xi} x_{n,G}^\zeta x_{n,G}^\xi a^{\zeta\xi} \quad \text{and} \quad b_m = \sum_i x_{n,G}^i b^i \quad (12)$$

127 where $a^{\zeta\zeta} = a^\zeta$ and $a^{\zeta\xi} = (1 - k^{\zeta\xi}) (a^\zeta a^\xi)^{0.5}$ with the binary interaction factor for non-aqueous
128 CO₂-water mixtures $k^{\zeta\xi} = 0.1896$ [39]. In the single phase region, (7) shows only one real root,
129 while in the two-phase region, the largest root yields the compressibility factor of the vapour phase
130 and the smallest positive root corresponds to that of the liquid phase. It can be solved directly
131 using Cardano's method or the method of Nickalls [29]. The density of the gas phase can then be

132 obtained from Z by

$$133 \quad \rho_G = \frac{M_G p_G}{ZRT} \quad (13)$$

134 using the average molar mass of the gas mixture

$$135 \quad M_G = x_{n,G}^C M^C + x_{n,G}^W M^W \quad (14)$$

136 The partial densities (or mass concentrations) of the constituents ζ in the gas phase can be deter-
137 mined by

$$138 \quad \rho_G^\zeta = \frac{x_{n,G}^\zeta M^\zeta}{M_G} \rho_G \quad (15)$$

139 3.2. Liquid phase

140 The first step is to find the density ρ_L of the liquid phase at a specific pressure p_L , temperature T ,
141 and mass concentration ρ_L^N conditions. Equations of state for such systems usually require iterative
142 solution procedures due to the complexity of that ternary system [40, 10]. However, Song et al [38]
143 found a closed-form correlation for brine density in presence of carbon dioxide, valid in a pressure
144 range from 10 to 18 MPa and a temperature range from 333 to 414 K. The correlation also considers
145 salt and carbon dioxide mass fractions in a range of 0.05 to 0.2 for salt and up to 0.03 for CO₂.
146 It is convenient to describe the aqueous phase composition at equilibrium in terms of molar fraction
147 $x_{n,L}$ or mass fraction $x_{m,L}$. Since brine composition is still unknown, the CO₂-content has to be
148 guessed initially, e. g. by assuming the brine to be free of CO₂ initially, so $x_{n,L}^C = x_{m,L}^C = 0$.
149 Following this, and assuming that ρ_L was known, the mass fraction of salt is found by

$$150 \quad x_{m,L}^N = \frac{\rho_L^N}{\rho_L} \quad (16)$$

151 and water mass fraction is simply

$$152 \quad x_{m,L}^W = 1 - x_{m,L}^C - x_{m,L}^N \quad (17)$$

153 Starting with an initial guess for ρ_L , (e. g. $\rho_L = 1000 \text{ kg m}^{-3}$), temporary values for the mass
154 fractions of all liquid phase components ζ_L are found, which can be transformed into molar fractions
155 using

$$156 \quad x_{n,L}^\zeta = \frac{x_{m,L}^\zeta M^{\zeta-1}}{\sum_\pi x_{m,L}^\pi M^{\pi-1}}, \quad \pi = N, C, W \quad (18)$$

157 or $x_{n,L}^W = 1 - x_{n,L}^C - x_{n,L}^N$, respectively. In order to find a better estimate for ρ_L , the empirical
158 equation of state presented by Song et al [38] is used (24), that takes salt molality as argument.

159 Molality b refers to the amount of a solute substance per mass of solvent. In the ternary system
160 consisting of N, W, and C constituents, the solvent can be described as one pure pseudo-substance
161 such that the ternary system is transformed into a binary system of solute and solvent. Therefore,
162 two new solvents ξ with $\xi = CW$ or $\xi = NW$ are defined in order to determine the molalities of N
163 and C, respectively (cf. Figure 2). The molar fraction of ξ in the binary system is simply

$$164 \quad x_{n,L}^\xi = 1 - x_{n,L}^\zeta \quad (19)$$

165 where ζ in this case is always that component, that is not part of ξ . It is clear that these solvents
166 are binary systems of themselves; their molar masses are found by averaging the molar masses
167 of their constituents (i. e. C and W for CW, N and W for NW) with the molar fractions of the
168 constituents within the solvent (not to be confused with the molar fractions of the liquid phase).

169 These auxiliary molar fractions $x_{n,\xi}^\zeta$ are found by³

$$170 \quad x_{n,\xi}^\zeta = x_{n,L}^\zeta x_{n,L}^\xi^{-1} \quad (20)$$

³ ξ has a double meaning: superscripted it denotes one constituent of the binary mixture α , when used as subscript it represents a binary mixture consisting of constituents ζ .

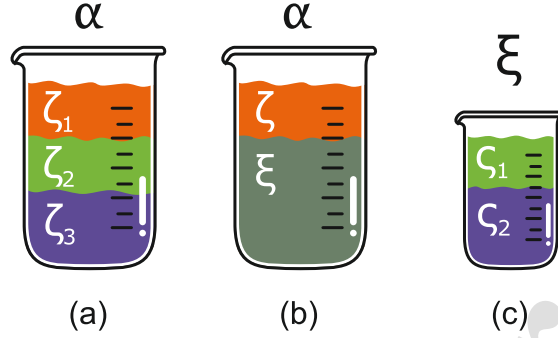


Figure 2: Phase α consists of three constituents ζ_n (a). This ternary mixture can be treated as a binary mixture of constituents ζ and ξ (b), where the pseudo-substance ξ itself is a binary mixture consisting of the constituents ζ_n (c).

and they must satisfy

$$\sum_{\varsigma} x_{n,\xi}^{\varsigma} = 1, \varsigma = C, W \text{ or } \varsigma = N, W \quad (21)$$

such that the molar mass of the pseudo-components yield

$$M_{\xi} = \sum_{\varsigma} x_{n,\xi}^{\varsigma} M^{\varsigma}, \varsigma = C, W \text{ for } \xi = CW \text{ and } \varsigma = N, W \text{ for } \xi = NW \quad (22)$$

The molality of salt in the solvent CW can be determined by

$$b_L^N = \frac{x_{n,L}^N}{M_{CW} x_{n,L}^{CW}} \quad (23)$$

With b_L^N known, a better estimate for the brine density can be determined by ⁴

$$\rho_L = \sum_{i=0}^2 \left(c_{1,i} + 0.1 c_{2,i} \tilde{p}_L + c_{3,i} \tilde{b}_L^N + c_{4,i} (\tilde{b}_L^N)^{1/3} + c_{5,i} (x_{m,L}^C)^{1/2} + c_{6,i} (x_{m,L}^C)^{1/3} \right) \tilde{T}^i \quad (24)$$

with $\tilde{p}_L = p_L p_{L0}^{-1}$, $\tilde{b}_L^N = b_L^N (b_{L0}^N)^{-1}$, and $\tilde{T} = T T_0^{-1}$ where $p_{L0} = 1 \text{ bar}$, $b_{L0}^N = 1 \text{ mol kg}^{-1}$, and

⁴(24) to (27) have been modified in order to establish unit consistency.

$T_0 = 1$ K. Dimensionless quantities $\tilde{p}_L$, $\tilde{b}_L^N$, and $\tilde{T}$ are used from here on in order to guarantee the consistency of units.

(24) is then used to find b_L^N more precisely using (16) to (23). These steps are performed repeatedly until the product $\rho_L x_{m,L}^N$ (using the updated value of ρ_L) approaches the known salt mass concentration ρ_L^N sufficiently. Knowing b_L^N , a better estimate for the amount of dissolved CO_2 can be obtained using the correlation of Duan and Sun [9] in terms of CO_2 -molality in brine at the equilibrium. It is given by

$$\ln b_L^C = \ln (x_{n,G}^C \varphi_{\text{CO}_2} \tilde{p}_L) - \mu_{\text{CO}_2}^{1(0)} R^{-1} T^{-1} - 2\lambda_{\text{CO}_2-\text{Na}^+} b_{\text{Na}^+}^L - \eta_{\text{CO}_2-\text{Na}^+-\text{Cl}^-} b_{\text{Cl}^-}^L b_{\text{Na}^+}^L \quad (25)$$

where $b_L^{\text{Na}^+} = b_L^{\text{Cl}^-} = b_L^N$, where φ_{CO_2} is the fugacity coefficient, $\mu_{\text{CO}_2}^{1(0)}$ is the standard chemical potential of CO_2 in the liquid phase, and $\lambda_{\text{CO}_2-\text{Na}^+}$ and $\eta_{\text{CO}_2-\text{Na}^+-\text{Cl}^-}$ are interaction parameters between CO_2 and Na^+ or between CO_2 and Na^+, Cl^- , respectively. A non-iterative correlation for the Fugacity coefficient φ_{CO_2} can be taken from Duan et al [11] which reads

$$\begin{aligned} \varphi_{\text{CO}_2} = & c_1 + \left(c_2 + c_3 \tilde{T} + c_4 \tilde{T}^{-1} + c_5 (\tilde{T} - 150)^{-1} \right) \tilde{p}_L \\ & + (c_6 + c_7 \tilde{T} + c_8 \tilde{T}^{-1}) \tilde{p}_L^2 + (c_9 + c_{10} \tilde{T} + c_{11} \tilde{T}^{-1}) \ln (\tilde{p}_L) \\ & + (c_{12} + c_{13} \tilde{T}) \tilde{p}_L^{-1} + c_{14} \tilde{T}^{-1} + c_{15} \tilde{T}^2 \end{aligned} \quad (26)$$

with coefficients c_n given in Table A.3. Correlations for interaction parameters $\lambda_{\text{CO}_2-\text{Na}^+}$ and $\eta_{\text{CO}_2-\text{Na}^+-\text{Cl}^-}$, as well as standard chemical potential $\mu_{\text{CO}_2}^{1(0)}$ of CO_2 as functions of temperature and pressure are taken from Duan and Sun [9]. The generic equation

$$\begin{aligned} \Upsilon = & c_1 + c_2 \tilde{T} + c_3 \tilde{T}^{-1} + c_4 \tilde{T}^2 + c_5 (630 - \tilde{T})^{-1} + c_6 \tilde{p}_L \\ & + c_7 \tilde{p}_L \ln (\tilde{T}) + c_8 \tilde{p}_L \tilde{T}^{-1} + c_9 \tilde{p} (630 - \tilde{T})^{-1} \\ & + c_{10} \tilde{p}_L^2 (630 - \tilde{T})^{-2} + c_{11} \tilde{T} \ln (\tilde{p}_L) \end{aligned} \quad (27)$$

can be used for all three quantities when different sets of coefficients c_n are applied. These coefficients can be found in Table A.4.

From CO_2 molality b_L^C , a better estimate of CO_2 mass fraction in the brine can be evaluated by

$$x_{m,L}^C = \frac{b_L^C M_{\text{CO}_2}}{1 + b_L^C M_{\text{CO}_2}} \quad (28)$$

which is now used to find better values for $x_{m,L}^N$ and ρ_L repeating the steps starting from (16); this procedure has to be performed iteratively until ρ_L converges. In Figure 3 the entire procedure is shown schematically in terms of a flow diagram.

The resulting distributions of constituents C and W are plotted in Figure 4 over a broad temperature range for two pressures $p_L = 10 \text{ MPa}$ and $p_L = 20 \text{ MPa}$. As expected, the water vapour amount in the gas phase rises with growing temperatures. At high pressures, this effect is less prominent since the distance to the phase boundary (the saturation pressure of water $p_{\text{vap},L}$) increases. The behaviour of CO_2 mole fraction is oppositional to that of water since the gas phase is a binary mixture and both constituents mole fractions add up to unity.

In the liquid phase, growing temperatures lead to a decrease of CO_2 content in the brine, since gas solubility in water is best at cold conditions. Note that in the liquid phase, the molar fractions of C and W constituents add up to $1 - x_{n,L}^N$.

4. A simplified non-iterative method

The method described in the last section consists of two nested iteration loops. Although it converges relatively fast, performing iteration loops during complex numerical simulations can in sum turn out to be very time consuming (cf. Figure 1). It is possible to further simplify the method in order to avoid iterations entirely at the cost of some accuracy. The acceptability of this loss of accuracy is subject to engineering judgement.

For this simplification, all salt-related composition parameters (mass and molar fraction, molality, and mass concentration) are evaluated at equilibrium for some or certain reference conditions using the iterative method from the previous section. These parameters are constant over the specified p -

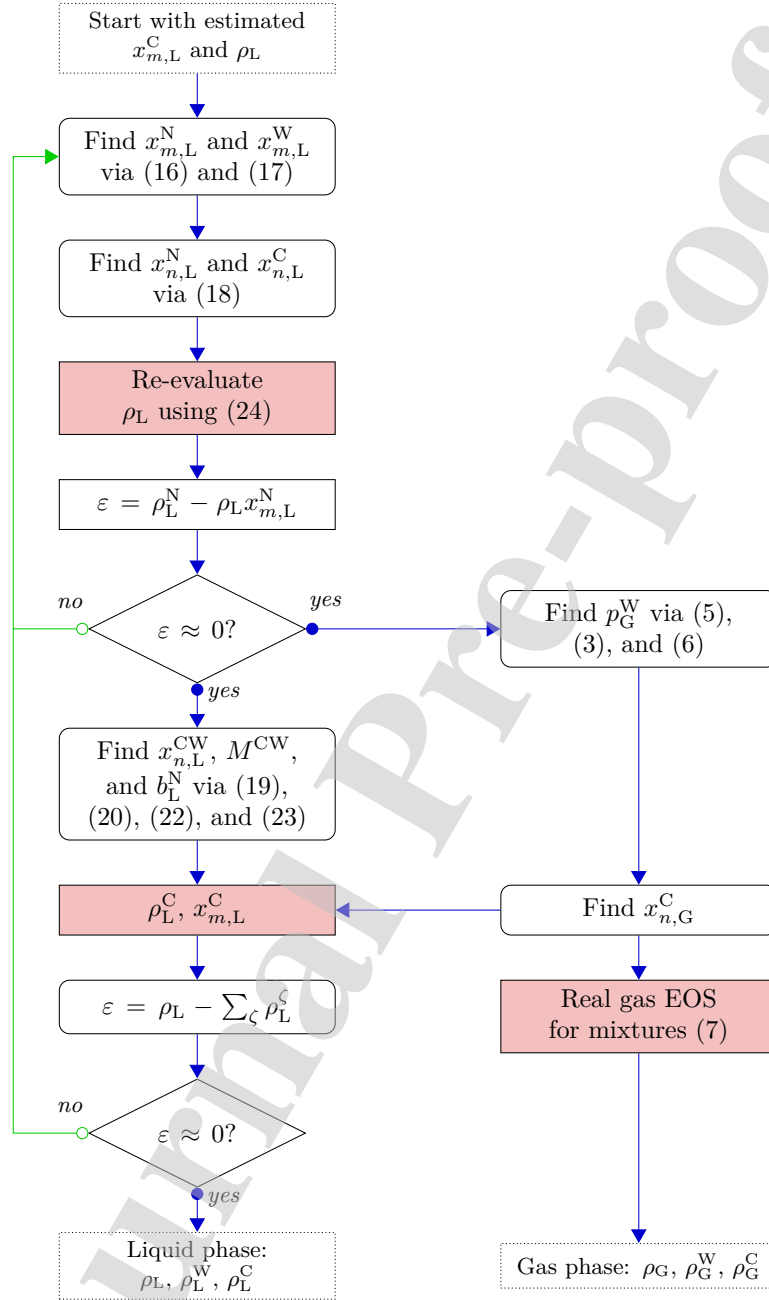


Figure 3: Flow chart for finding the contribution of components W and C among liquid and gas phases. Starting with rough estimates for ρ_L and $x_{m,L}^C$, e. g. $\rho_L = 1000 \text{ kg m}^{-3}$ and $x_{m,L}^C = 0$, an intermediate liquid mixture density ρ_L is found iteratively. Using this, gas phase composition and CO_2 -solubility can be found, which provides a better estimate for $x_{m,L}^C$ to start a new iteration of the entire loop. The loop continues until the calculated liquid density approximates the sum of all liquid components partial densities sufficiently.

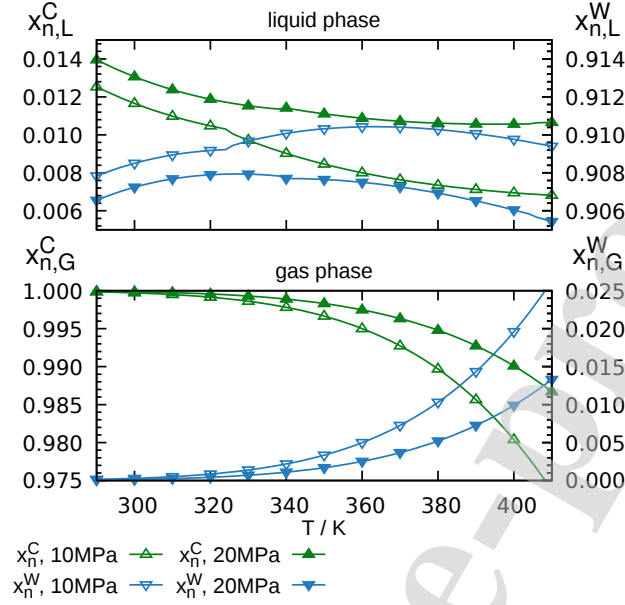


Figure 4: Molar fractions of CO₂ (C) and water (W) constituents among liquid phase (top) and gas phase (bottom) versus temperature at two reference pressures $p_L = 10$ MPa and $p_L = 20$ MPa

230 T -range. This simplification comes along with minor discrepancies if the ranges of phase pressure,
 231 capillary pressure, and temperature are not too broad. For $p_L^{\text{ref}} = 16$ MPa, $T^{\text{ref}} = 333$ K and
 232 $\rho_L^{\text{Nref}} = 250$ kg m⁻³, the resulting constant values are given in Table 1. The chosen reference values
 233 correspond to in-situ conditions of a saline aquifer at a depth 1600 m below the North Sea [6].
 234 Finding the composition of the gas phase follows the same steps as the iterative method, although
 235 for salinity in (5) the constant value from Table 1 was chosen. Furthermore, the correction for
 236 curved menisci of the liquid-gas interface was omitted since those effects are relevant in very dry

Table 1: Parameters describing the brine composition of the H₂O-CO₂-NaCl system at reference conditions.

mass concentration	$\rho_L^{\text{N}} = 250.0$ kg m ⁻³
molar fraction	$x_{n,L}^{\text{N}} = 0.08068$
mass fraction	$x_{m,L}^{\text{N}} = 0.2187$
salinity	$S = 218.7$ g kg ⁻¹
molality	$b_L^{\text{N}} = 4.7899$ mol kg ⁻¹

soils or media with very small pore sizes only. Practically, this assumption can be checked by evaluating the capillary pressure range during the simulation.

With known gas phase composition, the amount of dissolved CO_2 can be found directly using (25) for b_L^{Nref} . CO_2 mass fraction is found by (28), and the brine density can be computed directly using (24).

5. Results and discussion

In order to prove their accuracy, the results of the described methods are compared to experimental data as well as to results from more sophisticated models. One substantial component of VLE-models is the equation of state, which relates the state of a substance to a set of physical conditions. In contrast to complex, thermodynamically consistent EOS, the simple correlation presented by Song et al [38] which is used in this work shows surprisingly accurate results in the specified p_L - T -range. Figure 5 indicates the quality of the implemented EOS. It shows the relative deviation of calculated mixture densities (using the methods described in this work, primarily (24)) as well as density measurements from the literature [38] from the results of a reference density calculated by the established equation of state presented by Duan et al [12]. The figure shows comparisons for three different compositions and two pressures $p_L = 10$ MPa and $p_L = 18$ MPa versus temperature. Except for the highly saline, CO_2 -rich composition ($b_L^{\text{N}} = 4.0 \text{ mol kg}^{-1}$ and $x_{n,L}^{\text{C}} = 0.024$), both the measured densities as well as the densities computed by (24) show relative deviations from the reference EOS of less than 0.4%.

Another important module of the phase equilibrium model is the calculation of CO_2 -solubility in the liquid phase. For verification purposes, the ratio x_b^{C} is introduced as the ratio of equilibrium molality of CO_2 in the binary system CW to that of the ternary system CNW $\equiv$ L:

$$x_b^{\text{C}} = b_{\text{CW}}^{\text{C}} (b_L^{\text{C}})^{-1} \quad (29)$$

Figure 6 features a set of diagrams showing the absolute deviation $\Delta x_b^{\text{C}} = x_{b,\text{ref}}^{\text{C}} - x_b^{\text{C}}$ of this work's results from the results of the approved and sophisticated model presented by Akinfiev and

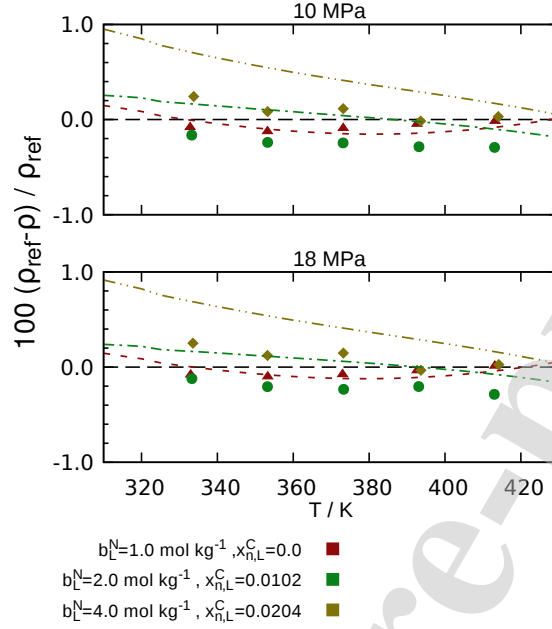


Figure 5: Relative deviation of calculated as well as measured densities presented by Song et al [38] from the reference equation of state presented by Duan et al [12]. Colors indicate the b_L^N - $x_{n,L}^C$ -conditions, symbols represent experimental values and lines correspond to densities calculated by (24).

Diamond [1] for six temperature ranges. Additionally, a large number of experimental data from the literature are shown for better contrast.

Both methods presented in this work show very good agreement only for low-salt compositions; from molalities of $b_L^N \gtrsim 2 \text{ mol kg}^{-1}$ on, the results start to deviate slightly from the reference method. Yet, this deviation does not exceed a value of $\Delta x_b^C \approx 12 \%$. Largest deviations occur at $T = 298 \text{ K}$ in highly saline mixtures. Applying the simplification from Section 4 downgrades the results from the iterative method only insignificantly.

However, these deviations are put into perspective when compared to the experimental data. Those measurements scatter in a range of approximately $\pm 35 \%$ around the reference value; this gives an appreciation for the complexity of this ternary system. It is therefore again subjected to the modeller's judgement whether the deviations of the described methods are acceptable or not.

For the conditions considered in this work, the iterative method requires never more than 12 inner,

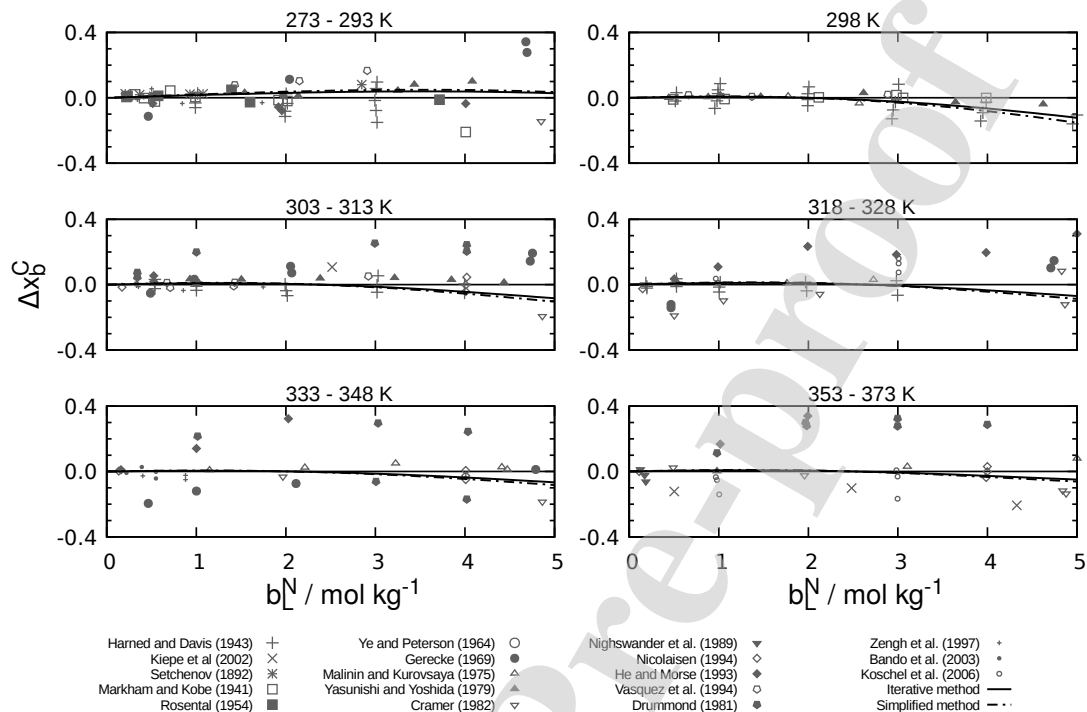


Figure 6: Absolute deviation of the ratios of CO₂ solubility in the binary system to that of the ternary system, plotted versus salt molality.

and never more than 6 outer iterations, resulting in 72 repetition loops at most. Since the simplification of this method allows to entirely avoid those iterations, one could argue that using the simple method results in a speed-up of about this factor. Though, the true saving in computation time always depends on the way the method is implemented and on the architecture of the utilized machine, among others.

Figure 7 to Figure 10 exemplarily compare the results of the iterative method to those of the simplification in terms of deviations of molar fraction, mass fraction, and of density. For the gas phase, one can say that there is no significant difference between both methods. Figure 7 and Figure 8 show absolute deviations of molar fraction and mass fraction for isobaric and isothermal conditions, respectively. The largest deviations for both quantities can be found at low pressures

and high temperatures, but they do not exceed values of about 0.01 %. However, this is no surprise, since most of the simplifications were applied to the liquid phase part of the method. In the liquid phase, the deviation between both methods is about one order of magnitude higher (cf. Figure 9), where the most significant deviations ($\Delta x_m \approx 0.7\%$) appear at high temperatures. Furthermore, it is notable that deviations in the liquid phase are almost independent from pressure. This behaviour is reflected in the density distribution. In Figure 10, the relative deviations of liquid phase density as well as liquid phase constituents partial densities is shown. With about 3.5 %, the partial density of salt (ρ_L^N) shows the largest deviation of all constituents, again most prominently at high temperatures. From Figure 10 it is also apparent that the reference conditions for the simplification were evaluated at a temperature of $T = 333\text{ K}$, since the deviations at this temperature are minimal.

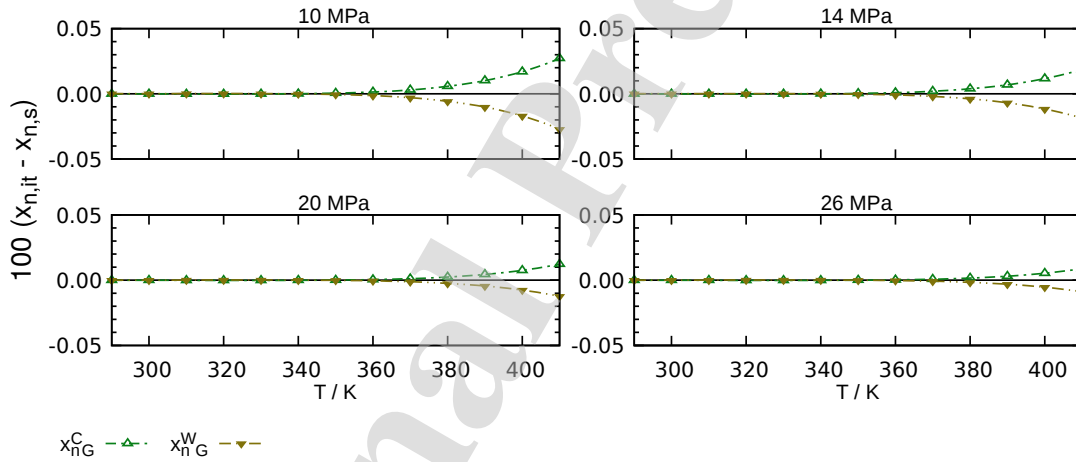


Figure 7: Absolute deviations of molar fractions of the gas phase constituents, where $x_{n,it}$ corresponds to results of the iterative method and $x_{n,s}$ corresponds to results of the simplified method.

6. Concluding remarks

The procedures presented in this article generate all relevant quantities to describe the phase equilibrium condition of ternary system water-salt-carbon dioxide. The iterative method allows computing

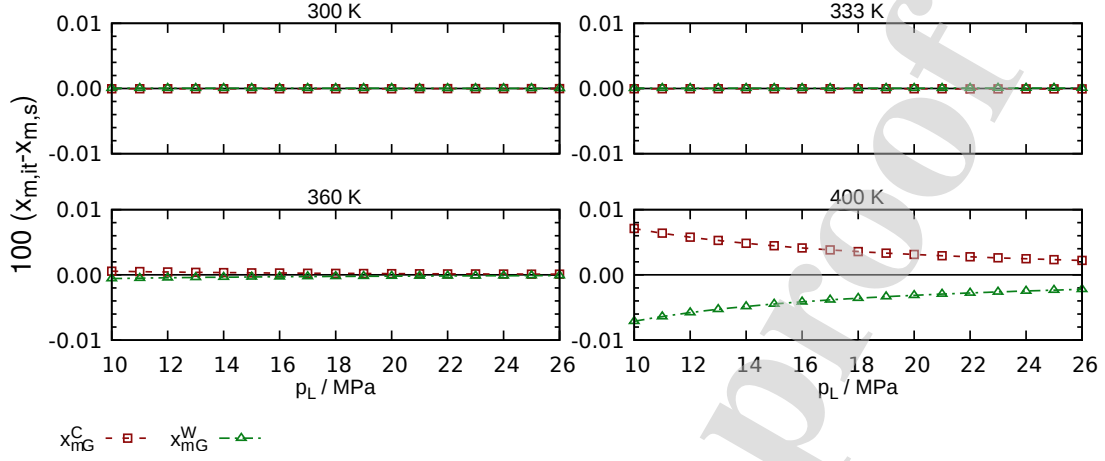


Figure 8: Absolute deviations of mass fractions of the gas phase constituents, where $x_{m,it}$ corresponds to results of the iterative method and $x_{m,s}$ corresponds to results of the simplified method.

the distribution of water and CO₂ constituents among gas and liquid phases for multiphase flow simulations, where pressure and temperature correspond to natural conditions. Compared to other, more sophisticated thermodynamic models as well as to experimental data, the method of this work produces appropriate results for engineering purposes. Although various numerical tests indicate that the iterative algorithm is very stable and its results are reliable, its general robustness has yet to be tested in an extensive convergence study.

In its simplified form, the computation time of the method is reduced by omitting iteration loops while the result quality is still acceptable. Thus, this work provides a constitutive phase equilibrium model that is suitable for large-scale THMC-simulations.

Declarations of interest

None.

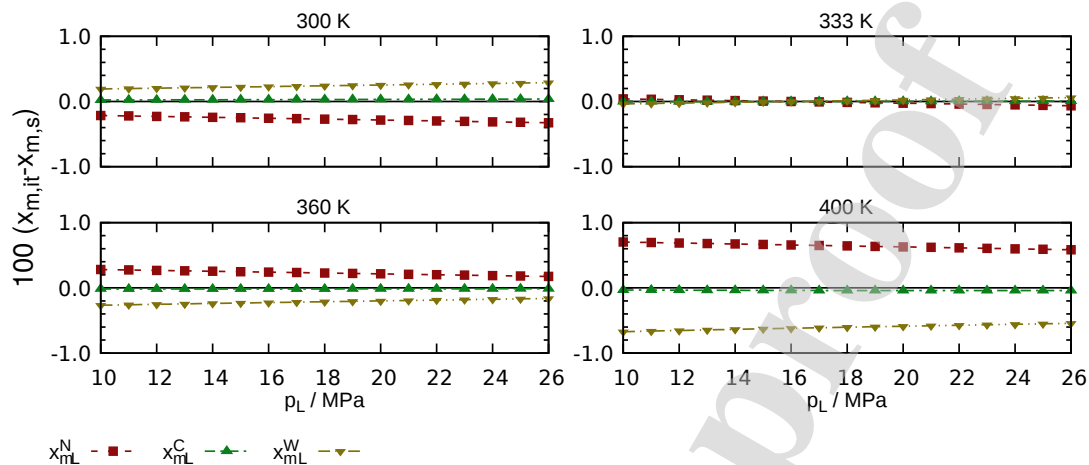


Figure 9: Relative liquid phase density and partial component densities deviations of the simplified method from the iterative method.

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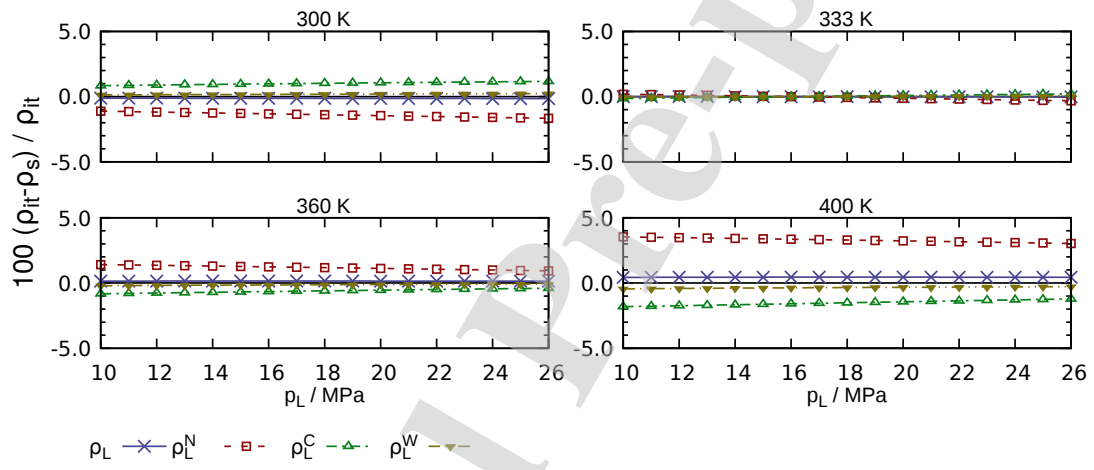


Figure 10: Relative liquid phase density and partial component densities deviations of the simplified method from the iterative method.

318 Appendix A. Coefficients

Table A.2: Coefficients for (24) presented by Song et al [38].

	i= 0	1	2
c_1	$8.8680 \cdot 10^{-1}$	$1.5789 \cdot 10^{-3}$	$-1.1438 \cdot 10^{-5}$
c_2	$4.6120 \cdot 10^{-4}$	$-1.9575 \cdot 10^{-6}$	$1.3304 \cdot 10^{-8}$
c_3	$5.0708 \cdot 10^{-3}$	$3.3686 \cdot 10^{-4}$	$-1.5925 \cdot 10^{-6}$
c_4	$1.4891 \cdot 10^{-1}$	$-2.0919 \cdot 10^{-3}$	$1.0504 \cdot 10^{-5}$
c_5	$1.1711 \cdot 10^{-2}$	$-5.3000 \cdot 10^{-5}$	$-1.1061 \cdot 10^{-7}$
c_6	$-7.4335 \cdot 10^{-3}$	$1.8936 \cdot 10^{-5}$	$1.5172 \cdot 10^{-7}$

Table A.3: Coefficients for (26) presented by Duan et al [11]. Those coefficients depend on a specific region in the $\tilde{p}_L, T$ -phase diagram.

coeff.	p_L, T -region					
	1	2	3	4	5	6
c_1	1.0000	$-7.1735 \cdot 10^{-1}$	$-6.5129 \cdot 10^{-2}$	5.0384	$-1.6063 \cdot 10^1$	$-1.5693 \cdot 10^{-1}$
c_2	$4.7587 \cdot 10^{-3}$	$1.5985 \cdot 10^{-4}$	$-2.1430 \cdot 10^{-4}$	$-4.4258 \cdot 10^{-3}$	$-2.7058 \cdot 10^{-3}$	$4.4621 \cdot 10^{-4}$
c_3	$-3.3570 \cdot 10^{-6}$	$-4.9286 \cdot 10^{-7}$	$-1.1445 \cdot 10^{-6}$	0.0000	0.0000	$-9.1081 \cdot 10^{-7}$
c_4	0.0000	0.0000	0.0000	1.9573	$1.4119 \cdot 10^{-1}$	0.0000
c_5	-1.3179	0.0000	0.0000	0.0000	0.0000	0.0000
c_6	$-3.8389 \cdot 10^{-6}$	$-2.7855 \cdot 10^{-7}$	$-1.1558 \cdot 10^{-7}$	$2.4223 \cdot 10^{-6}$	$8.1133 \cdot 10^{-7}$	$1.0647 \cdot 10^{-7}$
c_7	0.0000	$1.1877 \cdot 10^{-9}$	$1.1952 \cdot 10^{-9}$	0.0000	0.0000	$2.4273 \cdot 10^{-10}$
c_8	$2.2815 \cdot 10^{-3}$	0.0000	0.0000	$-9.3796 \cdot 10^{-4}$	$-1.1453 \cdot 10^{-4}$	0.0000
c_9	0.0000	0.0000	0.0000	-1.5026	2.3896	$3.5874 \cdot 10^{-1}$
c_{10}	0.0000	0.0000	0.0000	$3.0272 \cdot 10^{-3}$	$5.0527 \cdot 10^{-4}$	$6.3320 \cdot 10^{-5}$
c_{11}	0.0000	0.0000	0.0000	$-3.1377 \cdot 10^1$	$-1.7763 \cdot 10^1$	$-2.4990 \cdot 10^2$
c_{12}	0.0000	$-9.6540 \cdot 10^1$	$-2.2134 \cdot 10^2$	$-1.2847 \cdot 10^1$	$9.8592 \cdot 10^2$	0.0000
c_{13}	0.0000	$4.4775 \cdot 10^{-1}$	0.0000	0.0000	0.0000	0.0000
c_{14}	0.0000	$1.0181 \cdot 10^2$	$7.1820 \cdot 10^1$	0.0000	0.0000	$8.8877 \cdot 10^2$
c_{15}	0.0000	$5.3784 \cdot 10^{-6}$	$6.6089 \cdot 10^{-6}$	$-1.5057 \cdot 10^{-5}$	$-5.4965 \cdot 10^{-7}$	$-6.6348 \cdot 10^{-7}$

Region 1: $273 \text{ K} < T \leq 573 \text{ K}$, $p_L \leq p_L^{\text{sat}}$; Region 2: $273 \text{ K} < T \leq 340 \text{ K}$, $p_L^{\text{sat}} < p_L < 1000 \text{ bar}$;
 Region 3: $273 \text{ K} < T \leq 573 \text{ K}$, $p_L > 1000 \text{ bar}$; Region 4: $340 \text{ K} < T \leq 435 \text{ K}$, $p_L^{\text{sat}} < p_L < 1000 \text{ bar}$;
 Region 5: $340 \text{ K} < T \leq 435 \text{ K}$, $p_L > 1000 \text{ bar}$; Region 6: $T > 435 \text{ K}$, $p_L > p_L^{\text{sat}}$; with $p_L^{\text{sat}} = 75 \text{ bar} + (T - 305 \text{ K})1.25 \text{ bar K}^{-1}$

Table A.4: Coefficients for the chemical potential $\Upsilon = \mu_{\text{CO}_2}^{(0)}$ and for the interaction parameters $\Upsilon = \lambda_{\text{CO}_2-\text{Na}^+}$ and $\Upsilon = \eta_{\text{CO}_2-\text{Na}^+-\text{Cl}^-}$ (27) taken from Duan and Sun [9].

coeff.	$\Upsilon = \mu_{\text{CO}_2}^{(0)}$	$\lambda_{\text{CO}_2-\text{Na}^+}$	$\eta_{\text{CO}_2-\text{Na}^+-\text{Cl}^-}$
c_1	$2.8945 \cdot 10^1$	$-4.1137 \cdot 10^{-1}$	$3.3639 \cdot 10^{-4}$
c_2	$-3.5458 \cdot 10^{-2}$	$6.0763 \cdot 10^{-4}$	$-1.9830 \cdot 10^{-5}$
c_3	$-4.7707 \cdot 10^3$	$9.7535 \cdot 10^1$	0.0000
c_4	$1.0278 \cdot 10^{-5}$	0.0000	0.0000
c_5	$3.3813 \cdot 10^1$	0.0000	0.0000
c_6	$9.0404 \cdot 10^{-3}$	0.0000	0.0000
c_7	$-1.1493 \cdot 10^{-3}$	0.0000	0.0000
c_8	$-3.0741 \cdot 10^{-1}$	$-2.3762 \cdot 10^{-2}$	$2.1222 \cdot 10^{-3}$
c_9	$-9.0730 \cdot 10^{-2}$	$1.7066 \cdot 10^{-2}$	$-5.2487 \cdot 10^{-3}$
c_{10}	$9.3271 \cdot 10^{-4}$	0.0000	0.0000
c_{11}	0.0000	$1.4134 \cdot 10^{-5}$	0.0000

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