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Calculation of multiphase chemical equilibrium in electrolyte solutions with non-stoichiometric methods

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Abstract

Electrolyte systems constitute an important class of chemical and phase equilibrium mixtures. They usually involve complex speciation in the aqueous solution and the formation of solids phases. For geochemical systems in particular, the number of species, solids and speciation reactions is often large. In this study, we extend the application of two recently developed non-stoichiometric methods to multiphase chemical equilibrium in electrolyte systems: the first-order Lagrange multipliers method and the second-order modified RAND method. The methods are based on the Gibbs energy minimization approach with Lagrange multipliers as elemental chemical potentials and they are suitable to systems with many reactions and many phases. We demonstrate that the overall electroneutrality condition is always satisfied as long as the material balance is met. Therefore, the two methods can be directly applied to electrolyte systems while special caution is needed for the different reference states used in the electrolyte models. In addition, the stability analysis for pure solid formation can be expressed in a compact form using the Lagrange multipliers. We present three examples with emphasis on geochemical reactions. The aqueous phase can be at equilibrium with a vapor phase consisting of the volatile components and multiple solid phases. Formation of vapor and solid phases does not impede convergence or affect the convergence rate. For the geo-

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chemical system with three solid phases, our methods are orders of magnitude faster than PHREEQC.

Keywords: chemical equilibrium, phase equilibrium, electrolytes, geochemical reactions, algorithm, non-stoichiometric methods

1. Introduction

Simulation of numerous processes involves the coupling of chemical reactions and phase separation. Efficient calculation of simultaneous chemical and phase equilibrium (CPE) is necessary for the optimization of process parameters, such as maximization of yields, appropriate energy requirements and adequate safety. Systems of interest can include from simple singlephases with a few reactions to complex geochemical aqueous phase speciation at equilibrium with multiple minerals.

CPE calculations are usually encountered in reactive distillation [1, 2], reactive extraction [3], heterogeneous organic synthesis [4], biodiesel production [5], weak electrolyte/geochemical systems [6, 7], reactor design [8], metallurgy [9], reactive crystallization [10] or air pollution control equipment [11]. CPE is calculated by either solving the algebraic equations valid at equilibrium or minimizing the Gibbs energy. According to Smith and Missen [12], minimization of the total Gibbs energy is further divided into stoichiometric and non-stoichiometric methods. Stoichiometric methods minimize the Gibbs energy with respect to reaction extents, which are variables that indicate how far reactions progress. Although their use is advantageous for a small number of reactions, they are prone to round-off errors and initialization problems. A set of independent reactions based on the most abundant components can be selected to overcome round-off errors [13]. Nevertheless, this set might need to be modified, since the abundance of components can change between iterations. There have been studies in the literature concerning the selection of the proper basis [14, 15, 16]. On the other hand, non-stoichiometric methods minimize the Gibbs energy under material balance constraints. These methods can be efficient calculating the

CPE of systems with many reactions and do not require to keep track of the most abundant components.

Speciation equilibrium in electrolyte systems covers an extensive collection of chemical reaction systems that can involve the formation of multiple solid phases. Most research on chemical reaction in electrolyte systems has occurred in the area of geochemistry where the complex speciation in the aqueous phase and the reactions with rock minerals are the key focus. The study on CPE in geochemistry has established its own tradition and the methods used often differ from those commonly used in other disciplines, such as chemical engineering. According to a recent review from Leal et al. [17], CPE in geological systems has been mainly studied with two methods: the law of mass action (LMA) and the Gibbs energy minimization (GEM). In LMA methods, the main equations include chemical equilibrium constants which are equal to the activity product of the components. This method is referred to by Leal et al. [17] as a “stoichiometric method”. The term “stoichiometric” was originally coined by Smith and Missen [12] for methods that minimize the Gibbs energy, whereas LMA methods are usually presented as an equation-solving approach. GEM methods minimize the Gibbs energy under material balance constraints, equivalent to the non-stoichiometric methods of Smith and Missen [12]. A general practice in CPE calculations of geochemical systems is to usually treat the phase equilibrium of volatile solvents/solutes as a reaction.

In the same review, Leal et al. also presented the extended LMA (xLMA) [18], where stability factors are incorporated in the working equations. These factors are linked to the existence of a component in a specific phase. Similar stability factors are used in the GEM formulations and rigorous stability analysis at the end of the calculations is avoided. Although this approach might ensure local convergence, stability analysis on the converged phase set must be performed to validate that the global minimum of the Gibbs energy has been attained. The authors explain how to solve the equations of xLMA and GEM methods using a perturbed interior Newton method which directly takes into account the non-negativity constraints of the mole numbers. Additionally, for

the calculation of second order derivatives, composition independent fugacity or activity coefficients are assumed (ideal system approximation). Automatic differentiation is used instead of numerical derivatives for improved efficiency.

60 The authors claim that solving with the GEM methods is a robust and efficient method for CPE of electrolyte systems, however the ideal solution approximation is bound to be inefficient especially in highly non-ideal systems such as electrolyte aqueous phases. Quasi-Newton methods are computationally less expensive than full Newton methods, but they can attain at most superlinear
65 convergence which implies a larger number of iterations.

Examples of LMA-based methods for the CPE calculation of geochemical systems are MINEQL+ [19], CHESS [20] and PHREEQC [21]. Various GEM methods have been developed in Karpov et al. [22], Leal et al. [7] and the GEM-Selektor by Kulik et al. [23]. More specifically, PHREEQC and GEM-Selektor
70 are software packages coded in C/C++ that are widely used for geochemical calculations. Among their capabilities are the computation of electrolyte speciation in the aqueous phase, solid solutions, ion-exchange equilibria, surface complexation and mass-transfer/kinetically controlled processes. Both packages can take into account temperature and pressure dependence as well as
75 non-ideality of solutions. PHREEQC is based on LMA and GEM-Selektor is based on Gibbs energy minimization, as the name suggests. These methods can be coupled with Reaktoro (reaktoro.org), a unified framework which can perform chemical equilibrium and kinetic calculations for multiphase systems. It is developed in C++ for improved performance with a Python interface for
80 convenience.

A number of algorithms has also been applied to systems of interest in chemical engineering. White et al. [24] developed the RAND method intended for single ideal vapor phases with multiple reactions. Gautam and Seider [25] combined the ideal RAND method with a phase-splitting procedure that allowed
85 poor initial estimates for trial phases. The authors present results for non-ideal systems, however they explicitly set the derivatives of activity coefficients equal to zero. Although no information is provided about the implementation, one

possibility involves a nested loop, with constant activity coefficients in the inner loop and the update of their values in the outer loop. A second-order non-ideal formulation of the RAND method was shown by Greiner [26], which is
 90 also presented with a different derivation in Michelsen and Mollerup [13]. Recently Paterson et al. [27, 28] have presented formulations of TP- and TV-based thermodynamics, the modified RAND and the vol-RAND respectively. Their study is focused on the phase equilibrium of multicomponent systems. Pérez
 95 Cisneros et al. [29] presented two different procedures for the VLE of reaction systems: the chemical model with elemental compositions and the ideal system approximation with nested loops. Phoenix and Heidemann [30] developed a stoichiometric and non-stoichiometric algorithm for multiphase systems. Both were first-order algorithms with the usual nested-loop scheme (ideal system ap-
 100 proximation). Castier et al. [31] derived the only stoichiometric second-order method to our knowledge. Initial steps involve accelerated direct substitution with the General Dominant Eigenvalue Method (GDEM) [32]. The Rachford-Rice equation is solved in the inner loop and reaction extents with K-values are updated in the outer loop. The efficient Murry’s minimization is employed for
 105 final convergence. Yield factors are introduced to account for the separation of the components between the phases. Components need to be divided into primary or secondary and revision of their mole numbers is necessary when they attain negative values.

Modeling of electrolytes in single and mixed solvents is a challenging and
 110 active research area. Complex long- and short-range interactions are still not fully understood and it is an open question how to adequately account for them in modeling of electrolyte solutions. One of the first successful attempts to theoretically describe non-ideality in an electrolyte solution is attributed to Debye and Hückel [33]. “Debye-Hückel” activity coefficients can include up to three
 115 ion independent parameters that depend on temperature and solvent properties. The limiting Debye-Hückel law has one parameter and extended Debye-Hückel equations utilize the two additional parameters. However, its use is limited to low values of ionic strength. At higher electrolyte concentrations more com-

plicated models are more suitable, such as the Pitzer model. It was originally
 120 proposed by Pitzer [34] and it is worth mentioning one of its most extended
 variants presented in Felmy et al. [35]. Felmy et al. [35] show a number of
 different contributing terms to the activity coefficient: a Debye-Hückel based
 term as well as binary and ternary interaction terms between cations, anions
 and neutral solutes. Binary and ternary interaction parameters are regressed by
 125 fitting the model on experimental data. Simpler Pitzer-based equations might
 omit the ternary interaction parameters and include their own analysis for pre-
 dicting parameters when experimental data are scarce [36]. Electrolyte versions
 of local composition models have been also implemented such as the extended
 UNIQUAC [37] and the electrolyte NRTL [38]. Finally, there have been at-
 130 tempts to model electrolytes more consistently under the unified framework of
 an equation of state, combining different approaches to the modeling of the
 electrolyte interactions [39, 40, 41].

In our previous work [42, 43] we solved the CPE of non-electrolyte mix-
 tures using two non-stoichiometric methods, with Lagrange multipliers and
 135 phase amounts as independent variables. In the first-order Lagrange multi-
 pliers method, the working equations are obtained assuming constant fugacity or
 activity coefficients and their values are updated in an outer loop for non-ideal
 systems. In the modified RAND method, second-order derivatives are utilized
 and, since the material balance constraints are satisfied at every iteration, the
 140 Gibbs energy can be monitored. The focus of this study is on the application
 of the same methods to electrolyte/geochemical systems with multiple specia-
 tion reactions that take place in an aqueous liquid phase. We demonstrate how
 special features of electrolyte mixtures are handled, such as the satisfaction of
 the electroneutrality condition. Along with the aqueous phase, a vapor phase
 145 can also exist when there are volatile solvents/solutes present in the feed. Fur-
 thermore, multiple pure solid phases can precipitate from the aqueous phase or
 further dissolve in water. The modified RAND method is proven to be more
 robust for the highly non-ideal electrolyte systems that can reach values of ionic
 strengths up to 8 mol/kg H₂O in the tested examples.

150 2. Method

2.1. Minimization of the Gibbs energy with non-stoichiometric methods

Systems contain material entities with different chemical structure, physical and chemical properties. In chemical engineering practices, these entities are called “components” (e.g., water, carbon dioxide, calcium carbonate, etc.). The term “species” usually refers to a component in a specific phase. For example, 155 two different species are $\text{H}_2\text{O}_{(l)}$ and $\text{H}_2\text{O}_{(g)}$. It is not always necessary to know the composition of all the components to determine the state of a system. “Elements” represent the the minimum number of independent entities necessary to define compositions in all the phases. In the absence of reactions, the number 160 of elements is equal to the number of components. However, chemical reactions introduce dependencies between the components. According to the extended Gibbs phase rule [44], there are N_E independent entities in the system and their number is found by:

$$N_E = N_C - N_R \quad (1)$$

where N_C is the number of components and N_R the number of reactions. Elements can be chosen as single chemical elements (e.g., H, O, C) or groups 165 of atoms (e.g., OH, CO_2 , SO_4^{2-}). Elements can also share the same chemical composition as components but in such case, they are better understood as a formal definition rather than actual physical entities. It must be stressed that the selection of the elements for a specific reaction system is not unique.

170 The minimum of the Gibbs energy for specified temperature and pressure corresponds to the equilibrium state of a system. In non-stoichiometric methods,

the total Gibbs energy is minimized under material balance constraints:

$$\begin{aligned} \min_{\mathbf{n}} G(T, p, \mathbf{n}) &= \min_{n_{ik}} \sum_{k=1}^{N_P} \sum_{i=1}^{N_C} n_{ik} \mu_{ik}(T, p, \mathbf{n}_k) \\ \text{s.t. } \mathbf{A} \sum_{k=1}^{N_P} \mathbf{n}_k &= \mathbf{b} \\ n_{ik} &\geq 0, \quad i = 1, \dots, N_C \quad k = 1, \dots, N_P \end{aligned} \quad (2)$$

where G is the Gibbs energy, T the temperature, p the pressure, N_P the number of phases, $\mathbf{n}$ the component abundance matrix with columns $\mathbf{n}_k$ (the component abundance vector in phase k) and entries n_{ik} (the mole numbers of component i in phase k), μ_{ik} the chemical potential of component i in phase k , $\mathbf{A}$ the formula matrix and $\mathbf{b}$ the element abundance vector. The material balance constraints pertain to the conservation of the element amounts. The non-negativity constraints for the mole numbers in Eq. 2 can be satisfied by controlling the iteration step, and thus do not need to be treated explicitly. The reduced Gibbs energy, $G/(RT)$, is minimized for convenience and the constraints are incorporated into the Lagrangian:

$$\mathcal{L}(\mathbf{n}, \boldsymbol{\lambda}) = \frac{G}{RT} - \boldsymbol{\lambda}^T \left(\mathbf{A} \sum_{k=1}^{N_P} \mathbf{n}_k - \mathbf{b} \right) \quad (3)$$

where R is the gas constant and $\boldsymbol{\lambda}$ the Lagrange multipliers vector. The minimum of the reduced Gibbs energy is a stationary point of the Lagrangian:

$$\begin{aligned} \frac{\partial \mathcal{L}}{\partial n_{ik}} &= \frac{\mu_{ik}}{RT} - \sum_{j=1}^{N_E} A_{ji} \lambda_j = 0 \\ i &= 1, \dots, N_C \quad k = 1, \dots, N_P \end{aligned} \quad (4)$$

and

$$\begin{aligned} \frac{\partial \mathcal{L}}{\partial \lambda_j} &= - \sum_{k=1}^{N_P} \sum_{i=1}^{N_C} A_{ji} n_{ik} + b_j = 0 \\ j &= 1, \dots, N_E \end{aligned} \quad (5)$$

where A_{ji} is the number of elements j in the chemical formula of component i ,
 b_j the total amount of element j and λ_j the Lagrange multiplier of constraint
(element) j . The Lagrange multipliers are interpreted as the chemical potential
of the elements at equilibrium. The chemical potential of the components is
190 given by a general expression:

$$\mu_{ik} = \mu_{ik}^{\circ} + RT \ln \frac{x_{ik} \hat{\phi}_{ik} p}{f_{ik}^{\circ}} \quad (6)$$

where μ_{ik}° and f_{ik}° are the reference state chemical potential and fugacity, x_{ik} the
mole fraction and $\hat{\phi}_{ik}$ the fugacity coefficient of component i in phase k . In this
work, the Lagrange multipliers method and the modified RAND method are
used for CPE calculations. Both are numerical methods and their initialization
195 is reported in detail in Tsanas et al. [42, 43].

- The Lagrange multipliers methods [42]

In the Lagrange multipliers method, the working equations are the mate-
rial balance expressed in terms of mole fractions and phase amounts:

$$\sum_{k=1}^{N_P} n_{t,k} \sum_{i=1}^{N_C} A_{ji} x_{ik} - b_j = 0 \quad (7)$$

$$j = 1, \dots, N_E$$

and the sum of the mole fractions in each phase that is equal to one:

$$\sum_{i=1}^{N_C} x_{ik} - 1 = 0 \quad (8)$$

$$k = 1, \dots, N_P$$

200 where $n_{t,k}$ is the amount of phase k . Substituting Eq. 6 in 4, we obtain
after rearranging:

$$\ln x_{ik} = \sum_{j=1}^{N_E} A_{ji} \lambda_j - \frac{\mu_{ik}^{\circ}}{RT} - \ln \frac{\hat{\phi}_{ik} p}{f_{ik}^{\circ}} \quad (9)$$

Eq. 7 and 8 are solved for N_E Lagrange multipliers and N_P phase amounts:

$$\begin{bmatrix} \mathbf{A} \operatorname{diag} \left(\sum_{k=1}^{N_P} \mathbf{n}_k \right) \mathbf{A}^T & \mathbf{A} \mathbf{x} \\ (\mathbf{A} \mathbf{x})^T & \mathbf{0} \end{bmatrix} \begin{bmatrix} \Delta \boldsymbol{\lambda} \\ \Delta \mathbf{n}_t \end{bmatrix} = - \begin{bmatrix} \mathbf{A} \sum_{k=1}^{N_P} \mathbf{n}_k - \mathbf{b} \\ \mathbf{x}^T \mathbf{e}_{N_C} - \mathbf{e}_{N_P} \end{bmatrix} \quad (10)$$

where $\mathbf{x}$ is the mole fraction matrix with entries x_{ik} and $\mathbf{e}_N$ a vector of ones with dimensions $N \times 1$. The system of Eq. 10 is solved for constant fugacity or activity coefficients (ideal system approximation). When the phases are non-ideal, Eq. 10 is nested in a loop. The system is solved in the inner loop and fugacity or activity coefficients are updated in the outer loop. Therefore in the case of non-ideal systems, linear convergence rate is expected. Furthermore, the material balance is satisfied only when the inner loop converges and it is not possible to monitor the value of the reduced Gibbs energy, potentially compromising the robustness of the method. The error at iteration q is given by:

$$\text{error}^{(q)} = \sqrt{\sum_{j=1}^{N_E} \left[\lambda_j^{(q)} - \lambda_j^{(q-1)} \right]^2 + \sum_{k=1}^{N_P} \left[n_{t,k}^{(q)} - n_{t,k}^{(q-1)} \right]^2} \quad (11)$$

- The modified RAND method [43]

In the modified RAND method, Eq. 4 is linearized around the current estimate of the mole numbers:

$$\begin{aligned} \frac{\mu_k}{RT} + \mathbf{M}_k \Delta \mathbf{n}_k - s_k \mathbf{e}_{N_C} - \mathbf{A}^T \boldsymbol{\lambda} &= 0 \\ k &= 1, \dots, N_P \end{aligned} \quad (12)$$

with

$$M_{iqk} = \frac{\delta_{iq}}{n_{ik}} + \left(\frac{\partial \ln \hat{\phi}_{ik}}{\partial n_{qk}} \right)_{T,p} \quad (13)$$

and

$$s_k = \frac{\sum_{i=1}^{N_C} \Delta n_{ik}}{n_{t,k}} = \frac{\Delta n_{t,k}}{n_{t,k}} \quad (14)$$

where $\boldsymbol{\mu}_k$ is the vector of chemical potentials in phase k . We define the element abundance vector in phase k :

$$\mathbf{B}_k = \mathbf{A} \mathbf{n}_k \quad (15)$$

and the element abundance matrix:

$$\mathbf{B} = \mathbf{A} \mathbf{n} \quad (16)$$

Matrix $\mathbf{B}$ shows the distribution of the elements between the different phases. After rearranging Eq. 12, the correction vector for the mole numbers is given by:

$$\begin{aligned} \Delta \mathbf{n}_k &= \mathbf{n}_k s_k + \mathbf{M}_k^{-1} \left(\mathbf{A}^T \boldsymbol{\lambda} - \frac{\boldsymbol{\mu}_k}{RT} \right) \\ k &= 1, \dots, N_P \end{aligned} \quad (17)$$

The working equations of the modified RAND method are:

$$\mathbf{A} \sum_{k=1}^{N_P} \Delta \mathbf{n}_k = \Delta \mathbf{b} \quad (18)$$

and

$$\begin{aligned} \mathbf{e}_{N_C}^T \Delta \mathbf{n}_k &= \Delta n_{t,k} \\ k &= 1, \dots, N_P \end{aligned} \quad (19)$$

where

$$\Delta \mathbf{b} = \mathbf{b} - \sum_{k=1}^{N_P} \mathbf{B}_k \quad (20)$$

The full system of equations in the modified RAND method for multiple phases and non-ideal systems is solved for N_E Lagrange multipliers and N_P variables s :

$$\begin{bmatrix} \mathbf{A} \sum_{k=1}^{N_P} \mathbf{M}_k^{-1} \mathbf{A}^T & \mathbf{B} \\ \mathbf{B}^T & \mathbf{0} \end{bmatrix} \begin{bmatrix} \lambda \\ s \end{bmatrix} = \begin{bmatrix} \mathbf{A} \sum_{k=1}^{N_P} \mathbf{M}_k^{-1} [\mu_k / (RT)] + \Delta \mathbf{b} \\ \mathbf{d} \end{bmatrix} \quad (21)$$

where

$$d_k = \frac{\mathbf{n}_k^T \boldsymbol{\mu}_k}{RT} \quad (22)$$

In the derivation of Eq. 21 the ideal system approximation has not be used. Second-order derivatives have been considered in the calculations. As a result, this method is expected to exhibit quadratic convergence rate at the final iterations even for non-ideal systems. Furthermore, if the initial estimate satisfies the material balance, mole numbers will also satisfy it in the following iterations. In this way the reduced Gibbs energy can be monitored. If the Gibbs energy increases due to overstepping, the step size can be reduced to ensure a decrease in the objective function. Finally, the quantity $\Delta \mathbf{b}$ can be either omitted whenever the material balance is satisfied or preserved to mitigate round-off errors. A step-control parameter is used in Eq. 17 when updating mole numbers:

$$\begin{aligned} \mathbf{n}_k^{\text{new}} &= \mathbf{n}_k^{\text{old}} + \alpha \Delta \mathbf{n}_k \\ k &= 1, \dots, N_P \end{aligned} \quad (23)$$

In most cases α is equal to 1. When $\mathbf{n}^{\text{new}}$ has negative entries or when it results in higher Gibbs energy, the mole numbers are recalculated with $\alpha = \alpha/2$. The error at iteration q is given by:

$$\text{error}^{(q)} = \sqrt{\sum_{k=1}^{N_P} \sum_{i=1}^{N_C} [n_{ik}^{(q)} - n_{ik}^{(q-1)}]^2} \quad (24)$$

2.2. Electrolyte solutions

2.2.1. Electroneutrality

Although the dissociation of weak electrolytes and the dissolution of solids introduce charged components (ions), the total charge of the system must be conserved. It implies that for a feed with total charge equal to zero, the system should always be electroneutral. The electroneutrality condition can be described by the following equation:

$$\mathbf{q}^T \sum_{k=1}^{N_P} \mathbf{n}_k = 0 \quad (25)$$

where $\mathbf{q}$ is the charge vector of the components. The charges are not absolute but correspond to multiples of the absolute electron charge, e.g., $q_{\text{Ca}^{2+}} = 2$, $q_{\text{OH}^-} = -1$.

It is critical to consider whether the electroneutrality equation is an additional constraint which needs to be explicitly included in the current set of working equations. Mole number changes can be expressed as functions of the reaction extents:

$$\sum_{k=1}^{N_P} \mathbf{n}_k = \mathbf{n}_F + \mathbf{N}\boldsymbol{\xi} \quad (26)$$

where $\mathbf{n}_F$ is the component abundance vector in the feed, $\mathbf{N}$ the stoichiometric matrix with entries ν_{ir} , the stoichiometric coefficient of component i in reaction r , and $\boldsymbol{\xi}$ the reaction extent vector. If we multiply from the left with $\mathbf{q}^T$, we get:

$$\mathbf{q}^T \sum_{k=1}^{N_P} \mathbf{n}_k = \mathbf{q}^T \mathbf{n}_F + \mathbf{q}^T \mathbf{N}\boldsymbol{\xi} \quad (27)$$

The total charge in the feed is zero:

$$\mathbf{q}^T \mathbf{n}_F = 0 \quad (28)$$

265 and the chemical reactions are balanced in terms of electrons, which means that there is no charge produced or consumed for any value of ξ . Therefore:

$$\mathbf{q}^T \mathbf{N} = 0 \quad (29)$$

which proves Eq. 25. When non-stoichiometric methods are chosen for CPE calculations, the system is defined by the formula matrix. This matrix dictates how the components are decomposed into elements based on their chemical
270 composition. If this decomposition includes the charge as well, the total charge of a component must satisfy:

$$q_i = \sum_{j=1}^{N_E} \tilde{q}_j A_{ji} \quad (30)$$

$$i = 1, \dots, N_C$$

where $\tilde{q}_j$ is the charge of element j . For instance, water is composed of two elements, two H^+ and one O^{2-} . Its total charge is calculated by:

$$q_{\text{H}_2\text{O}} = 2\tilde{q}_{\text{H}^+} + \tilde{q}_{\text{O}^{2-}} = 2 + (-2) = 0 \quad (31)$$

Eq. 30 is written in matrix-vector form as:

$$\mathbf{q}^T = \tilde{\mathbf{q}}^T \mathbf{A} \quad (32)$$

275 The values of $\mathbf{q}^T$ are obtained by multiplying row j of $\mathbf{A}$ with $\tilde{q}_j$ and then adding all the new rows together. As a result, $\mathbf{q}^T$ is a linear combination of the rows of $\mathbf{A}$. If we would combine the electroneutrality equation with the current constraints, we would obtain:

$$\mathbf{A}' \sum_{k=1}^{N_P} \mathbf{n}_k = \mathbf{b}' \quad (33)$$

where

$$\mathbf{A}' = \begin{bmatrix} \mathbf{A} \\ \mathbf{q}^T \end{bmatrix} \quad (34)$$

280 and

$$\mathbf{b}' = \begin{bmatrix} \mathbf{b} \\ 0 \end{bmatrix} \quad (35)$$

However, we do not introduce a new constraint in the problem, since

$$\text{rank}(\mathbf{A}') = \text{rank}(\mathbf{A}) \quad (36)$$

Consequently, Eq. 25 is satisfied, implying that, when the material balance is satisfied, the electroneutrality equation is not required as an additional constraint. For a single aqueous phase, total electroneutrality of Eq. 25 coincides
 285 with the electroneutrality of the unique electrolyte phase. Both proofs based on stoichiometric or non-stoichiometric approaches show that the total charge will not change – the equilibrium system is electroneutral because the the feed is electroneutral. Although other researchers have also pointed out that the electroneutrality constraint is implicitly satisfied by the material balance [7, 17],
 290 they did not present a general proof.

2.2.2. Calculation procedure

In Tsanas et. al [42, 43], calculation of CPE in non-electrolyte systems followed the general procedure:

1. Assumption of a single phase
- 295 2. Initialization of $\boldsymbol{\lambda}$ and $\mathbf{n}_t$
3. Solve CPE
4. Stability analysis
 - If stable, end
 - If unstable, add a phase and go to step 3

300 We do not strictly follow the general procedure in the calculations with electrolyte systems. Although it is general and very efficient in the CPE of non-electrolyte systems, the analysis of electrolytes allows certain simplifications.

First, non-volatile electrolytes in the feed prevent us from starting calculations with a single vapor phase. Second, water-insoluble inert gases in the feed suggest
 305 the existence of a vapor phase. For partially soluble gases, it is also more effective in most cases to assume the existence of a vapor phase. Finally, we could force into a single liquid phase all the soluble gases and solids (undissociated or in the form of their ions). If the water concentration is appreciably reduced, electrolyte models will behave erratically. These models depend on water being
 310 the most abundant (solvent). Otherwise molalities will become large, which means that we can safely assume additional phases in the beginning of the calculations. In this work, a vapor, an aqueous and all potential solid phases were initially assumed. During calculations, it is possible that the vapor phase becomes a lighter liquid non-aqueous phase, or that specific solids completely
 315 dissolve in water. The current implementation allows for the deactivation and reintroduction of phases, whenever needed. Values of the phase amounts are assumed and the Lagrange multipliers are initialized through the minimization of a convex function. Afterward, the CPE solution is determined by:

- The successive substitution algorithm: only the first-order Lagrange multipliers method is used
 320
- The combined algorithm: the Lagrange multipliers method is used for a maximum of three outer-loop iterations and then calculations switch to the second-order modified RAND method

2.2.3. *Stability analysis for solids*

325 For electrolyte systems, stability analysis considering ordinary vapor and liquid phases is the same as described in Michelsen [45] and later in Michelsen and Mollerup [13]. The unique aspect in the stability analysis of electrolyte systems is to judge whether solid phases can form or not. The condition for a pure solid formation is a special case of the general stability analysis criterion.
 330 We demonstrate how the general criterion can be reduced to the special case with pure solid formation and chemical reaction. We also show the link to the

classical criterion using the solubility index.

A phase with composition $\mathbf{z}$ can be split into two phases, when there is composition $\mathbf{w}$ of the incipient that results in negative tangent plane distance [45, 13]:

$$tpd(\mathbf{w}) = \frac{1}{RT} \sum_{i=1}^{N_C} w_i [\mu_i(\mathbf{w}) - \mu_i(\mathbf{z})] \quad (37)$$

If the incipient phase is a pure solid, Eq. 37 becomes:

$$tpd = \frac{\mu_s^{\text{pure}}}{RT} - \frac{\mu_s(\mathbf{z})}{RT} = \frac{\mu_s^{\text{pure}}}{RT} - \sum_{j=1}^{N_E} A_{js} \lambda_j \quad (38)$$

In this case, the reduced tangent plane distance is simply the difference between the pure component chemical potential and the chemical potential of the solid in the aqueous phase. The equality

$$\frac{\mu_s(\mathbf{z})}{RT} = \sum_{j=1}^{N_E} A_{js} \lambda_j \quad (39)$$

is obtained from Eq. 4 and it is a convenient way to calculate the chemical potential of the solid in the aqueous phase. This equality is not concerned with the state that the solid appears in the aqueous phase, either as an undissociated solute or in the form of its ions. Consequently, Eq. 38 can readily utilize the values of the Lagrange multipliers to identify possible precipitations. The value of tpd is negative when precipitation must occur and positive when more solid can be dissolved in the aqueous phase. Its value reaches zero only when the precipitated solid is in equilibrium with other phases.

In the analysis of solid precipitation, the saturation index is often used:

$$SI_r = \log_{10} \frac{IAP_r}{K_r^{\text{eq}}} = \log_{10} \prod_{\substack{i=1 \\ i \neq s}}^{N_C} (m_i \gamma_i^m)^{\nu_{ir}} \frac{1}{K_r^{\text{eq}}} \quad (40)$$

where IAP is the ion activity product and K^{eq} the chemical equilibrium constant. The latter is equal to the equilibrium ion activity product (or solubility product), where pure solid activities are equal to one. The subscript r refers to

the corresponding reaction between the solid and its ions. Positive values of SI lead to precipitation (supersaturated solution), while negative values to dissolution (undersaturated solution). Similar to tpd in Eq. 38, the value of SI is zero at the solid-ion equilibrium. The criterion of the saturation index requires that the reaction corresponds to the dissolution of the solid in the aqueous phase (solid is a reactant). The saturation index can be expressed as a function of the Lagrange multipliers:

$$\begin{aligned}
 SI_r \ln 10 &= \ln \frac{IAP_r}{K_r^{eq}} = \ln IAP_r - \ln K_r^{eq} \\
 &= \sum_{\substack{i=1 \\ i \neq s}}^{N_C} \frac{\nu_{ir} \mu_i}{RT} - \sum_{\substack{i=1 \\ i \neq s}}^{N_C} \frac{\nu_{ir} \mu_i^o}{RT} + \sum_{i=1}^{N_C} \frac{\nu_{ir} \mu_i^o}{RT} = \\
 &= \sum_{\substack{i=1 \\ i \neq s}}^{N_C} \frac{\nu_{ir} \mu_i}{RT} + \frac{\nu_{sr} \mu_s^{pure}}{RT} = \\
 &= \sum_{\substack{i=1 \\ i \neq s}}^{N_C} \nu_{ir} \sum_{j=1}^{N_E} A_{ji} \lambda_j + \frac{\nu_{sr} \mu_s^{pure}}{RT}
 \end{aligned} \tag{41}$$

It is known that the formula matrix satisfies:

$$\mathbf{AN} = \mathbf{0} \tag{42}$$

OR

$$\sum_{i=1}^{N_C} A_{ji} \nu_{ir} = 0 \tag{43}$$

$$j = 1, \dots, N_E \quad r = 1, \dots, N_R$$

If we select r to be the reaction that includes the solid, we have:

$$\sum_{\substack{i=1 \\ i \neq s}}^{N_C} \nu_{ir} A_{ji} = -\nu_{sr} A_{js} \tag{44}$$

Introducing Eq. 44 to the last part of Eq. 41, we obtain:

$$\begin{aligned}
 \text{SI}_r \ln 10 &= \sum_{\substack{i=1 \\ i \neq s}}^{N_C} \nu_{ir} \sum_{j=1}^{N_E} A_{ji} \lambda_j + \frac{\nu_{sr} \mu_s^{\text{pure}}}{RT} = \\
 &= \sum_{j=1}^{N_E} \lambda_j \sum_{\substack{i=1 \\ i \neq s}}^{N_C} \nu_{ir} A_{ji} + \frac{\nu_{sr} \mu_s^{\text{pure}}}{RT} = \\
 &= -\nu_{sr} \left(\sum_{j=1}^{N_E} A_{js} \lambda_j - \frac{\mu_s^{\text{pure}}}{RT} \right)
 \end{aligned} \tag{45}$$

or

$$\text{SI}_r = \frac{\nu_{sr}}{\ln 10} \text{tpd} \tag{46}$$

Eq. 38 and 40 are performing essentially the same check on the aqueous phase: whether the precipitation of a solid will further decrease the Gibbs energy of the system. Nevertheless, Eq. 38 does not require reaction information, e.g., stoichiometry, chemical equilibrium constant and the assumption that the solid is the reactant of a single reaction. Furthermore, Eq. 38 utilizes directly the Lagrange multipliers, the independent variables of non-stoichiometric methods, which have been used in this work. If we suspect that an additional solid phase exists, we can use the Lagrange multipliers of the converged solution that correspond to the elements in the solid and compare them to the chemical potential of the pure solid, as it appears in Eq. 38.

2.3. Reference states

Chemical potentials (Eq. 6) can not only be calculated with different reference states between different phases but also between different components that belong to the same phase. It is important to clarify which reference state is chosen for each case, because this will influence the expression of the chemical potential. For components that exist in a vapor or a liquid phase described by an equation of state, the ideal gas reference state is used:

$$f_{ik}^{\circ} = p^* \quad \mu_{ik}^{\circ} = \mu_i^*(T, p^*) \tag{47}$$

and

$$\mu_{ik} = \mu_i^* + RT \ln \frac{x_{ik} \hat{\phi}_{ik} p}{p^*} \quad (48)$$

where p^* is the reference pressure (usually 1 bar or 1 atm) and μ_i^* the ideal gas chemical potential, calculated at the temperature of the system. In ideal vapor phases, the fugacity coefficient is equal to one.

385 For components in the liquid phase described by an activity coefficient model, there is a number of different reference states that can be used:

- Pure component reference state: component can exist as pure liquid (e.g. solvents)

$$f_{ik}^\circ = f_{ik}(T, p) \quad \mu_{ik}^\circ = \mu_{ik}^{\text{pure}}(T, p) \quad (49)$$

and

$$\mu_{ik} = \mu_{ik}^{\text{pure}} + RT \ln(x_{ik} \gamma_{ik}) \quad (50)$$

390 where f_{ik} and μ_{ik}^{pure} are the reference fugacity and chemical potential of pure component i in phase k , calculated at the temperature and pressure of the system. The symmetric activity coefficient is defined as:

$$\gamma_{ik} \equiv \frac{\hat{f}_{ik}}{x_{ik} f_{ik}} \quad (51)$$

The limiting behavior of the symmetric activity coefficient is described by the equation:

$$\lim_{x_{ik} \rightarrow 1} \gamma_{ik} = 1 \quad (52)$$

395 In ideal solutions, the symmetric activity coefficient is equal to one. Activity of a component is formally defined as the deviation of the fugacity

in the mixture from the pure state:

$$\alpha_{ik} \equiv \frac{\hat{f}_{ik}}{f_{ik}} = x_{ik}\gamma_{ik} \quad (53)$$

which results in:

$$\mu_{ik} = \mu_{ik}^{\text{pure}} + RT \ln \alpha_{ik} \quad (54)$$

- Infinite dilution reference state: volatile solutes

400 When a component cannot exist as pure liquid or the pure component is not of practical interest, we have:

$$f_{ik}^{\circ} = H_{ik}(T, p, \mathbf{n}_{\text{sol},k}) \quad \mu_{ik}^{\circ} = \tilde{\mu}_{ik}(T, p, \mathbf{n}_{\text{sol},k}) \quad (55)$$

and

$$\mu_{ik} = \tilde{\mu}_{ik} + RT \ln(x_{ik}\tilde{\gamma}_{ik}) \quad (56)$$

405 where H_{ik} and $\tilde{\mu}_{ik}$ are the Henry's constant and infinite dilution chemical potential of component i in phase k , calculated at the temperature and pressure of the system, and $\mathbf{n}_{\text{sol},k}$ the mole number vector of solvents in phase k . The Henry's constant is given by the general expression:

$$H_{ik} = H_{ik}^s \exp \left(\int_{p_{\text{sol}}^s}^p \frac{\bar{V}_{ik}^{\infty}}{RT} dp \right) \approx H_{ik}^s \exp \left[\frac{\bar{V}_{ik}^{\infty}(p - p_{\text{sol}}^s)}{RT} \right] \quad (57)$$

410 where H_{ik}^s is the saturation Henry's constant of component i in phase k , p_{sol}^s the vapor pressure of the solvent and $\bar{V}_{ik}^{\infty}$ the infinite dilution partial molar volume of component i in phase k . In contrast to the pure component reference state, the infinite dilution reference state depends on composition. Interactions in solutions of infinitely diluted solutes depend

on the solvent composition (Eq. 55). The asymmetric activity coefficient is defined as:

$$\tilde{\gamma}_{ik} \equiv \frac{\hat{f}_{ik}}{x_{ik}H_{ik}} \quad (58)$$

The limiting behavior of the asymmetric activity coefficient is described by the equation:

$$\lim_{\substack{x_{ik} \rightarrow 0 \\ x_{(j \neq i)k} \rightarrow 0}} \tilde{\gamma}_{ik} = 1 \quad (59)$$

where i is a solute. In the infinite dilution reference state activity is calculated in the literature as:

$$\alpha_{ik} = x_{ik}\tilde{\gamma}_{ik} \quad (60)$$

to match the expression of the chemical potential of Eq. 54. However, this is not consistent with the definition of Eq. 53.

- Unit molality reference state: solutes

Molality appears to be the preferred concentration measure in electrolyte solutions. It is defined as the mole numbers of solute per unit mass of the solvent:

$$m_{ik} = \frac{n_{ik}}{n_{\text{sol},k}M_{\text{sol},k}} \quad (61)$$

A molality reference state can be derived from the infinite dilution reference state which is based on mole fractions. The chemical potential is given by:

$$\mu_{ik} = \tilde{\mu}_{ik}^m + RT \ln \frac{m_{ik}\tilde{\gamma}_{ik}^m}{m^\circ} \quad (62)$$

with

$$\tilde{\mu}_{ik}^m = \tilde{\mu}_{ik} + RT \ln(M_{\text{sol},k} m^\circ) \quad (63)$$

and

$$\tilde{\gamma}_{ik}^m = x_{\text{sol},k} \tilde{\gamma}_{ik} \quad (64)$$

The value of m° is 1 mol/kg. In the unit molality reference state activity is calculated in the literature as:

$$\alpha_{ik} = \frac{m_{ik} \tilde{\gamma}_{ik}^m}{m^\circ} \quad (65)$$

to match the expression of the chemical potential of Eq. 54. However, this is not consistent with the definition of Eq. 53.

The symmetric and asymmetric activity coefficients are linked through:

$$\tilde{\gamma}_{ik} = \frac{\gamma_{ik}}{\gamma_{ik}^\infty} \quad (66)$$

and the infinite dilution with the pure component reference state through:

$$\tilde{\mu}_{ik} = \mu_{ik}^{\text{pure}} + RT \ln \gamma_{ik}^\infty \quad (67)$$

The symmetric infinite dilution activity coefficient is defined as:

$$\lim_{\substack{x_{ik} \rightarrow 0 \\ x_{(j \neq i)k} \rightarrow 0}} \gamma_{ik} = \gamma_{ik}^\infty \quad (68)$$

where i is a solute. For the derivatives of the asymmetric activity coefficients, we have:

$$\left(\frac{\partial \ln \tilde{\gamma}_{ik}}{\partial n_{qk}} \right)_{T,p} = \left(\frac{\partial \ln \gamma_{ik}}{\partial n_{qk}} \right)_{T,p} - \left(\frac{\partial \ln \gamma_{ik}^\infty}{\partial n_{qk}} \right)_{T,p} \quad (69)$$

and for the infinite dilution chemical potential, which also depends on composition:

$$\left(\frac{\partial \tilde{\mu}_{ik}}{\partial n_{qk}}\right)_{T,p} = RT \left(\frac{\partial \ln \gamma_{ik}^{\infty}}{\partial n_{qk}}\right)_{T,p} \quad (70)$$

440 Finally, derivatives of fugacity and symmetric activity coefficients are equivalent:

$$\left(\frac{\partial \ln \gamma_{ik}}{\partial n_{qk}}\right)_{T,p} = \left(\frac{\partial \ln \hat{\phi}_{ik}}{\partial n_{qk}}\right)_{T,p} \quad (71)$$

The methods described in Section 2.1 are based on reference states with mole fractions as concentration measure. Therefore, in order to use these methods unmodified, the molality reference state must be converted to the infinite dilution reference state through Eq. 63 and 64. Moreover, the modified RAND method
445 requires the composition derivatives of the chemical potentials. The Gibbs-Duhem equation must be satisfied to obtain Eq. 17. As a result, the derivatives of the symmetric activity coefficients are used. In this work we assume a single solvent, which results in a composition independent infinite dilution reference state:

$$\left(\frac{\partial \ln \gamma_{ik}^{\infty}}{\partial n_{qk}}\right)_{T,p} = 0 \quad (72)$$

450 Eq. 69 and 70 become:

$$\left(\frac{\partial \ln \tilde{\gamma}_{ik}}{\partial n_{qk}}\right)_{T,p} = \left(\frac{\partial \ln \gamma_{ik}}{\partial n_{qk}}\right)_{T,p} \quad (73)$$

and

$$\left(\frac{\partial \tilde{\mu}_{ik}}{\partial n_{qk}}\right)_{T,p} = 0 \quad (74)$$

3. Results and discussion

In this work, water is the only solvent in the unique aqueous phase of the multiphase systems. To validate the applicability of the algorithms to electrolyte systems, three different cases are examined. Common characteristics of
455

the systems are the existence of an aqueous phase with various electrolytes at equilibrium with a vapor phase or a CO₂-rich liquid phase, depending on the pressure. The complexity of each case gradually increases from vapor-liquid equilibrium, to vapor-liquid-solid/liquid-liquid-solid equilibrium and finally to
460 vapor-liquid-solid-solid-solid equilibrium. The pure solid phases introduced to the system could interact with the aqueous phase through precipitation or dissolution. The component and element numbering are presented in Table 1.

Table 1: Component and element numbering.

Number	H ₂ O / NH ₃ / CO ₂		CO ₂ solubility		Three-mineral system [7]	
	Component	Element	Component	Element	Component	Element
1	H ₂ O	CO ₂	H ₂ O	CO ₂	H ₂ O	CO ₂
2	NH ₃	CH ₄	CO ₂	H ⁺	CO ₂	SiO ₂
3	CO ₂	C ₂ H ₆	CaCl ₂	Ca ²⁺	MgCO ₃	H ⁺
4	CH ₄	H ⁺	CaCO ₃	Cl ⁻	H ₄ SiO ₄	Na ⁺
5	C ₂ H ₆	NH ₂ ⁻	H ⁺	O ²⁻	Calcite	K ⁺
6	H ⁺	O ²⁻	Ca ²⁺		Dolomite	Ca ²⁺
7	NH ₄ ⁺		OH ⁻		Quartz	Mg ²⁺
8	OH ⁻		Cl ⁻		H ⁺	Cl ⁻
9	HCO ₃ ⁻		HCO ₃ ⁻		Na ⁺	O ²⁻
10	CO ₃ ²⁻		CO ₃ ²⁻		K ⁺	SO ₄ ²⁻
11	NH ₂ COO ⁻				Ca ²⁺	
12					Mg ²⁺	
13					MgOH ⁺	
14					OH ⁻	
15					Cl ⁻	
16					HCO ₃ ⁻	
17					CO ₃ ²⁻	
18					HSO ₄ ⁻	
19					SO ₄ ²⁻	
20					H ₃ SiO ₄ ⁻	
21					H ₂ SiO ₄ ²⁻	

The Pitzer model [34], a widely used activity coefficient model in geochemical calculations, was chosen to describe the non-ideality in the electrolyte aqueous phases. Available geochemical calculations in the literature use the Pitzer model and its application in this work was primarily for consistent comparisons. The algorithms are not model-specific, therefore we can obtain fugacity or activity coefficients from different electrolyte models as well. A general implementation of the Pitzer model is presented in Felmy et al. [35]. Its various parameters can be interpreted as different contributions to the second and third virial coefficients:

- Second virial coefficients

- cation-anion: B_{ij}^ϕ , B_{ij} , $B'_{ij} = f(I)$
- cation-cation or anion-anion: θ_{ij} and ${}^E\theta_{ij}$, ${}^E\theta'_{ij} = f(I)$
- ion-neutral solute: λ_{ij}

- Third virial coefficients

- cation-anion: C_{ij}^ϕ
- cation-anion-anion or cation-cation-anion: ψ_{ijk}
- cation-anion-neutral solute: ζ_{ijk}

Furthermore, parameters $A^\phi = f(T, p)$ and $b = 1.2$ are used in the equations of the model. In this work, the Debye-Hückel slope for the osmotic coefficient is given by the equation:

$$A^\phi = \frac{1}{3} \sqrt{2\pi N_A \rho \left(\frac{e^2}{\epsilon_r k_B T} \right)^3} \quad (75)$$

where the numerical values for the constants were taken from PHREEQC [21]: Avogadro's constant $N_A = 6.022 \times 10^{23} \text{ mol}^{-1}$, electron charge $e = 4.803 \times 10^{-10} \text{ esu}$ and Boltzmann's constant $k_B = 1.38 \times 10^{-16} \text{ erg/K}$. To obtain the correct value for A^ϕ , the units of density must be kg/mL. Molar masses whenever needed were taken from the Pitzer database of PHREEQC [21]. The density of

pure water was taken from the correlation by Pátek et al. [46] and the relative permittivity from the correlation by Bradley and Pitzer [47]. The vapor phase
 490 is modeled with the Peng-Robinson equation of state [48].

3.1. Ammonia and carbon dioxide in water

Amine solutions can be utilized to capture carbon dioxide in an attempt to mitigate the greenhouse effect. Nevertheless, regeneration of amines requires high heat consumption and they can quickly degrade. To overcome these obsta-
 495 cles, ammonia solutions that could achieve high carbon dioxide capacity have been considered for the same purpose [49]. Xiao et al. [50] developed the KZ algorithm and applied it to the CPE of the aqueous ammonia/carbon dioxide system, encountered in industrial wastewater stream treatment. The volatile electrolytes and their ions react in the liquid phase according to the following
 500 reactions:

Methane and ethane were included in the analysis as inerts. All binary interaction parameters k_{ij} for the PR EoS were set to zero. The liquid phase is described by the Pitzer activity coefficient model [34] with the implementation presented in Edwards et al. [36]. The chemical equilibrium and Henry's
 505 constants were taken from Edwards et al. [36]. All solutes are considered non-volatile apart from ammonia and carbon dioxide. The inert hydrocarbons are insoluble in the liquid phase. Composition derivatives of activity coefficients are found by numerical differentiation. Table 2 compares the equilibrium solution of this work with the results of Xiao et al. [50].

Table 2: Vapor phase partial pressures, liquid phase molalities, phase amounts and phase fractions of the water/ammonia/carbon dioxide system at 373 K and 10 atm.

Component	Feed	Our work		Our work (++, -- interact)		Xiao et al. [50]	
		p_i (atm)	m_i (mol/kg)	p_i (atm)	m_i (mol/kg)	p_i (atm)	m_i (mol/kg)
H ₂ O	0.8473	0.9568	55.5062	0.9708	55.5062	0.9462	55.5550
NH ₃	0.0458	0.2544	0.8242	0.1863	0.5836	0.1543	0.6151
CO ₂	0.0458	2.1149	0.0240	1.5208	0.0176	1.8080	0.0183
CH ₄	0.0305	3.3370	0	3.6611	0	3.5457	0
C ₂ H ₆	0.0305	3.3370	0	3.6611	0	3.5457	0
H ⁺	0	0	3.29×10^{-8}	0	1.67×10^{-8}	0	5.34×10^{-8}
NH ₄ ⁺	0	0	1.8362	0	2.3436	0	2.2256
OH ⁻	0	0	3.84×10^{-5}	0	2.66×10^{-5}	0	4.61×10^{-5}
HCO ₃ ⁻	0	0	1.4167	0	2.0588	0	1.6712
CO ₃ ²⁻	0	0	0.0630	0	0.0863	0	0.1780
NH ₂ COO ⁻	0	0	0.2935	0	0.1121	0	0.1984
n_t (mol)	65.5084	5.9935	57.8034	5.4474	57.9161	–	–
β		0.0939	0.9061	0.0860	0.9140	–	–
I (mol/kg)		–	1.899	–	2.430	–	2.404

510 Xiao et al. [50] use a different equation of state, suitable for polar compounds. However, there is no explanation about the implementation of the activity coefficient model in the liquid phase, the parameters used or the correlations for the solvent properties. Following the instructions of Edwards et al. [36], like charges do not interact. This is achieved by setting the corresponding

 515 parameters equal to zero. If such interactions are allowed through the combining rules of Edwards et al. [36], our equilibrium solution appears to be closer to the results presented by Xiao et al. [50] (Table 2). This work is primarily concerned with the calculation of CPE and not with the models chosen to describe the phases. There was no further investigation why the results show

 520 these deviations. Given our implementation of the model, both the Lagrange multipliers and the modified RAND method could determine the equilibrium solution of this electrolyte system.

3.2. Carbon dioxide solubility

Storage of the carbon dioxide captured from various processes can take place
 525 inside geological formations. Carbon dioxide is injected into underground reser-
 voirs. Leaking of the gas back into the surface is prevented due to existence of a
 caprock (resistant rock). Experimental and modeling studies suggest that car-
 bonate minerals will react first with carbon dioxide. Precipitation takes place
 and it can decrease the porosity and permeability of the caprock, improving its
 530 robustness [51]. Carbon dioxide solubility was investigated for three distinct
 systems:

- CO₂ in pure water
- CO₂ in aqueous solution of CaCl₂ (different concentrations)
- CO₂ in 10.1% aqueous solution of CaCl₂ in the presence of CaCO₃

535 Calcium chloride can control the salinity of water, increasing the non-ideality
 of the aqueous phase. The full reaction scheme is:

The binary interaction parameters k_{ij} for the PR EoS were set to zero ex-
 cept for water/carbon dioxide that was set to 0.189 [52]. The liquid phase is
 described by the Pitzer activity coefficient model [34] with the implementation
 540 presented in Felmy et al. [35]. The reference chemical potentials were taken from
 Venkatraman et al. [6] and the Henry's constants from Duan and Sun [53]. All
 solutes are considered non-volatile apart from carbon dioxide. Calcium chloride
 exists only in the liquid phase as an undissociated solute. Calcium carbonate

exists in the liquid phase as an undissociated solute and as a pure solid phase.

545 Composition derivatives of activity coefficients are found by numerical differentiation. Calculations are compared with experimental data [54, 55] in Figures 1 to 3. Water/carbon dioxide ratio in the feed is always 2:1 for the calculations.

Carbon dioxide solubility in pure water in Figure 1 is determined without calcium chloride or calcium carbonate in the feed. Solubility is calculated as
550 the sum of carbon dioxide, bicarbonate and carbonate ions in the solution for different temperatures and a wide pressure range. Calculations can accurately capture the behavior of the experimental data. Relatively small ionic strengths are found at equilibrium due to the low concentration of the ions. Studying the system as a non-reaction mixture of water and carbon dioxide would yield very
555 similar solubilities for carbon dioxide, since the reactions do not progress much.

Including calcium chloride at different concentrations in the feed makes the system more complex and non-ideal (Figure 2). Experimental data are more sensitive to the calcium chloride concentrations than the temperature of the solution. Calculations predict higher dependence on temperature, since the
560 curves for constant calcium chloride concentration are more easily distinguishable compared with experimental data. As expected, lower solubilities are found at higher temperatures. However, in Figure 2 there are larger deviations between calculations and experimental data than the solubilities in pure water. High deviations between experimental data and calculations were also identified by Venkatraman et al. [6] that used the same model. The authors had
565 to tune binary and ternary parameters between carbon dioxide, calcium and chloride ions to obtain the desired results. Without regressing new parameters, calculations are not that sensitive to the calcium chloride concentration. As a result, at low concentrations there are under-predictions and at high concentrations over-predictions. The purpose of this work is not to model the behavior of
570 the systems in the most accurate way, but given a model, to produce the CPE solution of the electrolyte mixture. Ionic strengths are much higher, because the concentration of calcium chloride is high and its dissociation produces calcium and chloride ions.

Figure 1: Solubility of CO₂ (a, c) and ionic strength in water (b, d) [experimental data (points) and calculations (curves) at (a) 285.15 K (●, —), 291.15 K (■, - -), 298.15 K (▲, ····), 304.19 K (◆, - · - ·), 308.15 K (*, - · - ·), 313.15 K (×, ····), (b) 374.15 K (●, —), 393.15 K (■, - -)]

Figure 2: Solubility of CO₂ and ionic strength in CaCl₂ aqueous solutions: (a, b) 10.1%, (c, d) 20.2% and (e, f) 30.2% [experimental data (points) and calculations (curves) at 348.65 K (●, —), 349.15 K (■, - -), 374.15 K (▲, ···), 394.15 K (◆, - ·)].

575 Finally, calculations are made in the presence of both calcium chloride and
calcium carbonate in the solution. Comparison with experimental data is shown
in Figures 3. Experimental data and calculations with or without the solid
seem to lead to similar solubilities. There is no precipitation involved, the solid
is included in the feed and only a small amount is dissolved in the aqueous
580 phase. Calculations show that its presence influences the overall equilibrium
very little. Nevertheless, the pure solid phase is included in the calculations as
a separate distinct phase and there no problems observed as far as convergence
is concerned.

Figure 3: Solubility of CO_2 (a), ionic strength (b) and dissolved CaCO_3 (c) in 10.1% CaCl_2 aqueous solution [experimental data (points) and calculations (curves) at 393.15 K].

3.3. Multiple mineral phases

585 Leal et al. [7] has presented results for a system of three mineral phases at equilibrium with an aqueous and a vapor phase. The reactions occur between the solutes in the aqueous phase and the solid phases:

The binary interaction parameters k_{ij} for the PR EoS were set equal to zero except for water/carbon dioxide that was set equal to 0.19 [21]. The liquid phase is described by the Pitzer activity coefficient model [34] with the implementation presented in Felmy et al. [35]. The chemical equilibrium constants were taken from the Pitzer database of PHREEQC [21]. All solutes are considered non-volatile apart from carbon dioxide. Calcite, dolomite and quartz can only exist as pure solid phases. Composition derivatives of activity coefficients are found by numerical differentiation. No comparison is attempted with the results in Leal et al. [7]. We compare our results directly to PHREEQC for constant temperature and pressure specifications. Calculations are shown in Table 3. Figures 4 and 5 illustrate the absolute relative deviations of mole numbers and mole fractions from the calculations of PHREEQC.

Table 3: Equilibrium mole fractions, phase amounts and phase fractions in the three-mineral system at 298.15 K and 1 atm.

Component	Feed	V	L	Calcite	Dolomite	Quartz
H ₂ O	0.7324	0.0311	0.9786	0	0	0
CO ₂	0.0412	0.9689	5.18×10^{-4}	0	0	0
MgCO ₃	0	0	3.92×10^{-8}	0	0	0
H ₄ SiO ₄	9.74×10^{-7}	0	1.63×10^{-6}	0	0	0
Calcite	0.0132	0	0	1	0	0
Dolomite	0.0660	0	0	0	1	0
Quartz	0.1319	0	0	0	0	1
H ⁺	0	0	3.11×10^{-8}	0	0	0
Na ⁺	0.0064	0	0.0086	0	0	0
K ⁺	1.40×10^{-4}	0	1.87×10^{-4}	0	0	0
Ca ²⁺	1.41×10^{-4}	0	7.22×10^{-4}	0	0	0
Mg ²⁺	7.27×10^{-4}	0	5.61×10^{-4}	0	0	0
MgOH ⁺	0	0	1.56×10^{-10}	0	0	0
OH ⁻	0	0	2.44×10^{-10}	0	0	0
Cl ⁻	0.0075	0	0.0100	0	0	0
HCO ₃ ⁻	3.17×10^{-5}	0	2.86×10^{-4}	0	0	0
CO ₃ ²⁻	0	0	7.41×10^{-8}	0	0	0
HSO ₄ ⁻	0	0	8.72×10^{-9}	0	0	0
SO ₄ ²⁻	3.86×10^{-4}	0	5.17×10^{-4}	0	0	0
H ₃ SiO ₄ ⁻	0	0	3.98×10^{-10}	0	0	0
H ₂ SiO ₄ ²⁻	0	0	1.84×10^{-16}	0	0	0
n_t (mol)	75.7914	3.1890	56.6093	0.9465	5.0233	10.0000
β		0.0421	0.7471	0.0125	0.0663	0.1320
I (mol/kg)		–	0.7442	–	–	–

Figure 4: Deviations from PHREEQC for: (a) mole numbers of volatile solutes, (b) mole fractions of volatile solutes [vapor (■), liquid (▨)] and (c) mole numbers of solids.

Figure 5: Deviations from PHREEQC for the non-volatile solutes: (a) mole numbers, (b) mole fractions.

Results of this work are very close to PHREEQC with small deviations, proving that the solution determined is essentially the same. Modeling parameters were chosen as close to PHREEQC as possible. Feed composition in PHREEQC is a combination of kilograms, ppm and liters. In our method, we specify the feed as mole numbers. The conversion might lead to the small deviations. This can be seen for the sodium, potassium and chloride ions. These components are inerts and their mole numbers are constant at all iterations, but there are still some small deviations with PHREEQC (Figure 5). Finally, parameters ${}^E\theta(I)$ and ${}^E\theta'(I)$ in the Pitzer model were calculated from Eq. 47 in the work of Pitzer [56]. In PHREEQC, the Chebyshev approximation is used for the integrals in the higher-order electrostatic terms. These terms correspond to asymmetric interactions between like charges (cation-cation and anion-anion). The asymmetric interactions refer to ions that have different values of charges, e.g., between H^+ and Ca^{2+} or between OH^- and CO_3^{2-} .

3.4. Speed and convergence

CPU time can be used to assess the efficiency of an algorithm. The total time to initialize and solve the CPE of a system is presented in ms in Table 4. Although CPU time is necessary to support the claims of a fast algorithm, there are different factors that affect it. First, CPU time depends on the complexity of the thermodynamic model that calculates fugacity or activity coefficients and their derivatives. Simple models result in faster calculations while complicated models, especially with the use of numerical derivatives, can markedly slow down the calculations. Furthermore, the implementation of the method (e.g., solution of linear systems, matrix inversion, etc.) have an effect on CPU time. Finally, CPU time differs between hardware, computer language and compilers. The number of iterations, an additional index of efficiency, is shown in Figures 6 to 8. Iterations for the initialization procedure and the CPE calculation are shown. For the Lagrange multipliers method, iterations correspond to the outerloop, while the number of inner-loop (Newton) iterations per outer loop non-ideality update is also presented. Change of the error at each itera-

tion reveals the order of the convergence rate. The initialization [42, 43] and the modified RAND method are expected to have quadratic convergence rate, whereas the Lagrange multipliers method is expected to have linear convergence rate. Comparing the number of iterations of different methods is not enough to conclude about their efficiency. We must take into account the initial estimates and the convergence tolerance. Initial estimates close to the solution combined with high tolerance can lead to a small number of iterations and as a result, exaggerate the actual efficiency of the method. Finally, fewer iterations do not necessarily mean faster calculations. Iterations are not proportional to the CPU time. In the modified RAND method we expect fewer iterations due to the quadratic convergence rate but the inversion of matrices involved in the method is time-consuming.

- Ammonia and carbon dioxide in water

Xiao et al. [50] developed the KZ algorithm by modifying the S-C algorithm published by Sanderson and Chien [11]. The S-C algorithm follows the conventional stoichiometric approach using nested loops where phase equilibrium is solved in the inner loop with Rachford-Rice and reaction extents are updated in the outer loop. In the KZ algorithm the loops change: chemical equilibrium in the inner loop and phase equilibrium in the outer loop. Both algorithms are first-order methods.

There are no CPU time or iteration data in Xiao et al. [50]. However, we can expect fewer iterations in the KZ algorithm due to the high convergence tolerance. Xiao et al. calculated the K-factors of VLE as $K_i = y_i/x_i$ and the procedure stopped when $\sum_{i=1}^{N_C} (K_i^{\text{new}}/K_i - 1)^2 < 10^{-6}$. In our method, convergence was assumed when the error given by Eq. 11 is less than 10^{-10} . CPU times of the two algorithms in this work are comparable, with the combined algorithm being slightly faster. Use of analytical derivatives, would make the modified RAND method even faster and clearly more preferable for this system. In Figure 6 the observed convergence behavior is expected, with each algorithm requiring a sensible

number of iterations.

- Carbon dioxide in aqueous calcium chloride solution with solid calcium carbonate

Although the number of components is similar to the ammonia/carbon dioxide system, CPU time and iterations for the successive substitution algorithm are larger (Table 4 and Figure 7). However, a system with two liquid phases and a solid at 250 atm is highly non-ideal and requires more outer-loop fugacity and activity coefficient updates. The combined algorithm required 5 additional modified RAND iterations besides the 3 outer-loop updates of the Lagrange multipliers method in the beginning. These are relatively expensive iterations, since the CPU times between the two algorithms are comparable.

Oscillations were experienced with the Lagrange multipliers method for the 20.2% and 30.2% calcium chloride mixtures, where the method failed to converge. This could be attributed to the high ionic strength, therefore the high non-ideality of these solutions. Heidemann and Michelsen [57] have shown that for highly non-ideal systems, including electrolytes or polymers, successive substitution in phase equilibrium can fail to converge even with a good initial estimate. The CPE solution of such problems can be obtained with the combined algorithm when we reduce the number of the outer-loop updates in the Lagrange multipliers method (e.g. from three to one).

- Three-mineral system [7]

The only comparison possible for the CPU time is directly with PHREEQC, which required 179 ms to fully solve the three-mineral system. This is more than 195 times slower than the successive substitution algorithm and 38 times slower than the combined algorithm. The difference for the latter would be even larger if analytical derivatives of the Pitzer model were used instead of numerical central differences. Both algorithms required a small

number of steps to reach the solution, and the use of the modified RAND
method slightly reduced the total iterations.

Table 4: CPU time to obtain the equilibrium solution of the systems examined (SSA: successive substitution algorithm, CA: combined algorithm, processor: Intel®Core™ i7-7600U CPU@ 2.80 GHz).

System	T (K)	p (atm)	SSA (ms)	CA (ms)
H ₂ O/NH ₃ /CO ₂	373	10	0.398	0.391
H ₂ O/CO ₂ /CaCl ₂ /CaCO ₃	393.15	250	1.223	1.305
Three-mineral system	298.15	1	0.916	4.650

4. Conclusions

The non-stoichiometric Lagrange multipliers method and modified RAND method were recently presented for simultaneous CPE calculations in multiple phases. Both methods use the Lagrange multipliers or the elemental chemical potentials as independent variables, they are particularly suitable to systems with many reactions and multiple phases, and they were shown successful for non-electrolyte systems. In this study we have applied the two methods to multiphase chemical equilibrium in electrolyte systems. We prove that the overall electroneutrality constraint is implicitly satisfied if the material balance is met. Hence, no modification of the working equations is needed in either method when applied to electrolyte systems. Since electrolyte systems are often modeled with activity coefficient models using various reference states, precaution should be taken in the conversion between the reference states and the calculation of the composition derivatives of activity coefficients. Solid formation can be judged based on a simplified stability analysis criterion that involves the elemental chemical potentials. The two methods are used to construct a successive substitution algorithm (with only the first-order convergent Lagrange

Figure 6: Convergence in the water/ammonia/carbon dioxide system at 373 K and 10 atm: (a) successive substitution algorithm, (b) combined algorithm, (c) inner loop (Newton) iterations per outer loop update [initialization (—), vapor-liquid (---)].

Figure 7: Convergence in the water/carbon dioxide system with 10.1 % CaCl_2 in the presence of CaCO_3 at 393.15 K and 250 atm: (a) successive substitution algorithm, (b) combined algorithm, (c) inner loop (Newton) iterations per outer loop update [initialization (—), liquid-liquid-solid (---)].

Figure 8: Convergence in the three-mineral system at 298.15 K and 1 atm: (a) successive substitution algorithm, (b) combined algorithm, (c) inner loop (Newton) iterations per outer loop update [initialization (—), vapor-liquid-solid-solid-solid (---)].

multipliers method) and a combined algorithm (with both the Lagrange multipliers method and the second-order modified RAND method). The algorithms are tested with various highly non-ideal multiphase reactions in electrolyte systems, which always involve an aqueous electrolyte phase with an ordinary vapor or liquid phase, and up to three solid phases. The high non-ideality of the aqueous phase and the pure solid phases dissolving into or precipitating from the aqueous phase do not affect the convergence: the Lagrange multipliers method shows linear and the modified RAND quadratic convergence rate. The Gibbs energy can be monitored in the modified RAND method to control the convergence, because the material balance is always satisfied in its formulation. For the last complex geochemical reaction system with 21 components, 11 reactions and 5 phases (vapor, aqueous and three solid phases), the two algorithms converge smoothly and their speeds are much higher than PHREEQC. In the current study, numerical differentiation is used for the composition derivatives of the Pitzer model. This does not affect the overall iteration number but it increases the CPU time and can be improved in the future. The use of the Pitzer model is mainly for comparison with other geochemical calculations. Other more accurate and consistent models for electrolyte solutions can surely be adopted, since the algorithms discussed here are not bound to a particular model. Finally, the combined algorithm using both methods is recommended to robustly and efficiently solve the CPE in electrolyte systems.

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