

# Phase Equilibria Calculation of $\text{CO}_2 - \text{H}_2\text{O}$ System at Given Volume, Temperature, and Moles in $\text{CO}_2$ Sequestration

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**Abstract**—The paper deals with the investigation of multi-phase equilibrium of  $\text{CO}_2 - \text{H}_2\text{O}$  system at constant volume, temperature and moles (the so-called *VT-flash*), which is motivated by topical problem of  $\text{CO}_2$  sequestration. Studying  $\text{CO}_2 - \text{H}_2\text{O}$  mixture under natural geological conditions (pressures typically below 50 MPa and temperatures typically 298 – 383 K) for different system composition, two-phase and three-phase states were observed. Recently, we have developed a fast and robust algorithm for constant-volume two-phase split calculation, which is based on the direct minimization of the total Helmholtz free energy of the mixture with respect to the mole- and volume-balance constraints. The algorithm uses modified Newton-Raphson minimization method. To initialize the algorithm, an initial guess is constructed using the results of constant-volume stability testing. In this work, we extend the results for  $\text{CO}_2 - \text{H}_2\text{O}$  system and propose a fast and robust algorithm for three-phase equilibrium computation at constant volume, temperature and moles. The performance of the proposed strategy is shown on several examples of two- and three-phase equilibrium calculations of  $\text{CO}_2 - \text{H}_2\text{O}$  mixture under various conditions. Finally, we discuss the fact that the *VT*-approach seems more natural than the widely used classical formulation at constant pressure, temperature and moles (the so-called *PT-flash*), especially when using pressure-explicit equations of state.

**Index Terms**—phase equilibrium, constant volume flash,  $\text{CO}_2$  sequestration, Helmholtz free energy minimization, Newton-Raphson method, modified Cholesky factorization.

## I. INTRODUCTION

STUDYING  $\text{CO}_2 - \text{H}_2\text{O}$  system phase behaviour is motivated by  $\text{CO}_2$  sequestration, which is from an ecology point of view a possibility of protection against the greenhouse effect by capturing emissions of  $\text{CO}_2$  at the source and storing them into deep geological repositories (technology *CCS* - Carbon Capture and Storage) or salt-water reservoirs. For such operations, it is essential to fully understand the thermodynamics of the processes in the subsurface and to have a model which describes the behaviour of  $\text{CO}_2$  correctly under wide range of natural geological conditions.

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Injecting  $\text{CO}_2$  into a reservoir, it may dissolve in the water or it can mix and the  $\text{CO}_2 - \text{H}_2\text{O}$  mixture can split into two or more phases. Let us consider a closed system of total volume  $V$  containing a  $\text{CO}_2 - \text{H}_2\text{O}$  mixture with mole numbers  $N_w, N_c$  at temperature  $T$ . First, we are interested to find out whether the system is under given conditions in single-phase or splits into two phases. This is the problem of single-phase stability at constant volume, temperature and moles (the so-called *VT-stability*). In case of phase-splitting we want to establish volumes of both phases, mole numbers of each component in both phases, and consequently the equilibrium pressure of the system from the equation of state. This is the problem of two-phase split calculation at constant volume, temperature and moles (the so-called *VT-flash*). In our previous work [5], [6], [7], these problems were formulated and the algorithms were proposed and tested on many examples.

The formulation of phase stability investigation and phase-equilibria computation at constant volume, temperature and moles is alternative to the traditional formulation at constant pressure, temperature and chemical composition, which has been used in many applications [1], [2], [3], [4], [8], [9]. Despite the well-known fact that there is the possibility of using alternative variables, in most applications *PT-stability* and *PT-flash* have been used to solve the phase stability and phase-equilibria computation and the algorithms fully based on *VT* variables started to be developed only recently [5], [6], [7].

To demonstrate the shortcomings of the traditional variables, let us consider pure  $\text{CO}_2$  at temperature  $T = 280$  K and saturation pressure  $P_{sat}(T)$  corresponding to the temperature  $T = 280$  K. Using traditional *PT* variables, one cannot decide whether the system occurs in vapor or liquid state, or as a mixture of both, because all two-phase states and both saturated gas and saturated liquid occur at the same pressure, which is equal to the saturation pressure  $P_{sat}(T)$ , temperature and moles. Therefore, *PT-stability* and *PT-flash* cannot distinguish between these states, but *VT-stability* and *VT-flash* can, because these states have different volumes. This example shows that the *PT-stability* and *PT-flash* problems are not well posed since the volume of the system is not uniquely determined by specifying the pressure, temperature and moles. On the other hand, if volume, temperature and moles are specified, the equilibrium pressure is given uniquely by the equation of state. The non-uniqueness of volume at specified pressure, temperature and moles for the pure substances at saturation pressure has been discussed in [5], [6], [7]. In this work, we present a non-trivial example of a binary mixture of  $\text{CO}_2 - \text{H}_2\text{O}$  in

three phases, which exhibits the same behaviour as the pure substances at saturation pressure.

In [5], we have developed and successfully tested a numerical algorithm for constant-volume two-phase split calculation which is based on the constrained minimization of the total Helmholtz free energy of the mixture. The algorithm uses the Newton-Raphson method with line-search and modified Cholesky decomposition of the Hessian matrix to produce a sequence of states with decreasing values of the total Helmholtz free energy. Using of the Newton-Raphson method ensures fast convergence around the solution. Furthermore, as the method guarantees decreasing in the total Helmholtz free energy of the system in every iteration, it always converges to a state corresponding to at least a local minimum of the energy. To initialize the algorithm, we use the results of the constant-volume stability algorithm which has been developed in [7]. In this work, we extend these results to three phases for  $\text{CO}_2 - \text{H}_2\text{O}$  system, which provides us a better understanding of the thermodynamic behaviour of  $\text{CO}_2$  mixtures under geologic carbon storage conditions, and present an algorithm for three-phase equilibrium computation at constant volume, temperature and moles. The performance of the proposed strategy is shown on several examples of two- and three-phase equilibrium calculations of  $\text{CO}_2 - \text{H}_2\text{O}$  mixture under various conditions.

The paper is structured in the following way. In section 2, we formulate the  $VT$ -flash problem and derive the equilibrium conditions for binary mixture of  $\text{CO}_2 - \text{H}_2\text{O}$  using the Helmholtz free energy. In section 3, we describe a new computational algorithm for three-phase equilibrium calculation at constant volume, temperature, and moles. In section 4, we summarize key steps of the algorithm and propose a general strategy for the constant-volume phase-split calculation of  $\text{CO}_2 - \text{H}_2\text{O}$  system. In section 5, we present numerical results showing the performance of the algorithm on  $\text{CO}_2 - \text{H}_2\text{O}$  mixture under different conditions. In section 6, we discuss the results, especially, we point out advantages of using  $VT$ -variables instead of traditional  $PT$ -variables, and draw some conclusions. In the Appendix, we provide details of the Cubic-Plus-Association equation of state [12], [13] that was used in the work.

## II. PHASE EQUILIBRIUM CONDITIONS FOR $\text{CO}_2 - \text{H}_2\text{O}$ SYSTEM

Consider a closed system containing a binary mixture of water ( $\text{H}_2\text{O}$ ) and carbon dioxide ( $\text{CO}_2$ ) with mole numbers  $N_w$  and  $N_c$  occupying total volume  $V$  at temperature  $T$ . Let us assume that the mixture occurs in an  $N$ -phase state, where  $N = 2$  or  $N = 3$ , and denote the volumes of each phase  $V_\alpha$  and the mole numbers of each component in each phase  $N_{\alpha,w}$  and  $N_{\alpha,c}$ , where  $\alpha = 1, \dots, N$ . We are interested in deriving conditions of  $N$ -phase equilibrium in the mixture.

Let us denote by  $\mathbf{x}_0$  and  $\mathbf{x}_\alpha$  vectors with components  $N_w, N_c, V$  and  $N_{\alpha,w}, N_{\alpha,c}, V_\alpha$ , where  $\alpha = 1, \dots, N$ , respectively. Then, for the single-phase  $\text{CO}_2 - \text{H}_2\text{O}$  system, the Helmholtz free energy is given by

$$A^I = A(\mathbf{x}_0, T) = -PV + \sum_{i=w,c} N_i \mu_i, \quad (1)$$

where  $P = P(\mathbf{x}_0, T)$  is the pressure given by a pressure-explicit equation of state, and  $\mu_i = \mu_i(\mathbf{x}_0, T)$  is the chemical

TABLE I  
LIST OF NOTATION

Symbol	meaning
$A$	Helmholtz free energy
$b_i$	covolume parameter of the Peng-Robinson EOS
$c$	molar concentration
$\delta_{X-Y}$	binary interaction coefficient between components $X$ and $Y$
$i, j$	component indices; $w$ for water, $c$ for carbon dioxide
$k$	iteration index
$k_B$	Boltzmann constant
$\mu_{\alpha,i}$	chemical potential of the $i$ -th component in phase $\alpha$
$M_{w,i}$	molar weight of the $i$ -th component
$N_{\alpha,i}$	total mole number of the $i$ -th component in phase $\alpha$
$N$	number of phases
$\omega_i$	acentric factor of the $i$ -th component
$P$	pressure
$P_{i,crit}$	critical pressure of the $i$ -th component
$R$	universal gas constant
$T$	absolute temperature
$T_{i,crit}$	critical temperature of the $i$ -th component
$V$	total volume of the system
$V_\alpha$	volume of phase $\alpha$
$z_i$	overall mole fraction of the $i$ -th component

potential of the  $i$ -th component in the mixture. For the  $N$ -phase system, the total Helmholtz free energy reads as

$$A^N = \sum_{\alpha=1}^N A(\mathbf{x}_\alpha, T). \quad (2)$$

An equilibrium state of the  $N$ -phase system is such a state for which the increase in the total Helmholtz free energy with respect to an energy reference state

$$\Delta A = \sum_{\alpha=1}^N A(\mathbf{x}_\alpha, T) - A^{ref}, \quad (3)$$

where the energy reference state  $A^{ref}$  can be chosen for example as a single-phase state or an  $(N-1)$ -phase equilibrium state, is minimal among all states satisfying the following constraints expressing the volume balance and mole balance

$$\sum_{\alpha=1}^N V_\alpha = V, \quad (4)$$

$$\sum_{\alpha=1}^N N_{\alpha,i} = N_i, \quad i = w, c. \quad (5)$$

Using the Lagrange multiplier method, we derive the system of necessary conditions of the phase equilibrium

$$P(\mathbf{x}_1, T) = \dots = P(\mathbf{x}_N, T), \quad (6)$$

$$\mu_i(\mathbf{x}_1, T) = \dots = \mu_i(\mathbf{x}_N, T), \quad i = w, c. \quad (7)$$

Let us denote by  $P^{eq}$  the equilibrium pressure, which is the common value of pressures in each phase, and by  $\mu_i^{eq}$  the chemical potential of the  $i$ -th component in the equilibrium, which is the common value of chemical potentials of the  $i$ -th component in each phase.

III. NUMERICAL ALGORITHM FOR COMPUTATION OF THREE-PHASE EQUILIBRIUM FOR CO<sub>2</sub> – H<sub>2</sub>O SYSTEM

We derive a numerical algorithm for testing three-phase equilibrium of CO<sub>2</sub> – H<sub>2</sub>O system at constant volume, temperature and moles based on minimization of the total Helmholtz free energy of the three-phase system (3) which is subject to the volume and mole balance constraints (4) and (5). In all these equations, we set  $N = 3$  and we still denote by  $\mathbf{x}_\alpha$  a vector with components  $N_{\alpha,w}, N_{\alpha,c}, V_\alpha$ , where  $\alpha = 1, \dots, N$ . In general, the numerical procedure is based on transferring an  $n$ -dimensional problem of minimization of a twice-continuously differentiable objective function subject to a set of  $t$  linear equality constraints into an unconstrained minimization problem with the same objective function, but a lower dimension  $n - t$ .

The constraint equations (4) and (5) for  $N = 3$  can be written in the matrix form as  $\mathbb{A}\mathbf{x} = \mathbf{b}$ , or

$$\underbrace{\begin{pmatrix} 1 & 0 & 0 & 1 & 0 & 0 & 1 & 0 & 0 \\ 0 & 1 & 0 & 0 & 1 & 0 & 0 & 1 & 0 \\ 0 & 0 & 1 & 0 & 0 & 1 & 0 & 0 & 1 \end{pmatrix}}_{\mathbb{A}} \underbrace{\begin{pmatrix} \mathbf{x}_1 \\ \mathbf{x}_2 \\ \mathbf{x}_3 \end{pmatrix}}_{\mathbf{x}} = \underbrace{\begin{pmatrix} N_1 \\ N_2 \\ V \end{pmatrix}}_{\mathbf{b}}, \quad (8)$$

where  $\mathbb{A} \in \mathbb{R}^{3 \times 9}$  is the matrix formed by 3 blocks of the identity matrices in  $\mathbb{R}^3$ ,  $\mathbf{x} \in \mathbb{R}^9$  is the vector of unknowns, which is given as

$$\mathbf{x} = (N_{1,w}, N_{1,c}, V_1, N_{2,w}, N_{2,c}, V_2, N_{3,w}, N_{3,c}, V_3)^\top$$

and  $\mathbf{b} \in \mathbb{R}^3$  is the vector of right hand side. As the matrix  $\mathbb{A}$  has the full rank, the optimization problem with 9 unknowns and 3 linearly independent linear constraints can be transformed into an unconstrained problem with 6 variables. The reduction in dimensionality can be described in terms of two subspaces  $\mathcal{Y}$  and  $\mathcal{Z}$ , where  $\mathcal{Y}$  is the 3-dimensional subspace of  $\mathbb{R}^9$  spanned by the rows of matrix  $\mathbb{A}$  and  $\mathcal{Z}$  is the 6-dimensional subspace of  $\mathbb{R}^9$  of vectors orthogonal to the rows of matrix  $\mathbb{A}$ . The representation of  $\mathcal{Y}$  is not unique and it can be chosen for example as  $Y = A^T$ . As  $\mathcal{Y}$  and  $\mathcal{Z}$  define complementary subspaces

$$\mathbb{R}^9 = \mathcal{Y} \oplus \mathcal{Z}, \quad (9)$$

every 9-dimensional vector  $\mathbf{x}$  can be uniquely written as a combination of vectors from  $\mathcal{Y}$  and  $\mathcal{Z}$  as

$$\mathbf{x} = \mathbb{Y}\mathbf{x}_Y + \mathbb{Z}\mathbf{x}_Z, \quad (10)$$

where  $\mathbb{Y}$  and  $\mathbb{Z}$  denote matrices from  $\mathbb{R}^{9 \times 3}$  and  $\mathbb{R}^{9 \times 6}$ , respectively, whose columns represent bases of subspaces  $\mathcal{Y}$  and  $\mathcal{Z}$ , and the 3-dimensional vector  $\mathbf{x}_Y$  is called the range-space part of  $\mathbf{x}$ , and the 6-dimensional vector  $\mathbf{x}_Z$  is called the null-space part of  $\mathbf{x}$ .

The solution  $\mathbf{x}^*$  of the constrained optimization problem, given by

$$\mathbf{x}^* = \mathbb{Y}\mathbf{x}_Y^* + \mathbb{Z}\mathbf{x}_Z^*,$$

is feasible, whence

$$\mathbb{A}\mathbf{x}^* = \mathbb{A}(\mathbb{Y}\mathbf{x}_Y^* + \mathbb{Z}\mathbf{x}_Z^*) = \mathbf{b}.$$

From the definition of subspace  $\mathcal{Z}$  it follows that  $\mathbb{A}\mathbb{Z} = 0$ , therefore

$$\mathbb{A}\mathbb{Y}\mathbf{x}_Y^* = \mathbf{b}.$$

From the definition of subspace  $\mathcal{Y}$  it can be seen that the matrix  $\mathbb{A}\mathbb{Y}$  is non-singular, and thus the vector  $\mathbf{x}_Y^*$  is uniquely determined by the previous equation. Similarly, any feasible vector  $\mathbf{x}$  must have the same range-space part, which means  $\mathbf{x}_Y = \mathbf{x}_Y^*$ , and on the contrary, any vector with range-space component  $\mathbf{x}_Y^*$  satisfies the constraints of the optimization problem. Hence, the constraints uniquely determine the range-space part  $\mathbf{x}_Y^*$  of the solution, and only the 6-dimensional part  $\mathbf{x}_Z^*$  remains unknown. This way the expected reduction in dimensionality to 6 is performed.

To represent the null-space  $\mathcal{Z}$ , the LQ-factorization of matrix  $\mathbb{A}$  is used [10]. Let  $\mathbb{Q} \in \mathbb{R}^{9 \times 9}$  be an orthonormal matrix such that

$$\mathbb{A}\mathbb{Q} = (\mathbb{L} \ 0), \quad (11)$$

where  $\mathbb{L} \in \mathbb{R}^{3 \times 3}$  is a non-singular lower triangular matrix. From (11) one can see that the matrix  $\mathbb{Y}$  can be chosen as the first 3 columns of matrix  $\mathbb{Q}$  and the matrix  $\mathbb{Z}$  can be chosen as the remaining 6 columns of  $\mathbb{Q}$ , i.e.

$$\mathbb{Q} = (\mathbb{Y} \ \mathbb{Z}). \quad (12)$$

As the matrix of constraints  $\mathbb{A} \in \mathbb{R}^{3 \times 9}$  can be written as

$$\mathbb{A} = (\mathbb{I}_3 \ \mathbb{I}_3 \ \mathbb{I}_3),$$

then the matrices  $\mathbb{Y}$  and  $\mathbb{Z}$  may be chosen as

$$\mathbb{Y} = \frac{1}{\sqrt{3}}\mathbb{A}^T = \frac{1}{\sqrt{3}} \begin{pmatrix} \mathbb{I}_3 \\ \mathbb{I}_3 \\ \mathbb{I}_3 \end{pmatrix}, \quad \mathbb{Z} = \frac{1}{\sqrt{3}} \begin{pmatrix} \mathbb{I}_3 & \mathbb{I}_3 \\ -\mathbb{I}_3 & 0 \\ 0 & -\mathbb{I}_3 \end{pmatrix} \quad (13)$$

For solving the constrained optimization problem we use an iterative algorithm in which a feasible initial guess  $\mathbf{x}^{(0)}$  is given and the algorithm generates a sequence of feasible iterates  $\mathbf{x}^{(k)}$ . In every iteration, the solution  $\mathbf{x}^{(k)}$  is approximated as

$$\mathbf{x}^{(k+1)} = \mathbf{x}^{(k)} + \lambda^k \mathbf{d}^{(k)}, \quad (14)$$

where  $\lambda^k \in (0; 1)$  is the step size in the  $k$ -th iteration and  $\mathbf{d}^{(k)}$  is the direction vector in the  $k$ -th iteration. We assume that  $\mathbf{x}^{(k)}$  is feasible and the feasibility of  $\mathbf{x}^{(k+1)}$  is required, so the direction vector  $\mathbf{d}^{(k)}$  must be necessarily orthogonal to the rows of  $\mathbb{A}$ , i.e.

$$\mathbb{A}\mathbf{d}^{(k)} = 0, \quad (15)$$

which can be equivalently written as

$$\mathbf{d}^{(k)} = \mathbb{Z}\mathbf{d}_Z^{(k)}, \quad (16)$$

for some 6-dimensional vector  $\mathbf{d}_Z^{(k)}$ . It can be seen that the search direction  $\mathbf{d}^{(k)}$  is a 9-dimensional vector constructed to lie in the 6-dimensional subspace  $\mathcal{Z}$ . The columns of matrix  $\mathbb{Z}$ , which form an orthogonal basis of  $\mathcal{Z}$ , are given by (13), so it remains to determine the vector  $\mathbf{d}_Z^{(k)} \in \mathbb{R}^6$ . This way the constrained minimization problem is transferred to an unconstrained problem in a lower dimension.

To find the vector  $\mathbf{d}_Z^{(k)}$ , we use the modified Newton-Raphson method which is based on the quadratic approximation of function  $\Delta A$  around the point  $\mathbf{x}^{(k)}$ . Let us denote by  $\mathbf{g}(\mathbf{x}) \in \mathbb{R}^9$  the gradient of the function  $\Delta A$  which is obtained

by differentiating the  $\Delta A$  with respect to its variables, i.e.

$$\mathbf{g}(\mathbf{x}) = \nabla(\Delta A)^\top = \begin{pmatrix} \mu_w(\mathbf{x}_1, T) \\ \mu_c(\mathbf{x}_1, T) \\ -P(\mathbf{x}_1, T) \\ \mu_w(\mathbf{x}_2, T) \\ \mu_c(\mathbf{x}_2, T) \\ -P(\mathbf{x}_2, T) \\ \mu_w(\mathbf{x}_3, T) \\ \mu_c(\mathbf{x}_3, T) \\ -P(\mathbf{x}_3, T) \end{pmatrix}. \quad (17)$$

Further, let us denote by  $\mathbb{H}(\mathbf{x}) \in \mathbb{R}^{9 \times 9}$  the Hessian of the function  $\Delta A$  which is obtained by differentiating the  $\Delta A$  twice with respect to its variables in a block-diagonal form with 3 diagonal blocks given in the following form

$$\mathbb{H}(\mathbf{x}) = \nabla^2 \Delta A = \begin{pmatrix} \mathbb{H}_1 & & \\ & \mathbb{H}_2 & \\ & & \mathbb{H}_3 \end{pmatrix}, \quad (18)$$

$$\mathbb{H}_\alpha(\mathbf{x}) = \begin{pmatrix} \mathbb{B}^\alpha & \mathbb{C}^\alpha \\ \mathbb{C}^{\alpha \top} & \mathbb{D}^\alpha \end{pmatrix},$$

where  $\alpha \in \{1, 2, 3\}$  and

$$\begin{aligned} \mathbb{B}^\alpha &\in \mathbb{R}^{2 \times 2}, & \mathbb{B}_{ij}^\alpha &= \frac{\partial \mu_i}{\partial N_{\alpha,j}}(\mathbf{x}_\alpha, T) \\ \mathbb{C}^\alpha &\in \mathbb{R}^2, & \mathbb{C}_j^\alpha &= -\frac{\partial P}{\partial N_{\alpha,j}}(\mathbf{x}_\alpha, T), \\ \mathbb{D}^\alpha &\in \mathbb{R}^1, & \mathbb{D}^\alpha &= -\frac{\partial P}{\partial V_\alpha}(\mathbf{x}_\alpha, T), \end{aligned}$$

where  $i, j \in \{w, c\}$

Approximating the function  $\Delta A$  using the Taylor expansion around the point  $\mathbf{x}^{(k)}$  up to the quadratic terms, the search direction  $\mathbf{d}^{(k)} = \mathbb{Z} \mathbf{d}_Z^{(k)}$  can be found as a solution of the following minimization problem

$$\begin{aligned} \min_{\substack{\mathbf{d}^{(k)} \in \mathbb{R}^9 \\ \mathbb{A} \mathbf{d}^{(k)} = 0}} \Delta A(\mathbf{x}^{(k)} + \mathbf{d}^{(k)}) &= \min_{\mathbf{d}_Z^{(k)} \in \mathbb{R}^6} \Delta A(\mathbf{x}^{(k)} + \mathbb{Z} \mathbf{d}_Z^{(k)}) \approx \\ &\approx \min_{\mathbf{d}_Z^{(k)} \in \mathbb{R}^6} \Delta A(\mathbf{x}^{(k)}) + \mathbf{g}(\mathbf{x}^{(k)})^\top \mathbb{Z} \mathbf{d}_Z^{(k)} + \\ &+ \frac{1}{2} (\mathbb{Z} \mathbf{d}_Z^{(k)})^\top \mathbb{H}(\mathbf{x}^{(k)}) \mathbb{Z} \mathbf{d}_Z^{(k)}. \end{aligned} \quad (19)$$

Define a quadratic function  $\Phi$  as

$$\Phi(\mathbf{d}_Z) = \mathbf{g}(\mathbf{x}^{(k)})^\top \mathbb{Z} \mathbf{d}_Z + \frac{1}{2} \mathbf{d}_Z^\top \mathbb{Z}^\top \mathbb{H}(\mathbf{x}^{(k)}) \mathbb{Z} \mathbf{d}_Z,$$

then the vector  $\mathbf{d}_Z^{(k)}$  is the argument of its minimum. The function  $\Phi$  has a stationary point if and only if there is a  $\mathbf{d}_Z^{(k)}$  for which the gradient of  $\Phi$  vanishes, i.e.

$$\nabla \Phi(\mathbf{d}_Z^{(k)}) = 0. \quad (20)$$

The stationary point  $\mathbf{d}_Z^{(k)}$  is a solution of the following system of equations

$$\mathbb{H}_Z(\mathbf{x}^{(k)}) \mathbf{d}_Z^{(k)} = -\mathbf{g}_Z(\mathbf{x}^{(k)}), \quad (21)$$

where  $\mathbb{H}_Z(\mathbf{x}^{(k)}) \in \mathbb{R}^{6 \times 6}$  and  $\mathbf{g}_Z(\mathbf{x}^{(k)}) \in \mathbb{R}^6$  are the restrictions of the Hessian matrix and of the gradient vector to the subspace  $Z$  defined as

$$\mathbb{H}_Z(\mathbf{x}^{(k)}) = \mathbb{Z}^\top \mathbb{H}(\mathbf{x}^{(k)}) \mathbb{Z} \quad (22)$$

and

$$\mathbf{g}_Z(\mathbf{x}^{(k)}) = \mathbb{Z}^\top \mathbf{g}(\mathbf{x}^{(k)}). \quad (23)$$

Combining (13), (17), and (18), it follows from (23) that

$$\mathbf{g}_Z(\mathbf{x}^{(k)}) = \frac{1}{\sqrt{2}} \begin{pmatrix} \mu_w(\mathbf{x}_1, T) - \mu_w(\mathbf{x}_2, T) \\ \mu_c(\mathbf{x}_1, T) - \mu_c(\mathbf{x}_2, T) \\ -P(\mathbf{x}_1, T) + P(\mathbf{x}_2, T) \\ \mu_w(\mathbf{x}_1, T) - \mu_w(\mathbf{x}_3, T) \\ \mu_c(\mathbf{x}_1, T) - \mu_c(\mathbf{x}_3, T) \\ -P(\mathbf{x}_1, T) + P(\mathbf{x}_3, T) \end{pmatrix}, \quad (24)$$

and from (22) that the restricted Hessian matrix can be found in the following form

$$\mathbb{H}_Z(\mathbf{x}^{(k)}) = \frac{1}{2} \begin{pmatrix} \mathbb{H}_Z^2 & \mathbb{H}_1 \\ \mathbb{H}_1 & \mathbb{H}_Z^3 \end{pmatrix},$$

$$\mathbb{H}_Z^\alpha(\mathbf{x}^{(k)}) = \begin{pmatrix} \tilde{\mathbb{B}}^\alpha & \tilde{\mathbb{C}}^\alpha \\ \tilde{\mathbb{C}}^{\alpha \top} & \tilde{\mathbb{D}}^\alpha \end{pmatrix}, \quad (25)$$

where  $\alpha \in \{2, 3\}$ ,  $\mathbb{H}_1 \in \mathbb{R}^{3 \times 3}$  is given by (18) and

$$\begin{aligned} \tilde{\mathbb{B}}^\alpha &\in \mathbb{R}^{2 \times 2}, \quad \tilde{\mathbb{C}}^\alpha \in \mathbb{R}^2, \quad \tilde{\mathbb{D}}^\alpha \in \mathbb{R}^1, \\ \tilde{\mathbb{B}}_{ij}^\alpha &= \frac{\partial \mu_i}{\partial N_{1,j}}(\mathbf{x}_1, T) + \frac{\partial \mu_i}{\partial N_{\alpha,j}}(\mathbf{x}_\alpha, T), \\ \tilde{\mathbb{C}}_j^\alpha &= -\frac{\partial P}{\partial N_{1,j}}(\mathbf{x}_1, T) - \frac{\partial P}{\partial N_{\alpha,j}}(\mathbf{x}_\alpha, T) \\ \tilde{\mathbb{D}}^\alpha &= -\frac{\partial P}{\partial V_1}(\mathbf{x}_1, T) - \frac{\partial P}{\partial V_\alpha}(\mathbf{x}_\alpha, T), \end{aligned}$$

where  $i, j \in \{w, c\}$  The gradient vector in (17) depends on the values of chemical potentials which can be determined up to an arbitrary constant. Unlike in (17), the restricted gradient given by (24) is a function of differences of the chemical potentials between two states whose values can be evaluated uniquely using the equation of state.

If  $\mathbf{d}_Z^{(k)}$  solves the system of the equations (21) and the matrix  $\mathbb{H}_Z$  is positive definite, then the search direction  $\mathbf{d}_Z^{(k)}$  is a descent direction. If the matrix of the projected Hessian is not positive definite, then either the quadratic approximation of the function is not bounded from below, or a single minimum does not exist. In this case, it is necessary to modify the direction  $\mathbf{d}_Z^{(k)}$ . If the matrix  $\mathbb{H}_Z$  is indefinite,

then the vector  $\mathbf{d}_{\mathcal{Z}}^{(k)}$  is found as a solution of a modified system of equations

$$\widehat{\mathbb{H}}_{\mathcal{Z}}(\mathbf{x}^{(k)})\mathbf{d}_{\mathcal{Z}}^{(k)} = -\mathbf{g}_{\mathcal{Z}}(\mathbf{x}^{(k)}), \quad (26)$$

where  $\widehat{\mathbb{H}}_{\mathcal{Z}}(\mathbf{x}^{(k)})$  is a positive definite matrix obtained by the modified Cholesky decomposition of the matrix  $\mathbb{H}_{\mathcal{Z}}(\mathbf{x}^{(k)})$ . In this algorithm the usual Cholesky factorization is performed to decompose matrix  $\mathbb{H}_{\mathcal{Z}}(\mathbf{x}^{(k)})$  as

$$\mathbb{H}_{\mathcal{Z}}(\mathbf{x}^{(k)}) = \mathbb{L}\mathbb{L}^{\top},$$

where  $\mathbb{L}$  is a lower triangular matrix. If a negative element appears on the diagonal of  $\mathbb{L}$  during the Cholesky factorization, a suitable value is added to this element to ensure its positivity in the final decomposition. This way we obtain the Cholesky factorization of a positive definite matrix  $\widehat{\mathbb{H}}_{\mathcal{Z}}(\mathbf{x}^{(k)})$ , which is used instead of matrix  $\mathbb{H}_{\mathcal{Z}}(\mathbf{x}^{(k)})$  in (26) to determine the direction  $\mathbf{d}_{\mathcal{Z}}^{(k)}$  in the Newton-Raphson method. Due to this modification of the Newton-Raphson method, the obtained direction is a descent direction. Therefore, for a sufficiently small step size  $\lambda^k > 0$ , the decrease of  $\Delta A$  can be guaranteed. In this work, the line-search technique is used to find the step size  $\lambda^k$ . First, we set  $\lambda^k = 1$  and test if  $\Delta A(\mathbf{x}^{(k)} + \mathbf{d}^{(k)}) < \Delta A(\mathbf{x}^{(k)})$ . If this condition is satisfied, we set  $\mathbf{x}^{(k+1)} = \mathbf{x}^{(k)} + \mathbf{d}^{(k)}$ . If not, we halve the value of  $\lambda^k$  unless the condition  $\Delta A(\mathbf{x}^{(k)} + \lambda^k \mathbf{d}^{(k)}) < \Delta A(\mathbf{x}^{(k)})$  is satisfied and then set  $\mathbf{x}^{(k+1)} = \mathbf{x}^{(k)} + \lambda^k \mathbf{d}^{(k)}$ . Now, a single iteration of the Newton-Raphson method is completed.

The iterations are stopped when either the maximal number of iterations is achieved (500), or when a stopping criterion is satisfied and the required accuracy is achieved. In this work the stopping criterion is given by

$$\|\mathbf{d}^{(k)}\|_2 := \left( \sum_{j=1}^9 \mathbf{d}_j^{(k)2} \right)^{\frac{1}{2}} \leq 10^{-7}. \quad (27)$$

#### IV. ALGORITHM OF THE MODIFIED NEWTON METHOD FOR CONSTANT-VOLUME THREE-PHASE FLASH OF CO<sub>2</sub> – H<sub>2</sub>O SYSTEM

Now, we summarize the key steps of the algorithm.

**Step 1** Let  $N_w, N_c, V$  and  $T > 0$  be given. Set the number of iterations  $k = 0$ . Get an initial feasible solution  $\mathbf{x}^{(0)} \in \mathbb{R}^9$  from the  $VT$ -stability algorithm [7]

$$\mathbf{x}^{(0)} = \begin{pmatrix} N_{1,w} \\ N_{1,c} \\ V_1 \\ N_{2,w} \\ N_{2,c} \\ V_2 \\ N_{3,w} \\ N_{3,c} \\ V_3 \end{pmatrix}. \quad (28)$$

**Step 2** Assemble the Hessian matrix  $\mathbb{H}_{\mathcal{Z}}(\mathbf{x}^{(k)})$  and the gradient vector  $\mathbf{g}_{\mathcal{Z}}(\mathbf{x}^{(k)})$  of  $\Delta A$  in the  $k$ -th iteration projected to the subspace  $\mathcal{Z}$  using (25) and (24).

**Step 3** Compute the projected step direction  $\mathbf{d}_{\mathcal{Z}}^{(k)} \in \mathbb{R}^6$  and the feasible direction  $\mathbf{d}^{(k)} \in \mathbb{R}^9$  by

$$\mathbb{H}_{\mathcal{Z}}(\mathbf{x}^{(k)})\mathbf{d}_{\mathcal{Z}}^{(k)} = -\mathbf{g}_{\mathcal{Z}}(\mathbf{x}^{(k)}), \quad (29)$$

$$\mathbf{d}^{(k)} = \mathbb{Z}\mathbf{d}_{\mathcal{Z}}^{(k)}. \quad (30)$$

If the matrix  $\mathbb{H}_{\mathcal{Z}}(\mathbf{x}^{(k)})$  is not positive definite, find the vector  $\mathbf{d}_{\mathcal{Z}}^{(k)}$  by solving a modified system of equations

$$\widehat{\mathbb{H}}_{\mathcal{Z}}(\mathbf{x}^{(k)})\mathbf{d}_{\mathcal{Z}}^{(k)} = -\mathbf{g}_{\mathcal{Z}}(\mathbf{x}^{(k)}), \quad (31)$$

where  $\widehat{\mathbb{H}}_{\mathcal{Z}}(\mathbf{x}^{(k)})$  is a positive definite matrix obtained from the modified Cholesky decomposition of matrix  $\mathbb{H}_{\mathcal{Z}}(\mathbf{x}^{(k)})$ .

**Step 4** Determine the step length  $\lambda^k > 0$  for the  $k$ -th iteration satisfying

$$\Delta A(\mathbf{x}^{(k)} + \lambda^k \mathbf{d}^{(k)}) < \Delta A(\mathbf{x}^{(k)}). \quad (32)$$

First, set the step length to  $\lambda^k = 1$  and test if the condition (32) holds. If not, use the bisection method to find a value of  $\lambda^k$  satisfying (32).

**Step 5** Update the approximation as

$$\mathbf{x}^{(k+1)} = \mathbf{x}^{(k)} + \lambda^k \mathbf{d}^{(k)}. \quad (33)$$

**Step 6** Test the convergence using (27). If needed, increase  $k$  by 1 and go to Step 2. If not needed, the algorithm ends up with the solution  $\mathbf{x}^{(k+1)}$ .

Note that the constant-volume stability algorithm from [7] is used to test whether a single phase is stable or not at given conditions. If the mixture is unstable, the  $VT$ -stability provides an initial guess - the concentrations of a trial phase, which, if taken in a sufficiently small amount from the initial phase, lead to a two-phase system with lower value of the Helmholtz free energy  $A$  than the hypothetical single-phase state. From this, a criterion of stability at constant volume, temperature, and moles can be derived (see [7] for details).

#### General Strategy for Phase Equilibrium Computation of CO<sub>2</sub> – H<sub>2</sub>O System

Using the Gibbs phase rule [8], the maximal number of phases for the binary system of CO<sub>2</sub> – H<sub>2</sub>O is  $N = 3$  and the system can exist in single-, two- and three-phase states. The proposed general strategy for phase-equilibrium testing is based on repeated constant-volume stability testing and constant-volume phase-split calculation and can be summarized in the following steps:

**Step 1** Set the number of phases  $N = 1$  and perform the constant-volume single-phase stability using the algorithm, which is provided in [7]. If the single-phase state is stable, calculate the equilibrium pressure from the equation of state and the procedure ends.

**Step 2** If the single phase is unstable, an initial two-phase split is provided from the phase-stability algorithm and the constant-volume two-phase flash algorithm is performed using the method described in [5].

**Step 3** Perform the phase-stability algorithm on one of the two equilibrium phases. If it is unstable, an initial guess for the three-phase split calculation is provided.

**Step 4** Perform the constant-volume three-phase flash calculation to establish composition, densities and amounts of the phases using the algorithm described above.

TABLE II  
PARAMETERS OF THE PHYSICAL PART OF THE  
CUBIC-PLUS-ASSOCIATION EQUATION OF STATE FOR THE H<sub>2</sub>O AND  
CO<sub>2</sub> MIXTURE (THE NOTATION IS EXPLAINED IN THE APPENDIX).

Component	$T_{i,crit}$ [K]	$P_{i,crit}$ [MPa]	$\omega_i$ [-]	$M_{w,i}$ [g.mol <sup>-1</sup> ]
H <sub>2</sub> O	647.29	22.09	0.3440	18.02
CO <sub>2</sub>	304.14	7.375	0.2390	44.0

## V. RESULTS

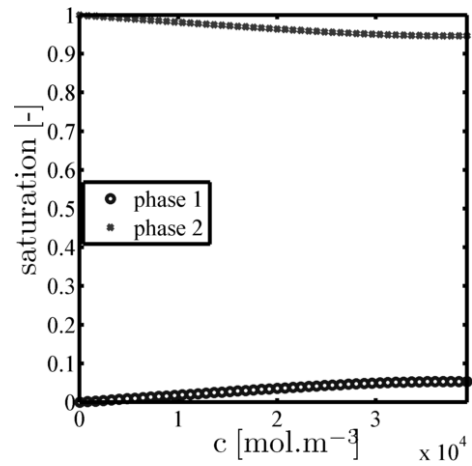
Studying a binary mixture of CO<sub>2</sub> – H<sub>2</sub>O under different conditions, we have tested the proposed algorithm in several examples of general phase-stability testing and phase-split calculation both at constant volume, temperature and moles of CO<sub>2</sub> – H<sub>2</sub>O system. In all simulations we perform isothermal compression of a CO<sub>2</sub> – H<sub>2</sub>O mixture of a given chemical composition  $z_w, z_c$  in a closed cell, where  $z_w = N_w/N$ ,  $z_c = N_c/N$  and  $N = N_w + N_c$ . Changing the overall concentration  $c$  at a given temperature  $T$ , we provide the results of the constant-volume two- and three-phase flash calculations for the CO<sub>2</sub> – H<sub>2</sub>O mixture at temperature  $T$  and molar concentrations  $c_i = cz_i$ . For the CO<sub>2</sub> – H<sub>2</sub>O system, we use the Cubic-Plus-Association (CPA) equation of state [12], [13]. Parameters for the physical part used are presented in Table II. Details for the equation of state can be found in the Appendix.

### Two-Phase Equilibrium of the CO<sub>2</sub> – H<sub>2</sub>O System

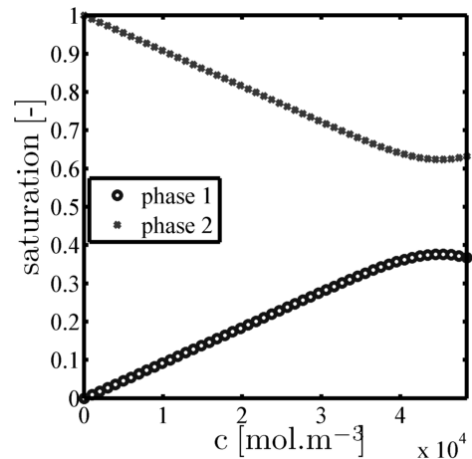
First, we investigate phase equilibrium for a binary mixture of water (H<sub>2</sub>O) and carbon dioxide (CO<sub>2</sub>) with mole fractions  $z_{H_2O}$  ranging from 0.1 to 1.0 and  $z_{CO_2} = 1 - z_{H_2O}$  at temperature  $T = 308.15$  K. For this temperature, the binary interaction coefficient is  $\delta_{H_2O-CO_2} = 0.09850$  and the cross association factor used in the CPA equation of state is  $s_{CO_2} = 0.025936802$ . Note that  $\delta_{H_2O-CO_2}$  and  $s_{CO_2}$  are strongly dependent on temperature. For  $T = 308.15$  K and mole fractions of water  $z_{H_2O}$  ranging from 0.1 to 1.0, the mixture splits in all cases into two phases except from very low overall molar concentrations  $c$ .

Changing the mole fraction of water  $z_{H_2O}$  from 0.1 to 0.9, the mixture behaviour does not change very much. In all cases it can be seen that the mutual solubility of CO<sub>2</sub> and water is limited. Saturations (volume fractions) of both phases as functions of the overall molar concentration  $c$  are presented for three different mole fractions  $z_{H_2O}$  (0.1, 0.5 and 0.9) in Figure 1. Mole fractions of both water and carbon dioxide components in both phases as functions of the overall molar concentration  $c$  are presented for the same three values of mole fractions  $z_{H_2O}$  in Figure 2. In Figure 3, mass densities of both phases as functions of the overall molar concentration  $c$  are presented for  $z_{H_2O} = 0.9$ . Note that while compressing the mixture, its composition in both phases and mass densities of the phases almost do not vary, only slight variations of volume fractions in both phases can be seen. The equilibrium pressure as a function of the overall molar concentration  $c$  is presented for mole fraction  $z_{H_2O} = 0.9$  in Figure 4 illustrating a steady increase of the equilibrium pressure during compression.

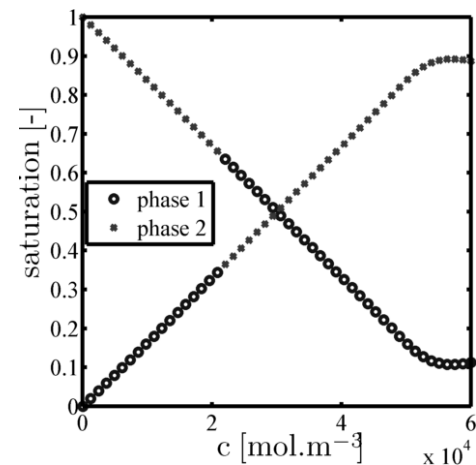
In all cases, quadratic convergence of the Newton-Raphson method has been observed. Thus, numerical errors can be estimated from the size of increment in the last few iterations.



(a)  $z_{H_2O} = 0.1$



(b)  $z_{H_2O} = 0.5$



(c)  $z_{H_2O} = 0.9$

Fig. 1. Saturation of both phases as a function of the overall molar concentration  $c$  for the binary mixture of CO<sub>2</sub> – H<sub>2</sub>O with three different values of  $z_{H_2O}$  at  $T = 308.15$  K.

Using the Euclidean norm, the estimated error is approximately  $10^{-14}$ .

### Three-Phase Equilibrium of the CO<sub>2</sub> – H<sub>2</sub>O System

Now, we investigate phase equilibrium for a binary mixture of water (H<sub>2</sub>O) and carbon dioxide (CO<sub>2</sub>) with low mole fractions  $z_{H_2O}$  ranging from 0.003 to 0.008

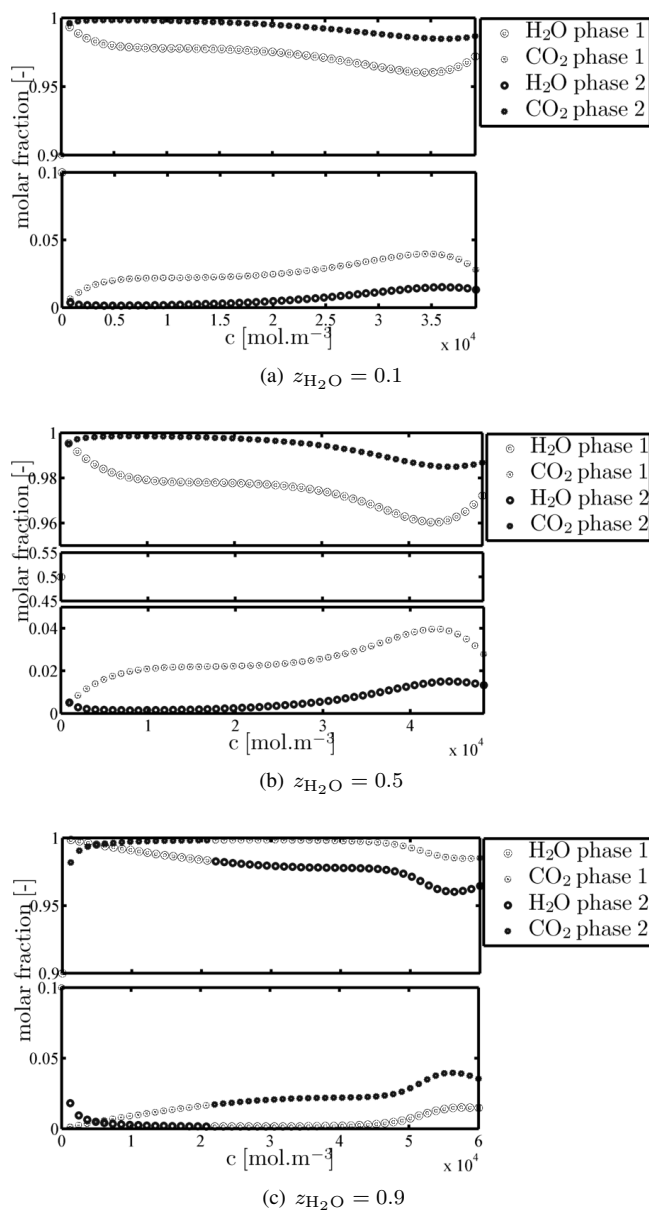


Fig. 2. Mole fractions of both components in each phase as functions of the overall molar concentration  $c$  for the binary mixture of  $\text{CO}_2 - \text{H}_2\text{O}$  with three different values of  $z_{\text{H}_2\text{O}}$  at  $T = 308.15$  K.

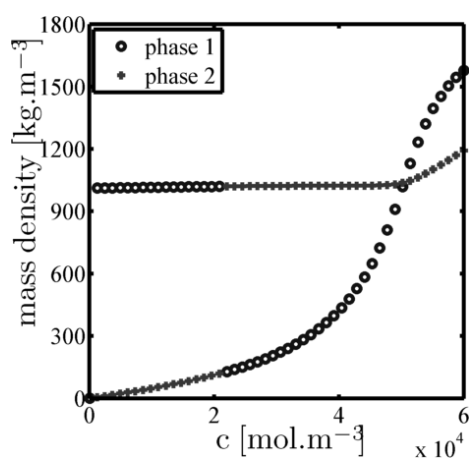


Fig. 3. Mass densities of both phases as a function of the overall molar concentration  $c$  for the binary mixture of  $\text{CO}_2 - \text{H}_2\text{O}$  with  $z_{\text{H}_2\text{O}} = 0.9$  at  $T = 308.15$  K.

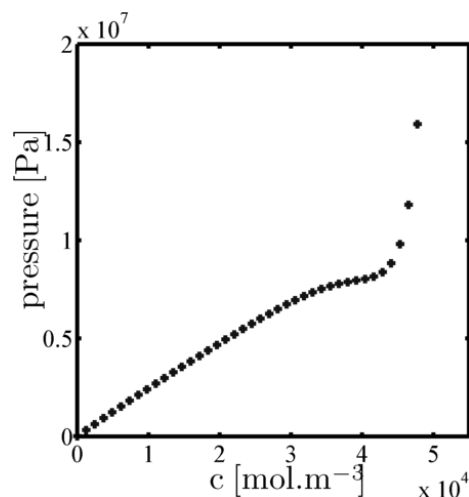


Fig. 4. Equilibrium pressure as a function of the overall molar concentration  $c$  for the binary mixture of  $\text{CO}_2 - \text{H}_2\text{O}$  with  $z_{\text{H}_2\text{O}} = 0.9$  at  $T = 308.15$  K.

and  $z_{\text{CO}_2} = 1 - z_{\text{H}_2\text{O}}$  at temperature  $T = 298.15$  K. For this temperature, the binary interaction coefficient is  $\delta_{\text{H}_2\text{O}-\text{CO}_2} = 0.078795$  and the cross association factor used in the CPA equation of state is  $s_{\text{CO}_2} = 0.021141$ . For  $T = 298.15$  K and very low mole fractions of water  $z_{\text{H}_2\text{O}}$  ranging from 0.003 to 0.008, the mixture splits in all cases into two or three phases except from very low overall molar concentrations  $c$ .

Changing the mole fraction of water  $z_{\text{H}_2\text{O}}$  from 0.003 to 0.008 and compressing the mixture at temperature  $T = 298.15$  K, the mixture occurs in two-phase from the lowest molar concentrations up to approximately  $9000 \text{ mol.m}^{-3}$ , then becomes three-phase, while at molar concentrations higher than  $14000 \text{ mol.m}^{-3}$  the mixture becomes two-phase again. Finally, from the molar concentrations approximately  $18500 \text{ mol.m}^{-3}$ ,  $23500 \text{ mol.m}^{-3}$  and  $29000 \text{ mol.m}^{-3}$ , the mixture with  $z_{\text{H}_2\text{O}} = 0.003$ ,  $z_{\text{H}_2\text{O}} = 0.005$  and  $z_{\text{H}_2\text{O}} = 0.008$ , respectively, becomes single-phase (see Figure 5, 6 or 7).

In Figure 5, mass densities of each phase as functions of the overall molar concentration  $c$  are presented for three values of  $z_{\text{H}_2\text{O}}$ , i.e. 0.003; 0.005 and 0.008. Note that in case of  $z_{\text{H}_2\text{O}} = 0.008$  while at lower molar concentrations  $c$  the two-phase region corresponds to a gas-liquid two-phase region, at high molar concentrations  $c$  we can observe a second two-phase area corresponding to a liquid-liquid two-phase region as can be seen from the values of mass densities of the phases (see Figure 5(c)).

Mole fractions of water and carbon dioxide components in each phase as functions of the overall molar concentration  $c$  are presented for the same three values of  $z_{\text{H}_2\text{O}}$  in Figure 6 in which the limited mutual solubility of  $\text{CO}_2$  and water can be seen. Saturations (volume fractions) of each phase and also equilibrium pressures as functions of the overall molar concentration  $c$  look similar for different values of  $z_{\text{H}_2\text{O}}$ , so we present them for  $z_{\text{H}_2\text{O}} = 0.003$  in Figure 7 and 8. In Figure 8, the equilibrium pressure as a function of the overall molar concentration  $c$  is presented illustrating a steady rise of the equilibrium pressure during the compression in two-phase area, followed by the constant value of pressure within the

three-phase area (for molar concentrations between approximately  $9000 \text{ mol.m}^{-3}$  and  $14000 \text{ mol.m}^{-3}$ ), demonstrating the similar behaviour as pure components, and the substantial increase at molar concentrations higher than  $14000 \text{ mol.m}^{-3}$  when the gas phase is depleted. Notice again that as the pressure is constant during the compression in the three-phase region, the mass densities of each phase and the composition of each phase remain constant as well.

Numerical errors are comparable to those from the two-phase examples.

## VI. DISCUSSION AND CONCLUSION

To draw some conclusion from the results, it can be seen from Figure 3 that the mass densities of both phases intersect at molar density approximately  $50000 \text{ mol.m}^{-3}$  and switch, i.e. the heavier phase, which is rich in water, becomes the lighter one and the lighter phase, which is rich in  $\text{CO}_2$ , becomes the heavier one. The pressure corresponding to this molar concentration is approximately 40.86 MPa. Similarly, when consider the  $\text{CO}_2 - \text{H}_2\text{O}$  system with  $z_{\text{H}_2\text{O}} = 0.008$ , the mass densities of both phases intersect in the two-phase region at molar density approximately  $24000 \text{ mol.m}^{-3}$  and switch (see Figure 5(c)). The pressure corresponding to this molar concentration is approximately 37.83 MPa. The switching of phases is an important evidence for  $\text{CO}_2$  sequestration because if the  $\text{CO}_2 - \text{H}_2\text{O}$  mixture is compressed at the level for which the mass densities of both phases intersect and switch (i.e. for molar concentrations higher than  $50000 \text{ mol.m}^{-3}$  in case of the  $\text{CO}_2 - \text{H}_2\text{O}$  mixture from Figure 3 and for molar concentrations higher than  $24000 \text{ mol.m}^{-3}$  in case of the  $\text{CO}_2 - \text{H}_2\text{O}$  mixture from Figure 5(c)), then the phase rich in  $\text{CO}_2$  becomes heavier and goes down in the reservoir. Consequently, the phase rich in water becomes lighter and goes up, so that another amount of  $\text{CO}_2$  can be dissolved into it.

As explained in the Introduction, specification of pressure, temperature and moles may not determine uniquely the equilibrium state of the system. In our previous work [5], we have observed this issue in pure substances at saturation pressure in two phases. In this work, the behaviour similar to that of pure components has been observed in case of  $\text{CO}_2 - \text{H}_2\text{O}$  system in three phases, proving that there exist mixtures more complex than the trivial ones which cannot be fully described using the  $PT$  variables. In the plot illustrating pressure as a function of the overall molar concentration (see Figure 8), we can observe the constant plateau within the three-phase area like in the case of pure  $\text{CO}_2$  within the two-phase region. All these three-phase states occur at the same pressure, temperature and moles, therefore, they are indistinguishable in terms of the  $PT$  variables, but can be distinguished using the  $VT$  variables because the volumes are different in these states. The results of the algorithm testing provide an important evidence that the  $PT$  and  $VT$  variables are definitely not equivalent and that by specifying the pressure, temperature and moles the equilibrium state cannot be uniquely determined in pure component as well as in more complex systems.

To conclude, in this work we have extended the results of the previous work, in which we have dealt with the problem of single-phase stability and two-phase split calculation in a multicomponent mixture in a closed cell, both at constant

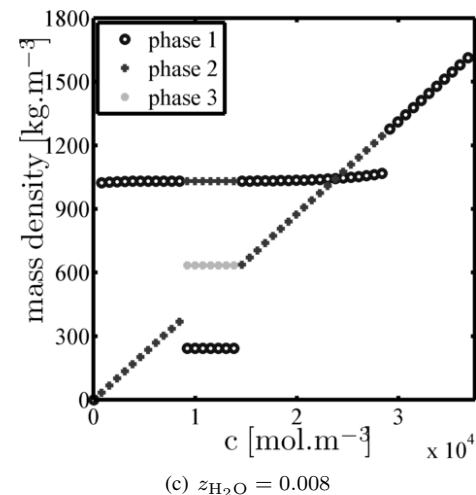
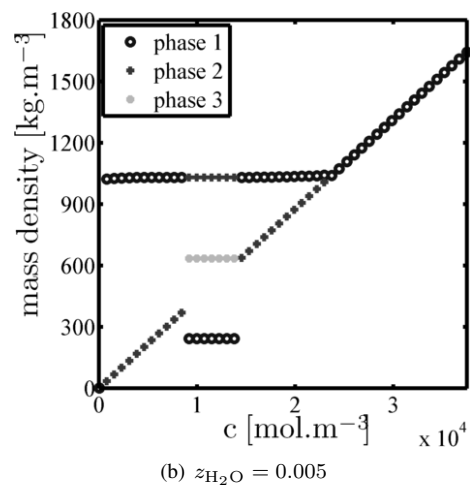
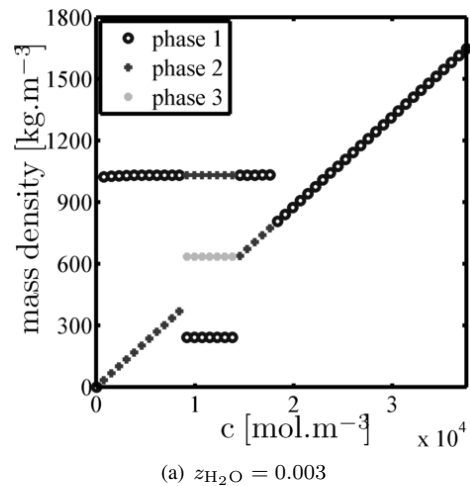


Fig. 5. Mass densities of each phase as a function of the overall molar concentration  $c$  for the binary mixture of  $\text{CO}_2 - \text{H}_2\text{O}$  with three different values of  $z_{\text{H}_2\text{O}}$  at  $T = 298.15 \text{ K}$ .

volume, temperature and moles (the so-called  $VT$ -stability and  $VT$ -flash), to the constant-volume three-phase equilibrium computation for the binary mixture of  $\text{CO}_2 - \text{H}_2\text{O}$  under geologic sequestration conditions. The performance of the algorithm is shown on several examples of two- and three-phase equilibrium computations of the mixture which is described using the Cubic-Plus-Association equation of state. In future work, the algorithm will be generalized and



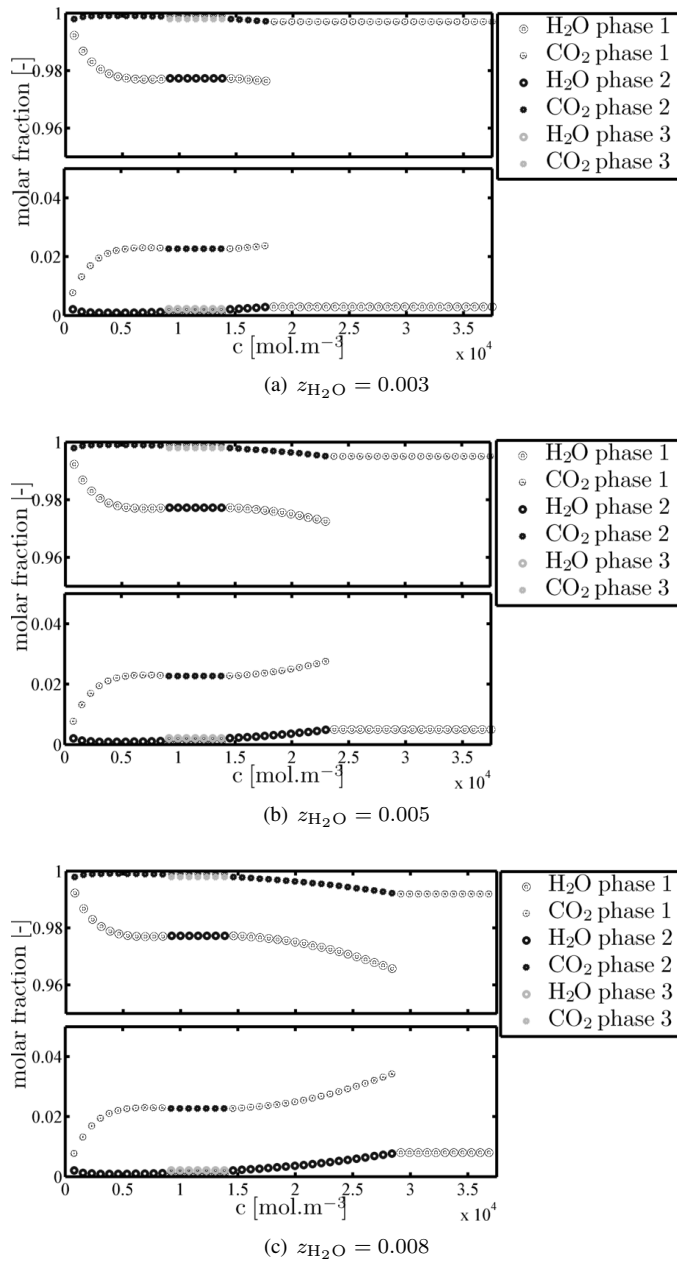


Fig. 6. Mole fractions of both components in each phase as functions of the overall molar concentration  $c$  for the binary mixture of CO<sub>2</sub> – H<sub>2</sub>O with three different values of  $z_{H_2O}$  at  $T = 298.15$  K.

the behaviour of mixtures in three and more phases is to be investigated to draw some general conclusions.

#### APPENDIX EQUATION OF STATE

In this work we use for the mixture of water (H<sub>2</sub>O) and carbon dioxide (CO<sub>2</sub>) the Cubic-Plus-Association (CPA) equation of state [12], [13].

This equation is based on the Peng-Robinson equation of state [11] to describe the physical interactions and the thermodynamic perturbation theory to describe the bonding of water molecules. We assume that each water molecule has four association sites of two types (mark them  $\alpha$  and  $\beta$ ), so each type has two sites. We assume the same for each molecule of carbon dioxide, whose association sites can be marked as  $\alpha'$  and  $\beta'$ . Let  $\chi_\alpha$  and  $\chi_\beta$  be the mole fractions of water not bonded at site  $\alpha$  and  $\beta$ , respectively,

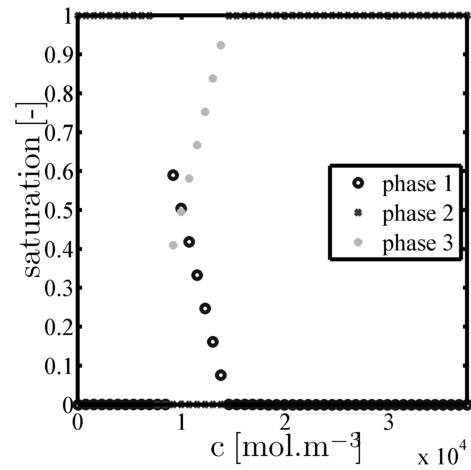


Fig. 7. Saturation of each phase as a function of the overall molar concentration  $c$  for the binary mixture of CO<sub>2</sub> – H<sub>2</sub>O with  $z_{H_2O} = 0.003$  at  $T = 298.15$  K.

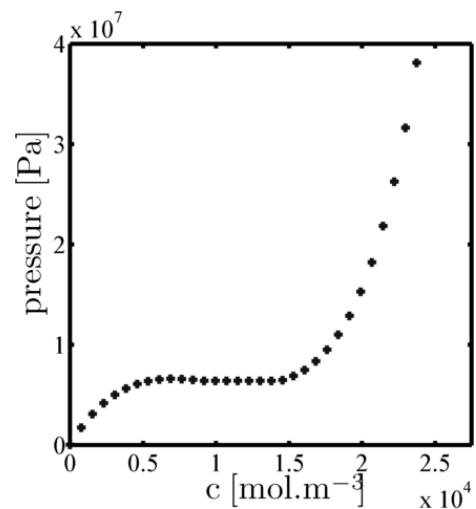


Fig. 8. Equilibrium pressure as a function of the overall molar concentration  $c$  for the binary mixture of CO<sub>2</sub> – H<sub>2</sub>O with  $z_{H_2O} = 0.003$  at  $T = 298.15$  K.

and let  $\chi_{\alpha'}$  and  $\chi_{\beta'}$  be the mole fractions of carbon dioxide not bonded at site  $\alpha'$  and  $\beta'$ , respectively. Assuming neither cross association nor self association between carbon dioxide molecules, and symmetric cross association between the two sites of different type of water and carbon dioxide, we obtain the following simplified expressions for the symmetric association model

$$\chi_\alpha = \chi_\beta = \chi_w = \frac{1}{1 + 2\frac{N_w}{V}\chi_w\Delta^{\alpha\beta} + 2\frac{N_c}{V}\chi_c\Delta^{\alpha\beta'}},$$

$$\chi_{\alpha'} = \chi_{\beta'} = \chi_c = \frac{1}{1 + 2\frac{N_w}{V}\chi_c\Delta^{\alpha\beta'}}.$$

In these equations the association strength between molecules of water is given by

$$\Delta^{\alpha\beta} = g\kappa^{\alpha\beta}[\exp(\epsilon^{\alpha\beta}/k_B T) - 1],$$

where  $k_B$  is the Boltzmann constant,  $\kappa^{\alpha\beta}$  and  $\epsilon^{\alpha\beta}$  are the bonding volume and energy parameters of water, respectively, and  $g$  is the contact value of the radial distribution function of hard-sphere mixture that can be approximated

TABLE III

PARAMETERS OF THE CPA EQUATION OF STATE FOR THE H<sub>2</sub>O AND CO<sub>2</sub> MIXTURE (THE NOTATION IS EXPLAINED IN THE APPENDIX).

Symbol	Units	Value
$\kappa^{\alpha\beta}$	[m <sup>3</sup> mol <sup>-1</sup> ]	1.801506 · 10 <sup>-6</sup>
$\epsilon^{\alpha\beta}/k_B$	[K]	1738.393603
$a_w^0$	[J·m <sup>-3</sup> ·mol <sup>-2</sup> ]	0.096273
$c_1$	[-]	1.755732
$c_2$	[-]	0.003518
$c_3$	[-]	-0.274636

as  $g = g(\eta) \approx \frac{1-0.5\eta}{(1-\eta)^3}$ , where  $\eta = \frac{\mathcal{B}}{4V}$  and  $\mathcal{B}$  is the parameter from the Peng-Robinson equation of state which will be explained later. The association strength between water and carbon dioxide molecules is related to the strength between water molecules as  $\Delta^{\alpha\beta'} = s_i \Delta^{\alpha\beta}$  where  $s_i$  is the temperature-dependent cross association coefficient which can be determined together with the binary interaction coefficient by fitting the experimental data. Finally, the CPA equation of state for the H<sub>2</sub>O – CO<sub>2</sub> system is given by

$$P(V, T, N_w, N_c) = \frac{NRT}{V - \mathcal{B}} - \frac{\mathcal{A}}{V^2 + 2\mathcal{B}V - \mathcal{B}^2} + 2RT \left( \frac{\eta}{g} \frac{\partial g}{\partial \eta} + 1 \right) \left[ \frac{N_w}{V} (\chi_w - 1) + \frac{N_c}{V} (\chi_c - 1) \right],$$

where  $N_w$  and  $N_c$  are the mole numbers of water and carbon dioxide, respectively,  $N = N_w + N_c$ , and  $\frac{\partial g}{\partial \eta} = \frac{2.5-\eta}{(1-\eta)^4}$ ,  $R$  is the universal gas constant,  $\mathcal{A}$  and  $\mathcal{B}$  are the parameters from the Peng-Robinson equation of state given by

$$\mathcal{A} = \sum_{i=w,c} \sum_{j=w,c} N_i N_j a_{ij}, \quad a_{ij} = (1 - \delta_{i-j}) \sqrt{a_i a_j}$$

$$\mathcal{B} = \sum_{i=w,c} N_i b_i.$$

The coefficients  $a_i$  and  $b_i$  for nonwater species (in our case for carbon dioxide) read as

$$a_i = 0.45724 \frac{R^2 T_{i,crit}^2}{P_{i,crit}} \left[ 1 + m_i \left( 1 - \sqrt{T_{r,i}} \right) \right]^2,$$

$$b_i = 0.0778 \frac{RT_{i,crit}}{P_{i,crit}} \quad T_{r,i} = \frac{T}{T_{i,crit}},$$

$$m_i = \begin{cases} 0.37464 + 1.54226\omega_i - 0.26992\omega_i^2, & \text{for } \omega_i < 0.5, \\ 0.3796 + 1.485\omega_i - 0.1644\omega_i^2 + 0.01667\omega_i^3, & \text{for } \omega_i \geq 0.5. \end{cases}$$

In these equations  $\delta_{i-j}$  denotes the binary interaction parameter between the components  $i$  and  $j$ ,  $T_{i,crit}$ ,  $P_{i,crit}$ , and  $\omega_i$  are the critical temperature, critical pressure, and acentric factor of the  $i$ -th component, respectively.

The coefficients  $a_i$  and  $b_i$  for water read as

$$a_w = a_w^0 \left[ 1 + c_1 \left( 1 - \sqrt{T_{r,w}} \right) + c_2 \left( 1 - \sqrt{T_{r,w}} \right)^2 + c_3 \left( 1 - \sqrt{T_{r,w}} \right)^3 \right]^2,$$

$$b_w = 1.458431 \cdot 10^{-5},$$

where  $a_w^0$ ,  $c_1$ ,  $c_2$ ,  $c_3$  are the parameters of the equation of state given in Table III.

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