Calculation of Phase and Chemical Equilibrium for Multiple Ion-Containing Phases Including Stability Analysis

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Abstract

A reactive flash algorithm based on the work of Gautam, Seider, White (Gautam and Seider, 1979a, 1979b, 1979c; White and Seider, 1981) and Barreau et al. (2006) is presented. The original algorithm minimizes the total Gibbs energy of the system with respect to an elemental material balance constraint and the overall system electroneutrality. In our approach, we perform the minimization taking into account the charge/electric potential contribution to the Gibbs energy to allow application to multiple electrolyte phases. Moreover, the composition derivatives of fugacity coefficients are not ignored in the derivation of the working equations. Finally, the need of the overall electroneutrality equation is discussed. The algorithm is applied to a demixing amine system (water/DEEA/MAPA) with carbon dioxide, modeled with eNRTL for both phases (Mouhoubi et al., 2020). At LLE, both phases are electroneutral, chemical reaction equilibrium is satisfied and phase equilibrium of each molecule and ion individually has been established. Stability analysis based on the electrochemical potential allows the determination of an electroneutral ion-containing phase. Although calculations are compared with experimental data, the purpose of the work was not the parameterization of the model, and therefore its accuracy is not addressed. Since our implementation of eNRTL did not satisfy the Gibbs-Duhem equation, its composition derivatives were incompatible with the algorithm and certain terms had to be ignored. Even though the algorithm is generally expected to converge quadratically, convergence in this work resembles the one of a partial Newton method due to the omitted derivative terms.

keywords: phase equilibrium, chemical equilibrium, flash algorithm, liquid-liquid equilibrium, electrolytes

1 Introduction

Electrolyte liquid-liquid equilibrium (LLE) has been studied in the literature for both aqueous (Peng et al., 1995; Riazi and Moshfeghian, 2009; Hamta et al., 2018; Bülow et al., 2019) and mixed solvent solutions (Govindarajan and Sabarathinam, 1995; Chou et al., 1998; Salabat and Hashemi, 2007; Simoni et al., 2009b; Simoni et al., 2009a). Applications of electrolyte mixtures that split into two liquid phases include protein separation and purification (Peng et al., 1995), metal ion recovery with solvent extraction (Liddell, 2005), systems with aminoacids or polymers with salts (Pazuki et al., 2008; Sadeghi and Jamehbozorg, 2009; Liu et al., 2019), ionic liquids (Riazi and Moshfeghian, 2009; Bülow et al., 2019), and water/oil/surfactant systems with surfactant dissociation (Riazi and Moshfeghian, 2009). Even in classical single liquid systems like miscible azeotropic mixtures (e.g. water/1-propanol), the presence of salts can introduce a liquid-liquid split (Maribo-Mogensen et al., 2015). The phase diagrams exhibit LLE with upper, lower or even no critical points (Peng et al., 1994). Up to three liquid phases at

equilibrium have also been reported (van Bochove et al., 2002). Finally, in polymer solutions we can expect LLE between two aqueous phases with polymer/salt systems exhibiting certain advantages over polymer/polymer systems (biocompatible, nontoxic, nonflammable, low viscosity, etc.) (Hamta et al., 2018).

In terms of thermodynamic modeling, there is still no general consensus on the best strategy in LLE. It is not straightforward to accurately describe simultaneously short- and long-range forces of charged particles, which inevitably leads to approximate theories. The most widely used models for electrolyte solutions appear to be Debye-Hückel (Pazuki et al., 2008), Pitzer (Peng et al., 1994; Salabat and Hashemi, 2007; Hao et al., 2016) and Pitzer-Debye-Hückel (Ingram et al., 2012; Hamta et al., 2018). When the models are applied to a mixed-solvent, its properties are estimated based on the properties of the pure solvents. Other more complex theories have been used for aqueous and mixed solvent solutions, such as NRTL/eNRTL (Ishidao et al., 2001; van Bochove et al., 2002; Simoni et al., 2007; Chen and Chen, 2008; Zafarani-Moattar et al., 2013), UNIQUAC/extended UNIQUAC (Simoni et al., 2008; Pirahmadi et al., 2010; Hamta et al., 2018; Liu et al., 2019), Wilson activity coefficient model (Chou et al., 1998; Salabat and Hashemi, 2007; Zafarani-Moattar et al., 2013; Zafarani-Moattar and Jafari, 2014), and LIQUAC/LIFAC (Kiepe et al., 2006). Apart from activity coefficient models, calculations with equations of state have also been published, such as PC-SAFT (Held et al., 2014; Mohammad et al., 2016a; Mohammad et al., 2016b) and eCPA with Peneloux translation (Maribo-Mogensen et al., 2015). LLE in polymer solutions with salts can be modeled with Fluory-Huggins combined with Debye-Hückel (Pazuki et al., 2008). The Othmer-Tobias correlation has been used only for estimating tie lines (Vakili-Nezhaad et al., 2004; Zafarani-Moattar et al., 2013). Furthermore, COSMO-RS with the electrolyte extension has been applied to solvent screening (Mohammad et al., 2016b).

Compared to VLE modeling, results in LLE systems are much more sensitive to the ionic strength of the phases, which affects the correct representation of chemical equilibrium in each phase. The behavior of complexes or ion pairs is not captured adequately by models that do not take into account chemical speciation (Liddell, 2005). Association models that implicitly incorporate speciation reactions, attempt to overcome this challenge. Approaches such as the SAFT-VR (Mac Dowell et al., 2010; Rodriguez et al., 2012) and the SAFT γ-SW (Rodriguez et al., 2012) have been successfully applied to the carbon dioxide capture using amine solutions (adsorption/desorption with e.g., MEA, DEA, AMP), providing a good match to the experimental data. When parameters in LLE are regressed only from VLE data, results are expected to be poor (Liddell, 2005). Although there have been studies for high molalities (Mohammad et al., 2016a), correlations still seem unsatisfactory in high salt content (Gomis et al., 2004). Experiments face challenges as well. Ion solvation might be slow, especially in mixed solvent solutions (Gomis et al., 2004) and small amounts of salts should be expected in organic phases (Chou et al., 1998; van Bochove et al., 2002; Chen and Chen, 2008; Hamta et al., 2018). In general, LLE data are scarce (Kiepe et al., 2006).

Despite the diversity of the published electrolyte LLE studies, the common focus is the description of the systems in terms of apparent compositions (e.g., partitioning of a salt between two phases). In this work we generalized a reactive flash algorithm for application to a system with multiple electrolyte phases by minimizing the Gibbs energy with the charge/electric potential contribution. Individual molecules and ions satisfy phase equilibrium, without constraining the analysis to a single salt or salts with different ions. Our purpose was to test an adequately complex system that exhibits an LLE split. The available system came from the work of Mouhoubi et al. (2020), who provided parameters for the eNRTL activity coefficient model. The working

equations and stability analysis are rigorously derived for a model that satisfies the Gibbs-Duhem equation and the composition derivatives of fugacity/activity coefficients are symmetric. Although the algorithm eventually convergences to two electroneutral liquid phases at equilibrium, the expected quadratic convergence behavior of the algorithm was not observed. The implementation of eNRTL that was used, does not satisfy the Gibbs-Duhem, therefore it is incompatible with the algorithm. The use of such models in Gibbs energy minimization is discussed.

2 Method

2.1 Electrostatic energy

To extend the procedure to phase equilibrium for individual ions, we need to take into account additional terms in the Gibbs energy differential. In phase α, it will include the charge/electric potential term:

$$dG^{\alpha} = -S^{\alpha}\,\mathrm{d}T + V^{\alpha}\mathrm{d}p + \sum_{i=1}^{N_C}\mu_i^{\alpha}\mathrm{d}n_i^{\alpha} + \psi^{\alpha}\mathrm{d}q^{\alpha} \qquad \alpha = 1,...,N_P \tag{1}$$

where i is the component, α the phase, q the charge and ψ the electric potential. Textbooks usually present the Gibbs energy of Eq. (1) with temperature, pressure, mole numbers and charges as natural variables (Michelsen and Mollerup, 2018). However, the new work term does not introduce any new natural variables (Alberty, 1997), since:

$$\mathrm{d}q^{\alpha} = F\sum_{i=1}^{N_C} z_i \mathrm{d}n_i^{\alpha} \qquad \alpha = 1,...,N_P \tag{2}$$

where F is the Faraday constant and z the relative charge. We cannot report Maxwell equations such as:

$$\left(\frac{\partial\psi^{\alpha}}{\partial n_i^{\alpha}}\right)_{T,p,n_{j\neq i}^{\alpha}} = \left(\frac{\partial\mu_i^{\alpha}}{\partial q^{\alpha}}\right)_{T,p,n_i^{\alpha}} \qquad i = 1,...,N_C \qquad \alpha = 1,...,N_P \tag{3}$$

because the charges are not natural variables. The notation "$n_{j\neq i}^{\alpha}$" means that we keep constant all n_j^{α} apart from n_i^{α}. Collecting all the coefficients of dn, we obtain:

$$dG^{\alpha} = -S^{\alpha}\,\mathrm{d}T + V^{\alpha}\mathrm{d}p + \sum_{i=1}^{N_C}\left(\mu_i^{\alpha} + z_i\psi^{\alpha}F\right)\mathrm{d}n_i^{\alpha} \qquad \alpha = 1,...,N_P \tag{4}$$

The term in the parenthesis is usually referred to as the "electrochemical potential", μ^{el}:

$$\mu_i^{\mathrm{el},\alpha} \equiv \mu_i^{\alpha} + z_i \psi^{\alpha} F \qquad i = 1,...,N_C \qquad \alpha = 1,...,N_P \tag{5}$$

The integrated form of a thermodynamic potential differential can be found with the help of Euler's theorem. In systems with PV work, the thermodynamic potentials are first-order homogeneous to their extensive variables. For the internal energy this means that, if:

$$\mathrm{d}U^{\alpha}\left(S,V,\mathbf{n}^{\alpha}\right) = \mathrm{d}U_{TS}^{\alpha} + \mathrm{d}U_{pV}^{\alpha} + \mathrm{d}U_{\mu n}^{\alpha} = T\mathrm{d}S^{\alpha} - p\mathrm{d}V^{\alpha} + \sum_i \mu_i^{\alpha}\mathrm{d}n_i^{\alpha} \qquad \alpha = 1,...,N_P \tag{6}$$

the integrated form of the internal energy would be:

$$U^{\alpha} = U_{TS}^{\alpha} + U_{pV}^{\alpha} + U_{\mu n}^{\alpha} \qquad \alpha = 1,...,N_P \tag{7}$$

According to Euler's theorem, the integrated function multiplied by the homogeneity degree will be given as the product of intensive/extensive variables. Since the internal energy is first-order homogeneous with respect to S, V and n_i, we have:

$$\begin{aligned} 1\times U_{TS}^{\alpha} &= TS^{\alpha} \\ 1\times U_{pV}^{\alpha} &= -pV^{\alpha} \\ 1\times U_{\mu n}^{\alpha} &= \sum_i \mu_i^{\alpha} n_i^{\alpha} \\ \alpha &= 1,...,N_P \end{aligned} \tag{8}$$

However, Sørensen and Compañ (1997) address the particularity of involving the $\psi \mathrm{d}q$ work term. The electrostatic energy must be given as:

$$U_{\psi q}^{\alpha} = \frac{1}{2} q^{\alpha} \psi^{\alpha} \qquad \alpha = 1,...,N_P \tag{9}$$

That would mean that the Euler's theorem resulted in the following integration:

$$2\times U_{\psi q}^{\alpha} = q^{\alpha} \psi^{\alpha} \qquad \alpha = 1,...,N_P \tag{10}$$

making the internal energy second-order homogenous with respect to the charge. This observation of Sørensen and Compañ is valid in the derivative potentials, such as the Gibbs energy used in this work. There are two direct consequences:

- We obtain the correct "Gibbs-Duhem" equations. This "situation of mixed Euler order" as mentioned by the authors, does not allow one generalized Gibbs-Duhem equation, but

two variation equations, one for each homogeneity degree. First- and second-order variables are included in different equations, given as

$$\begin{gathered} -S^{\alpha}\mathrm{d}T + V^{\alpha}\mathrm{d}p + \sum_{i=1}^{N_C} n_i^{\alpha}\mathrm{d}\mu_i^{\alpha} = 0 \\ \alpha = 1,...,N_P \end{gathered} \tag{11}$$

and

$$\begin{gathered} q^{\alpha}\mathrm{d}\psi^{\alpha} = \psi^{\alpha}\mathrm{d}q^{\alpha} \\ \alpha = 1,...,N_P \end{gathered} \tag{12}$$

Sørensen and Compañ explicitly stress the "confusion" in the literature about the correct integration of thermodynamic potentials and the resulting incorrect Gibbs-Duhem equation, which is usually presented as:

$$\begin{gathered} -S^{\alpha}\mathrm{d}T + V^{\alpha}\mathrm{d}p + \sum_{i=1}^{N_C} n_i^{\alpha}\mathrm{d}\left(\mu_i^{\alpha} + z_i\psi^{\alpha}F\right) = 0 \\ \alpha = 1,...,N_P \end{gathered} \tag{13}$$

- We obtain the correct expression for the Gibbs energy. In the work of Sørensen and Compañ, the integrated internal energy is given by:

$$U = TS - pV + \sum_{\alpha=1}^{N_P}\sum_{i=1}^{N_C}\mu_i^{\alpha}n_i^{\alpha} + \frac{1}{2}\sum_{\alpha=1}^{N_P}\psi^{\alpha}q^{\alpha} + ... \tag{14}$$

which results in the Gibbs energy being:

$$G = \sum_{\alpha=1}^{N_P}\sum_{i=1}^{N_C}\left(\mu_i^{\alpha} + \frac{1}{2}z_i\psi^{\alpha}F\right)n_i^{\alpha} \tag{15}$$

compared to the incorrect expression:

$$G = \sum_{\alpha=1}^{N_P}\sum_{i=1}^{N_C}\left(\mu_i^{\alpha} + z_i\psi^{\alpha}F\right)n_i^{\alpha} = \sum_{\alpha=1}^{N_P}\sum_{i=1}^{N_C}\mu_i^{\mathrm{el},\alpha}n_i^{\alpha} \tag{16}$$

Eventually, the partial molar Gibbs energy is given by:

$$\left(\frac{\partial G^{\alpha}}{\partial n_j^{\alpha}}\right)_{T,p,n_{i\neq j}^{\alpha}} = \frac{\partial}{\partial n_j^{\alpha}}\left[\sum_{i=1}^{N_C}\left(\mu_i^{\alpha} + \frac{1}{2} z_i \psi^{\alpha} F\right) n_i^{\alpha}\right]$$

$$= \mu_j^{\alpha} + \sum_{i=1}^{N_C} n_i^{\alpha}\left(\frac{\partial \mu_i^{\alpha}}{\partial n_j^{\alpha}}\right)_{T,p,n_{i\neq j}^{\alpha}} \tag{17}$$

$$+ \frac{1}{2} z_j \psi^{\alpha} F + \frac{1}{2}\left(\frac{\partial \psi^{\alpha}}{\partial n_j^{\alpha}}\right)_{T,p,n_{i\neq j}^{\alpha}} F \sum_{i=1}^{N_C} z_i n_i^{\alpha}$$

At constant temperature and pressure, Eq. (11) takes the form:

$$\sum_{i=1}^{N_C} n_i^{\alpha}\left(\frac{\partial \mu_i^{\alpha}}{\partial n_j^{\alpha}}\right)_{T,p,n_{i\neq j}^{\alpha}} = 0 \tag{18}$$

$$\alpha = 1,\ldots,N_P$$

The same procedure for Eq. (12) gives:

$$\left(\frac{\partial \psi^{\alpha}}{\partial n_j^{\alpha}}\right)_{T,p,n_{i\neq j}^{\alpha}} \sum_{i=1}^{N_C} z_i n_i^{\alpha} = z_j \psi^{\alpha} \tag{19}$$

$$j = 1,\ldots,N_C \qquad \alpha = 1,\ldots,N_P$$

Using Eq. (18) and (19) in Eq. (17), we obtain:

$$\left(\frac{\partial G^{\alpha}}{\partial n_i^{\alpha}}\right)_{T,p,n_{j\neq i}^{\alpha}} = \mu_i^{\alpha} + z_i \psi^{\alpha} F = \mu_i^{\mathrm{el},\alpha} \tag{20}$$

$$\alpha = 1,\ldots,N_P$$

In systems with charged components, equilibrium is established at the minimum of the Gibbs energy, where the partial molar Gibbs energies are equal between the phases. Alberty (1997) prefers to call the partial molar Gibbs energy "chemical potential" to be compatible with non-electrolyte analysis. In this work we will refer to the partial molar Gibbs energy as "electro-chemical potential" μ^{el} [Eq. (5)] to avoid ambiguities with the classical contribution (μ) given by a thermodynamic model.

The separation of μ^{el} into μ and an electric term must be addressed. First, Michelsen and Mollerup (2018) present the electrochemical potential μ^{el} of this work under the Helmholtz natural variables with the symbol μ_j^{ec} and as a combination of different contributions:

$$\mu_j^{ec} = \mu_j^{c}\left(T,V,n\right) + \mu_j^{self}\left(\varepsilon,q_j\right) + \mu_j^{el}\left(T,V\varepsilon,\mathbf{q}\right) + \mu_j^{dip}\left(T,V,\varepsilon,\mathbf{q}\right) + z_j F\psi \tag{21}$$

starting with the classical contribution μ_j^c, the energy of charging each ion in the solution μ_j^{self}, the background potential energy μ_j^{el} and the dipole-ion interactions μ_j^{dip}. Thermodynamic modeling of the excess Gibbs/Helmholtz energy uses charges and potentials to describe the non-ideality in such mixtures, but the last term ($z_jF\psi$) is not included in the models implicitly. It is the work term that was initially included in the internal energy differential. Second, according to Denbigh (1981) and Guggenheim (1986), the measurement of a potential ψ difference between phases makes sense only when the phases have identical compositions, to exclude the influence of the chemical work. Otherwise, the authors claim that this separation is arbitrary and does not have a physical meaning. A calculated value of $\Delta\psi$ based on our analysis does not correspond to a measurable quantity. The only thermodynamic requirement is the equality of μ^{el} at equilibrium. Nevertheless, ψ differences have been identified experimentally in the literature (Haynes et al., 1991).

The classical term μ is given by:

$$\mu_i^\alpha = \mu_i^{\mathrm{ref}} + RT \ln \frac{x_i^\alpha \hat{\varphi}_i^\alpha p}{f_i^{\mathrm{ref}}} \qquad i = 1,...,N_C \qquad \alpha = 1,...,N_P \tag{22}$$

and its composition derivatives are:

$$\left(\frac{\partial \mu_i^\alpha}{\partial n_j^\alpha} \right)_{T,p,n_{i\neq j}^\alpha} = \frac{\delta_{ij}}{n_i^\alpha} - \frac{1}{n^\alpha} + \left(\frac{\partial \ln \hat{\varphi}_i^\alpha}{\partial n_j^\alpha} \right)_{T,p,n_{i\neq j}^\alpha} \qquad i = 1,...,N_C \qquad j = 1,...,N_C \qquad \alpha = 1,...,N_P \tag{23}$$

where δ_{ij} is the Kronecker delta and the phase amounts are found as the sum of mole numbers:

$$n^\alpha = \sum_{i=1}^{N_C} n_i^\alpha \qquad \alpha = 1,...,N_P \tag{24}$$

Second-order composition derivatives of the Gibbs energy (Maxwell relations) result in symmetric composition derivatives of μ^{el}:

$$\frac{\partial^2 G}{\partial n_j^\alpha \partial n_i^\alpha} = \frac{\partial^2 G}{\partial n_i^\alpha \partial n_j^\alpha} \tag{25}$$

or:

$$\left(\frac{\partial \mu_i^{\mathrm{el},\alpha}}{\partial n_j^\alpha} \right)_{T,p,n_{i\neq j}^\alpha} = \left(\frac{\partial \mu_j^{\mathrm{el},\alpha}}{\partial n_i^\alpha} \right)_{T,p,n_{j\neq i}^\alpha} \qquad i = 1,...,N_C \qquad j = 1,...,N_C \qquad \alpha = 1,...,N_P \tag{26}$$

Differentiating Eq. (5), we get:

$$\left(\frac{\partial \mu_i^\alpha}{\partial n_j^\alpha}\right)_{T,p,n_{i\neq j}^\alpha} + z_i F\left(\frac{\partial \psi^\alpha}{\partial n_j^\alpha}\right)_{T,p,n_{i\neq j}^\alpha} = \left(\frac{\partial \mu_j^\alpha}{\partial n_i^\alpha}\right)_{T,p,n_{j\neq i}^\alpha} + z_j F\left(\frac{\partial \psi^\alpha}{\partial n_i^\alpha}\right)_{T,p,n_{j\neq i}^\alpha} \qquad (27)$$

$$i = 1,...,N_C \qquad j = 1,...,N_C \qquad \alpha = 1,...,N_P$$

It must be mentioned that Alberty (1997) uses ψ as a constant and resorts to a Legendre transform to make ψ a (natural) variable of a different thermodynamic potential. Sørensen and Compañ (1997) have considered an additional constant external ψ, as a "pseudo first-order" term in the context of Euler's theorem. In our analysis we use only the internal ψ that arises from the solution charges, which could be a function of mole numbers. Therefore, we do not eliminate ψ composition derivatives.

The term μ should behave the same whether $\psi = 0$ or $\psi \neq 0$:

$$\left(\frac{\partial \mu_i^\alpha}{\partial n_j^\alpha}\right)_{T,p,n_{i\neq j}^\alpha} = \left(\frac{\partial \mu_j^\alpha}{\partial n_i^\alpha}\right)_{T,p,n_{j\neq i}^\alpha} \qquad (28)$$

$$i = 1,...,N_C \qquad j = 1,...,N_C \qquad \alpha = 1,...,N_P$$

This has a direct consequence on the derivatives of fugacity coefficients, which must be symmetric as well:

$$\left(\frac{\partial \ln \hat{\varphi}_i^\alpha}{\partial n_j^\alpha}\right)_{T,p,n_{i\neq j}^\alpha} = \left(\frac{\partial \ln \hat{\varphi}_j^\alpha}{\partial n_i^\alpha}\right)_{T,p,n_{j\neq i}^\alpha} \qquad (29)$$

$$i = 1,...,N_C \qquad j = 1,...,N_C \qquad \alpha = 1,...,N_P$$

Therefore, Eq. (27) becomes:

$$z_i F\left(\frac{\partial \psi^\alpha}{\partial n_j^\alpha}\right)_{T,p,n_{i\neq j}^\alpha} = z_j F\left(\frac{\partial \psi^\alpha}{\partial n_i^\alpha}\right)_{T,p,n_{j\neq i}^\alpha} \qquad (30)$$

$$i = 1,...,N_C \qquad j = 1,...,N_C \qquad \alpha = 1,...,N_P$$

2.2 Gibbs energy minimization

The equilibrium state corresponds to the minimum of the Gibbs energy. For constant temperature, we can minimize the equivalent reduced Gibbs energy:

$$Q = \frac{G}{RT} = \sum_{\alpha=1}^{N_P}\sum_{i=1}^{N_C}\left(\frac{\mu_i^\alpha}{RT} + \frac{1}{2} z_i \pi^\alpha\right) n_i^\alpha = \sum_{\alpha=1}^{N_P}\sum_{i=1}^{N_C}\frac{\mu_i^\alpha n_i^\alpha}{RT} + \frac{1}{2F}\sum_{\alpha=1}^{N_P}\pi^\alpha q^\alpha \qquad (31)$$

where:

$$\pi^{\alpha} = \frac{\psi^{\alpha} F}{RT} \tag{32}$$

The purpose of this derivation is to generalize the equations shown in Gautam, Seider and White (Gautam and Seider, 1979a, 1979b, 1979c; White and Seider, 1981) which were also used in Barreau et al. (2006). The final system of equations is similar to the one of the modified RAND method(White et al., 1958; Tsanas et al., 2017a; Paterson et al., 2018; Medeiros et al., 2021). Function Q is linearized truncating after the second term of a Taylor expansion around the current estimate of mole numbers:

$$Q(\mathbf{n}) = Q^0 + \sum_{\alpha=1}^{N_P}\sum_{i=1}^{N_C} \left.\frac{\partial Q}{\partial n_i^{\alpha}}\right|_{\mathbf{n}^0} \Delta n_i^{\alpha} + \frac{1}{2}\sum_{\alpha=1}^{N_P}\sum_{i=1}^{N_C}\sum_{\beta=1}^{N_P}\sum_{q=1}^{N_C} \left.\frac{\partial^2 Q}{\partial n_i^{\alpha}\partial n_q^{\beta}}\right|_{\mathbf{n}^0} \Delta n_i^{\alpha}\Delta n_q^{\beta} \tag{33}$$

where:

$$\Delta n_i^{\alpha} = n_i^{\alpha} - n_i^{0,\alpha} \tag{34}$$

Superscript 0 denotes the current estimate of mole numbers, chemical potentials, etc. In the expansion of the terms in Eq. (33), we make use of μ symmetric derivatives [Eq. (28), (29)], the classical Gibbs-Duhem equation [Eq. (18)] and the consequence of the symmetric μ^{el} derivatives [Eq. (30)]. The approximation of function Q becomes:

$$\begin{aligned} Q(\mathbf{n}) = Q^0 &+ \sum_{\alpha=1}^{N_P}\sum_{i=1}^{N_C}\left(\frac{\mu_i^{\alpha,0}}{RT} + z_i\pi^{\alpha}\right)\Delta n_i^{\alpha} + \frac{1}{2}\sum_{\alpha=1}^{N_P}\sum_{i=1}^{N_C}\frac{\left(\Delta n_i^{\alpha}\right)^2}{n_i^{\alpha,0}} \\ &- \frac{1}{2}\sum_{\alpha=1}^{N_P}\frac{\left(\Delta n^{\alpha}\right)^2}{n^{\alpha,0}} + \frac{1}{2}\sum_{\alpha=1}^{N_P}\sum_{i=1}^{N_C}\sum_{q=1}^{N_C} n_i^{\alpha} n_q^{\alpha} \left.\frac{\partial \ln \hat{\varphi}_i^{\alpha}}{\partial n_q^{\alpha}}\right|_{\mathbf{n}^0} \\ &+ \frac{1}{F}\sum_{\alpha=1}^{N_P}\sum_{i=1}^{N_C}\left.\frac{\partial \pi^{\alpha}}{\partial n_i^{\alpha}}\right|_{\mathbf{n}^0}\left(\frac{1}{2}q^{\alpha} n_i^{\alpha} - q^{\alpha,0} n_i^{\alpha} + \frac{1}{2}q^{\alpha,0} n_i^{\alpha,0}\right) \end{aligned} \tag{35}$$

In the last two terms of Eq. (35), the composition derivatives are calculated at the current estimate $\mathbf{n}^0$. In the publications of Gautam, Seider and White (Gautam and Seider, 1979a, 1979b, 1979c; White and Seider, 1981) derivatives of fugacity coefficients are completely ignored in the derivatives of the chemical potential. Such an approach is a "partial Newton's method", because only a part of the full second-order derivatives is utilized. A partial Newton's method has the advantage of simpler implementation, but it requires more iterations to converge compared with the full Newton's method.

The approximation of function Q is minimized under an elemental material balance constraint:

$$\mathbf{A}\sum_{\alpha=1}^{N_P}\mathbf{n}^{\alpha} = \mathbf{b} \tag{36}$$

The elemental material balance states that the amount of the chemical elements cannot change due to reaction. The methods that minimize the Gibbs energy with respect to an elemental

material balance are called non-stoichiometric (Smith and Missen, 1982). In such cases there is no need of explicitly specifying which reactions take place in the system. In the presence of a constraint, the Lagrangian of the system is defined as:

$$\mathcal{L}\left(\mathbf{n},\boldsymbol{\lambda}\right)=Q\left(\mathbf{n}\right)-\boldsymbol{\lambda}^{\mathrm{T}}\left(\mathbf{A}\sum_{\alpha=1}^{N_P}\mathbf{n}^{\alpha}-\mathbf{b}\right) \tag{37}$$

At the minimum:

$$\begin{aligned}&\frac{\partial\mathcal{L}}{\partial n_i^{\alpha}}=0 && \frac{\partial\mathcal{L}}{\partial\lambda_j}=0\\ &i=1,\ldots,N_C && j=1,\ldots,N_E\\ &\alpha=1,\ldots,N_P\end{aligned} \tag{38}$$

or:

$$\begin{aligned}\frac{\partial\mathcal{L}}{\partial n_i^{\alpha}}=\frac{\mu_i^{\alpha,0}}{RT}+z_i\pi^{\alpha}+\frac{n_i^{\alpha}}{n_i^{\alpha,0}}-\frac{n^{\alpha}}{n^{\alpha,0}}+\sum_{q=1}^{N_C}n_q^{\alpha}\left.\frac{\partial\ln\hat{\varphi}_q^{\alpha}}{\partial n_i^{\alpha}}\right|_{\mathbf{n}^0}\\ +\left.\frac{\partial\psi^{\alpha}}{\partial n_i^{\alpha}}\right|_{\mathbf{n}^0}\left(q^{\alpha}-q^{\alpha,0}\right)-\sum_{j=1}^{N_E}A_{ji}\lambda_j=0\\ i=1,\ldots,N_C\qquad\alpha=1,\ldots,N_P\end{aligned} \tag{39}$$

and

$$\begin{aligned}\frac{\partial\mathcal{L}}{\partial\lambda_j}=-\sum_{\alpha=1}^{N_P}\sum_{i=1}^{N_C}A_{ji}n_i^{\alpha}+b_j=0\\ j=1,\ldots,N_E\end{aligned} \tag{40}$$

Throughout the calculations, we keep the phase charges equal to 0. We note:

- Eq. (31) reduces to the classical Gibbs energy. The values of the Gibbs energy are not affected by the values of ψ^{α}. Every phase charge is kept at 0 and the electric term vanishes without contributing to the Gibbs energy itself. However, the values of ψ^{α} affect the ion phase equilibrium.
- The coefficients of the ψ^{α} composition derivatives in Eq. (35) and (39) are always a function of charge (current or initial estimate of charge). These terms can be ignored when the phase charge is always kept at 0.

At equilibrium, the current estimate should be approaching the next estimate:

$$\frac{\mu_i^{\alpha,0}}{RT}\to\frac{\mu_i^{\alpha}}{RT}\qquad\frac{n_i^{\alpha}}{n_i^{\alpha,0}}\to 1\qquad\frac{n^{\alpha}}{n^{\alpha,0}}\to 1 \tag{41}$$

Since the terms with the derivatives are eliminated in Eq. (39) due to the Gibbs-Duhem equation, we obtain:

$$\frac{\mu_i^{\alpha}}{RT} + z_i \pi^{\alpha} = \frac{\mu_i^{\mathrm{el},\alpha}}{RT} = \sum_{j=1}^{N_E} A_{ji} \lambda_j$$
$$i = 1, ..., N_C \qquad \alpha = 1, ..., N_P \tag{42}$$

Eq. (42) shows that the reduced μ^{el} at equilibrium will be given by the appropriate linear combination of the Lagrange multipliers. The Lagrange multipliers at equilibrium represent the chemical potential of the elements which were chosen in the formula matrix **A**. Since their values are phase-independent, the corresponding electrochemical potentials at equilibrium are the same for all phases. When the distribution of the ions is not uniform between the different solvent media (phases), ψ^{α} are in principle different (Haynes et al., 1991; Michelsen and Mollerup, 2018). Consequently, different ψ^{α} would result in different μ. It is necessary to remember that the equilibrium criterion is based on μ^{el} and not on μ.

Isolating the mole numbers from Eq. (39), we get:

$$\mathbf{n}^{a} = \mathbf{n}^{\alpha,0} u^{\alpha} + \left(\mathbf{M}^{\alpha}\right)^{-1} \left(\mathbf{A}^{\mathrm{T}} \boldsymbol{\lambda} - \frac{\boldsymbol{\mu}^{\alpha,0}}{RT} - \pi^{\alpha} \mathbf{z} \right)$$
$$\alpha = 1, ..., N_P \tag{43}$$

where:

$$u^{\alpha} \equiv \frac{n^{\alpha}}{n^{\alpha,0}}$$
$$\alpha = 1, ..., N_P \tag{44}$$

and

$$M_{iq}^{\alpha} \equiv \frac{\delta_{iq}}{n_i^{\alpha,0}} + \left. \frac{\partial \ln \hat{\varphi}_i^{\alpha}}{\partial n_q^{\alpha}} \right|_{\mathbf{n}^0}$$
$$i = 1, ..., N_C \qquad q = 1, ..., N_C \tag{45}$$

Matrix $\mathbf{M}^{\alpha}$ satisfies:

$$\sum_{i=1}^{N_C} \left(M_{ij}^{\alpha} \right)^{-1} = n_j^{\alpha}$$
$$j = 1, ..., N_C \tag{46}$$

Eq. (43) is substituted in Eq. (40) to obtain:

$$\left[\mathbf{A} \sum_{\alpha=1}^{N_P} \left(\mathbf{M}^{\alpha} \right)^{-1} \mathbf{A}^{\mathrm{T}} \right] \boldsymbol{\lambda} + \mathbf{C}\boldsymbol{\pi} + \mathbf{B}\mathbf{u} = \mathbf{b} + \mathbf{A} \sum_{\alpha=1}^{N_P} \left(\mathbf{M}^{\alpha} \right)^{-1} \frac{\boldsymbol{\mu}^{\alpha,0}}{RT} \tag{47}$$

where:

$$B_i^\alpha \equiv \sum_{j=1}^{N_C} A_{ij} n_j^{\alpha,0}$$
$$i = 1,...,N_E \qquad \alpha = 1,...,N_P \tag{48}$$

and

$$C_i^\alpha \equiv -\sum_{j=1}^{N_C}\sum_{q=1}^{N_C} A_{ij} \left(M_{jq}^\alpha\right)^{-1} z_q$$
$$i = 1,...,N_E \qquad \alpha = 1,...,N_P \tag{49}$$

The mole numbers must satisfy two additional equations. First, a relevant subset of the phases $N_P^{\mathrm{el}} < N_P$ must be electroneutral (for more details, see section 2.4):

$$\mathbf{z}^{\mathrm{T}}\mathbf{n}^\alpha = 0$$
$$\alpha = 1,...,N_P^{\mathrm{el}} \tag{50}$$

Eq. (43) is substituted in Eq. (50) to obtain:

$$\mathbf{C}^{\mathrm{T}}\boldsymbol{\lambda} + \mathrm{diag}(\mathbf{s})\boldsymbol{\pi} = \mathbf{r} \tag{51}$$

where:

$$s^\alpha \equiv \sum_{i=1}^{N_C}\sum_{j=1}^{N_C} z_i z_j \left(M_{ij}^\alpha\right)^{-1}$$
$$\alpha = 1,...,N_P \tag{52}$$

and

$$r^\alpha \equiv -\sum_{i=1}^{N_C}\sum_{j=1}^{N_C} z_i \left(M_{ij}^\alpha\right)^{-1}\left(\mu_j^{\alpha,0}/RT\right)$$
$$\alpha = 1,...,N_P \tag{53}$$

Second, the sum of the mole numbers in all phases must be equal to the phase amount:

$$\sum_{i=1}^{N_C} n_i^\alpha = n^\alpha$$
$$\alpha = 1,...,N_P \tag{54}$$

Eq. (43) is substituted in Eq. (54) to obtain:

$$\left(\mathbf{B}^\alpha\right)^{\mathrm{T}}\boldsymbol{\lambda} = d^\alpha$$
$$\alpha = 1,...,N_P \tag{55}$$

where:

$$d^{\alpha} \equiv \frac{1}{RT}\sum_{i=1}^{N_C} n_i^{\alpha,0}\mu_i^{\alpha,0} \qquad \alpha = 1,...,N_P \tag{56}$$

Eq. (47), (51) and (55) are combined in a system of equations with unknowns the Lagrange multipliers, the reduced electric potentials and variables *u*:

$$\begin{bmatrix} \mathbf{A}\sum_{\alpha=1}^{N_P}\left(\mathbf{M}^{\alpha}\right)^{-1}\mathbf{A}^{\mathrm{T}} & \mathbf{C} & \mathbf{B} \\ \mathbf{C}^{\mathrm{T}} & \mathrm{diag}(\mathbf{s}) & \mathbf{0} \\ \mathbf{B}^{\mathrm{T}} & \mathbf{0} & \mathbf{0} \end{bmatrix} \begin{bmatrix} \boldsymbol{\lambda} \\ \boldsymbol{\pi} \\ \mathbf{u} \end{bmatrix} = \begin{bmatrix} \mathbf{b} + \mathbf{A}\sum_{\alpha=1}^{N_P}\left(\mathbf{M}^{\alpha}\right)^{-1}\left(\boldsymbol{\mu}^{\alpha,0}/RT\right) \\ \mathbf{r} \\ \mathbf{d} \end{bmatrix} \tag{57}$$

The dimensions of the system are $N_E + N_P^{\mathrm{el}} + N_P$.

2.3 Formula matrix, reactions and electroneutrality

In stoichiometric methods the Gibbs energy is minimized with respect to reaction extents, whereas in non-stoichiometric methods, the Gibbs energy is minimized under the material balance constraint (Smith and Missen, 1982). We can view a reactive system either from the perspective of the elements or the reactions. When working on a system of N_C components, we must make one of the following decisions:

1. Our system can be described by N_E independent entities (elements). The elements are used to define the formula matrix **A** and they can be interpreted as building blocks of the components. Assuming the number of elements, we implicitly acknowledge that a number of $N_R = N_C - N_E$ equilibrium reactions must take place in our system. It is not necessary to know these reactions to solve with a non-stoichiometric method.
2. Our system can be described by N_R linearly independent reactions. The reactions are collected in the stoichiometric matrix **N**, which includes the stoichiometric coefficients of all components in all the reactions. Stoichiometric coefficients are negative for reactants, positive for products and zero for inerts. Assuming the number of reactions, we implicitly acknowledge that there are $N_E = N_C - N_R$ independent entities (elements) in the system. It is not necessary to know these elements to solve with a stoichiometric method.

As Smith and Missen (1982) have pointed out, the two problems are not independent. The two matrices must satisfy:

$$\mathbf{AN} = \mathbf{0} \tag{58}$$

For a given **A** matrix, we can find infinite consistent **N** matrices from Eq. (58) and vice versa. Matrix **N** is the null space of matrix **A** and any appropriate method can be used for this calculation. Some studies (Smith and Missen, 1982) begin their analysis by listing the reactions in the system, but instead of using Eq. (58) to directly extract a consistent **A** matrix from the given **N** matrix, they construct matrix **A** themselves. However, **A** and **N** are not independent, therefore

we must make sure that the selected **A** matrix actually corresponds to the reactions we wish to equilibrate. First, the number of elements must be given by:

$$N_E = N_C - N_R \tag{59}$$

Examples in Smith and Missen (1982) begin with setting chemical elements as elements. To demonstrate an issue with blindly following such an approach, we find in the literature the synthesis of MTBE from isobutene and methanol:

$$i\text{-}\mathrm{C_4H_8} + \mathrm{CH_4O} \rightleftharpoons \mathrm{C_5H_{12}O} \tag{60}$$

If the formula matrix was built directly from chemical elements, we would have:

$$\mathbf{A} = \begin{array}{c|ccc|} & i\text{-}\mathrm{C_4H_8} & \mathrm{CH_4O} & \mathrm{C_5H_{12}O} & \\ \hline & 4 & 1 & 5 & \mathrm{C} \\ & 8 & 4 & 12 & \mathrm{H} \\ & 0 & 1 & 1 & \mathrm{O} \\ \hline \end{array} \tag{61}$$

According to Eq. (59), we would end up satisfying $N_R = N_C - N_E = 3-3 = 0$ reactions. This of course does not correspond to the original system we intended to solve for. A correct formula matrix would include 2 elements for the 3 components, so that we can satisfy $N_R = N_C - N_E = 3-2 = 1$ reactions at equilibrium:

$$\mathbf{A} = \begin{array}{c|ccc|} & i\text{-}\mathrm{C_4H_8} & \mathrm{CH_4O} & \mathrm{C_5H_{12}O} & \\ \hline & 1 & 0 & 1 & i\text{-}\mathrm{C_4H_8} \\ & 0 & 1 & 1 & \mathrm{CH_4O} \\ \hline \end{array} \tag{62}$$

The following remark is relevant only in ion-containing systems. When we construct ourselves the formula matrix, we can potentially separate it in an atomic part (chemical elements, combination of chemical elements) and a row of the component charges (considering the electrons as additional elements):

$$\mathbf{A} = \begin{bmatrix} \mathbf{A}_{\text{atom}} \\ \mathbf{z}^{\mathrm{T}} \end{bmatrix} \tag{63}$$

The charge row corresponds to the overall electroneutrality constraint: the total charge of the system. Overall electroneutrality is implicitly satisfied in two cases:

- constructing a formula matrix with chemical elements: if the oxidation number of the atoms is the same in all components, the charge row in Eq. (63) is not needed. A proof for an equivalent statement is mentioned in Tsanas et al. (2019): if a constant charge can be assigned to the elements, the total system electroneutrality is unnecessary. The oxidation number is used here as the "apparent" charge of the atom.
- constructing a stoichiometric matrix with the desired reactions: if the reactions are balanced in terms of atoms and charges, then a consistent formula matrix can be determined from Eq. (58) and the charge row is implicitly included.

Satisfying the overall electroneutrality means that:

$$\operatorname{rank}\left(\begin{bmatrix}\mathbf{A}_{\text{atom}}\\ \mathbf{z}^{\mathrm{T}}\end{bmatrix}\right)=\operatorname{rank}(\mathbf{A}_{\text{atom}}) \tag{64}$$

When we specify chemical elements as elements, but the oxidation number of the atoms changes, then the charge must be included as an element. To demonstrate the necessity of the charge element, assume the following redox reaction:

$$\mathrm{Fe}^{3+}+\mathrm{V}^{2+}\rightleftharpoons\mathrm{Fe}^{2+}+\mathrm{V}^{3+} \tag{65}$$

We identify the components and the chemical elements of the system. The formula matrix with only chemical elements is:

$$\mathbf{A}=\begin{array}{cccc:c} \mathrm{Fe}^{2+} & \mathrm{Fe}^{3+} & \mathrm{V}^{2+} & \mathrm{V}^{3+} & \\ \hline 1 & 1 & 0 & 0 & \mathrm{Fe}\\ 0 & 0 & 1 & 1 & \mathrm{V}\end{array} \tag{66}$$

This formula matrix will satisfy $N_R=N_C-N_E=4-2=2$ reactions at equilibrium, and one consistent reaction set is:

$$\begin{aligned}\mathrm{Fe}^{3+}&\rightleftharpoons\mathrm{Fe}^{2+}\\ \mathrm{V}^{2+}&\rightleftharpoons\mathrm{V}^{3+}\end{aligned} \tag{67}$$

which is not physical, because it is not electrically balanced. The correct formula matrix must include the charge, to satisfy $N_R=N_C-N_E=4-3=1$ reaction at equilibrium.

$$\mathbf{A}=\begin{array}{cccc:c} \mathrm{Fe}^{2+} & \mathrm{Fe}^{3+} & \mathrm{V}^{2+} & \mathrm{V}^{3+} & \\ \hline 1 & 1 & 0 & 0 & \mathrm{Fe}\\ 0 & 0 & 1 & 1 & \mathrm{V}\\ 2 & 3 & 2 & 3 & z\end{array} \tag{68}$$

For some readers this discussion might appear trivial. However, others may start their analysis by specifying their elements instead of their reactions. For a reaction scheme found in the literature of $N_R^{\text{literature}}$ reactions that has $N_C^{\text{literature}}$ components, the reader needs only $N_C^{\text{literature}}$ and their chemical formulas to define a formula matrix in terms of chemical elements. We want to stress that it is important to verify that $N_E^{\text{defined}}=N_C^{\text{literature}}-N_R^{\text{literature}}$. Otherwise, the reader will not satisfy the same chemical equilibrium that inspired their study.

In our work, we construct the formula matrix with chemical elements and make sure they correspond to the literature reactions. The separation of the formula matrix into an atomic part and a charge row was done only for demonstration purposes. If the charges need to be included in the formula matrix, they are treated as regular elements. In all equations, they appear as A_{ji} and not as z_i (j is the charge row).

2.4 Electric potential

As mentioned earlier, ψ^{α} does not affect the value of the Gibbs energy when the phases are kept electroneutral. In the system of Eq. (57) we always determine Lagrange multipliers for all elements (N_E) and variables u for all phases (N_P). However, enforcing electroneutrality [Eq. (50)] is not necessary for every phase. Only the relevant phases (N_P^{el}) must be included in the equations for the determination of π. We note the following for the determination of the electric potential:

- electroneutrality of a single electrolyte phase is enforced by the material balance and its ψ can be arbitrary.

When the overall electroneutrality is satisfied by the formula matrix, the single ion-containing phase is electroneutral due to the material balance. In this phase, ions take part only in chemical equilibrium. Any consistent stoichiometric matrix to the formula matrix [Eq. (58)]:

$$\mathbf{N} = f\left(\mathbf{A}\right) \tag{69}$$

must satisfy the charge balance as well:

$$\mathbf{N}^{\mathrm{T}}\mathbf{z} = 0 \tag{70}$$

The condition of chemical equilibrium based on μ^{el} is:

$$\mathbf{N}^{\mathrm{T}}\left(\boldsymbol{\mu}^{\alpha} + \mathbf{z}\,\psi^{\alpha}F\right) = 0 \tag{71}$$

or

$$\mathbf{N}^{\mathrm{T}}\boldsymbol{\mu}^{\alpha} = -\mathbf{N}^{\mathrm{T}}\mathbf{z}\,\psi^{\alpha}F \tag{72}$$

Using Eq. (70), the right-hand-side of Eq. (72) is zero for any value of ψ:

$$\mathbf{N}^{\mathrm{T}}\boldsymbol{\mu}^{\alpha} = 0 \tag{73}$$

which is the condition of chemical equilibrium in non-electrolyte systems, based on μ. Therefore, the first ion-containing phase should be excluded from the calculation of π in Eq. (57). Of course, the same phase is included for the calculation of u.

- non-ionic phases that are always electroneutral (e.g. vapor, solids) are not included in the system of Eq. (57) for the calculation of π.

- values of ψ are required for the second phase with ionic species and each ion-containing phase after that.

An arbitrary value of ψ for the first ion-containing phase will affect the ψ in any subsequent ion-containing phase. However, the different $\Delta\psi$ at equilibrium depend on the equilibrium distribution of ions and will be the same.

2.5 Stability analysis

Stability analysis in non-electrolyte systems is based on the minimization of the reduced tangent plane distance:

$$tpd\left(\mathbf{w}\right)=\frac{1}{RT}\sum_{i=1}^{N_C}w_i\left[\mu_i\left(\mathbf{w}\right)-\mu_i\left(\mathbf{x}\right)\right] \tag{74}$$

where **x** is the composition of the feed phase and **w** the composition of the trial phase. If we can find a trial phase composition that results in a negative tangent plane distance, a phase split is thermodynamically favored. When a phase does not contain charges, stability analysis is performed as an unconstrained minimization of the modified *tpd* shown by Michelsen (1982).

Michelsen's method in electrolyte mixtures might lead to accumulation of charges during iterations, because compositions are allowed to vary independently during minimization. This subsequently leads to numerical issues either in the calculation of activity coefficients or solving the linear systems of the modified *tpd* minimization. When ions exist in the trial phase, we employ a different method. The problem is defined in terms of μ^{el} [Eq. (5)], and we need to minimize:

$$\begin{aligned}&\min_{\mathbf{w}} tpd\left(\mathbf{w}\right)=\frac{1}{RT}\sum_{i=1}^{N_C}w_i\left[\mu_i^{\mathrm{el}}\left(\mathbf{w}\right)-\mu_i^{\mathrm{el}}\left(\mathbf{x}\right)\right]\\&\text{s.t.}\sum_{i=1}^{N_C}w_i=1\end{aligned} \tag{75}$$

In this section, our previous observations are still valid and details will be omitted for brevity:

- ψ of the trial and feed phase does not affect the value of the *tpd* as long as we keep the trial phase electroneutral.
- in the working equations, due to electroneutrality being met at each iteration, terms with composition derivatives of ψ vanish.

The Lagrangian is:

$$\mathcal{L}\left(\mathbf{w},\lambda_w\right)=tpd\left(\mathbf{w}\right)-\lambda_w\left(\sum_{i=1}^{N_C}w_i-1\right) \tag{76}$$

We define:

$$t_i=\ln w_i+\ln\hat{\varphi}_i\left(\mathbf{w}\right)-d_i+1 \tag{77}$$

with:

$$d_i=\ln x_i+\ln\hat{\varphi}_i\left(\mathbf{x}\right)+z_i\pi_x \tag{78}$$

At the minimum, the Lagrangian gradients are zero:

$$t_i + z_i\pi_w - \lambda_w = 0 \qquad i = 1,...,N_C \qquad\qquad \sum_{i=1}^{N_C} w_i - 1 = 0 \tag{79}$$

For the first iterations, we use a successive substitution method as initialization, similar to the approach in Tsanas et al. (2017b). Eq. (79) becomes:

$$\ln w_i = d_i + \lambda_w - \ln\hat{\varphi}_i\left(\mathbf{w}\right) - z_i\pi_w - 1 \tag{80}$$

We keep the fugacity coefficients constant. For the Lagrange multiplier and π of the trial phase as independent variables, we have:

$$\frac{\partial w_i}{\partial \lambda_w} = w_i \qquad\qquad \frac{\partial w_i}{\partial \pi_w} = -z_i w_i \tag{81}$$

In a nested-loop approach, we solve in the inner loop the equations:

$$\sum_{i=1}^{N_C} w_i = 1 \tag{82}$$

and

$$\sum_{i=1}^{N_C} z_i w_i = 0 \tag{83}$$

or equivalently:

$$\begin{bmatrix} \sum_{i=1}^{N_C} w_i^0 & -\sum_{i=1}^{N_C} z_i w_i^0 \\ -\sum_{i=1}^{N_C} z_i w_i^0 & \sum_{i=1}^{N_C} z_i^2 w_i^0 \end{bmatrix} \begin{bmatrix} \lambda_w \\ \pi_w \end{bmatrix} = \begin{bmatrix} 1 - \sum_{i=1}^{N_C} w_i^0 \\ \sum_{i=1}^{N_C} z_i w_i^0 \end{bmatrix} \tag{84}$$

Mole fractions are updated by Eq. (80). In the outer loop, the fugacity coefficients are updated and we enter the inner loop again. For a second-order approach, we base our analysis on the modified RAND method (White et al., 1958; Tsanas et al., 2017a; Paterson et al., 2018; Medeiros et al., 2021). The modified RAND method itself is not used here. What we use is a similar derivation strategy as the modified RAND, to take advantage of the constraints in the minimization of *tpd*. We linearize Eq. (77) and substitute it in Eq. (82) and (83). We obtain:

$$\mathbf{t}^0 + \mathbf{M}^w\Delta\mathbf{w} + \mathbf{z}\pi_w - \mathbf{e}_{N_C}\lambda_w = 0 \tag{85}$$

$$\sum_{i=1}^{N_C} \Delta w_i = 1 - \sum_{i=1}^{N_C} w_i^0 \tag{86}$$

and

$$\sum_{i=1}^{N_C} z_i \Delta w_i = -\sum_{i=1}^{N_C} z_i w_i^0 \tag{87}$$

with

$$M_{iq}^{w} \equiv \frac{\delta_{iq}}{w_i^0} + \left.\frac{\partial \ln \hat{\varphi}_i}{\partial w_q}\right|_{\mathbf{n}^0} \tag{88}$$

Eq. (85) becomes:

$$\Delta \mathbf{w} = \left(\mathbf{M}^{w}\right)^{-1} \left(\mathbf{e}_{N_C} \lambda_w - \mathbf{z}\pi_w - \mathbf{t}^0\right) \tag{89}$$

By substituting Eq. (89) in (86) and (87), and taking into account that:

$$\begin{gathered} \sum_{i=1}^{N_C} \left(M_{ij}^{w}\right)^{-1} = w_j \\ j = 1, \ldots, N_C \end{gathered} \tag{90}$$

we have the final system of the second-order method:

$$\begin{bmatrix} \sum_{i=1}^{N_C} w_i^0 & -\sum_{i=1}^{N_C} z_i w_i^0 \\ -\sum_{i=1}^{N_C} z_i w_i^0 & \sum_{i=1}^{N_C}\sum_{j=1}^{N_C} z_i M_{ij}^{w} z_j \end{bmatrix} \begin{bmatrix} \lambda_w \\ \pi_w \end{bmatrix} = \begin{bmatrix} 1 - \sum_{i=1}^{N_C} w_i^0 + \left(\mathbf{M}^{w}\right)^{-1} \mathbf{t}^0 \\ \sum_{i=1}^{N_C} z_i w_i^0 + \mathbf{z}^{\mathrm{T}} \left(\mathbf{M}^{w}\right)^{-1} \mathbf{t}^0 \end{bmatrix} \tag{91}$$

After solving the system, updates of the mole fractions are calculated from Eq. (89). Michelsen (1982) incorporated a single linear constraint in the *tpd* objective function. This gave rise to a simpler problem: the unconstrained minimization of the modified *tpd*. In our work, we solve the full constrained minimization with two linear constraints. Refinements can follow to match the simplicity and efficiency of Michelsen's work. Nevertheless, the contribution of this study is the inclusion of the electroneutrality constraint, which is necessary when searching for a phase split to an ion-containing phase.

2.6 Algorithm

The system in Eq. (57) is solved iteratively. Then, the values of λ, π, and u are substituted in Eq. (43) to obtain the new estimates of the mole numbers. In the next iteration, the matrix and vector of Eq. (57) are updated with the new mole numbers. The procedure repeats until the error:

$$\text{error} = \sqrt{\sum_{\alpha=1}^{N_P}\sum_{i=1}^{N_C}\left(\frac{\mu_i^{\alpha}}{RT} + z_i \pi^{\alpha} - \sum_{j=1}^{N_E} A_{ji}\lambda_j\right)^2} \tag{92}$$

becomes less than a tolerance. The step must be controlled by the following equation:

$$\begin{gathered} n_i^\alpha = n_i^{\alpha,0} + \omega \Delta n_i^\alpha \\ i = 1,...,N_C \qquad \alpha = 1,...,N_P \end{gathered} \tag{93}$$

to avoid negative mole numbers or accepting a step that increases the Gibbs energy. Default value of ω is 1 and when the step is not acceptable, ω is halved.

Since the method is numerical, an initial estimate is necessary. Guessing a good starting value is not straightforward, therefore an initialization procedure is employed. Initialization is performed by solving the original system of Eq. (57) considering constant fugacity coefficients (composition derivatives of fugacity coefficients are ignored). The chemical potentials are found during initialization by:

$$\frac{\mu_i^\alpha}{RT} = \text{const}_i^\alpha + \ln x_i^\alpha \tag{94}$$

where:

$$\text{const}_i^\alpha = \frac{\mu_i^{\text{ref}}}{RT} + \ln \frac{\hat{\varphi}_i^\alpha p}{f_i^{\text{ref}}} \tag{95}$$

The fugacity coefficients are calculated based on the composition in the feed. The thermodynamic model is therefore called only once per phase in Eq. (95) and the chemical potential will depend only on the logarithm of the mole fractions. The solution of the initialization corresponds to the equilibrium of a hypothetical system, where the equilibrium fugacity coefficients are equal to the ones assumed initially.

In principle, we could begin calculations with a multiphase system. However, to increase reliability, a single phase is initially assumed. The initial estimate is refined with the initialization procedure and then the Gibbs energy is minimized for the single phase. Finally, stability analysis is used to identify convergence to a local minimum. If stability analysis detects a phase split, the new phase is included in the system and a new minimization is attempted. Initialization is not called again. The procedure is repeated until stability cannot identify any further phase split (stable system).

2.7 Violation of the Gibbs-Duhem theorem

In our work we minimize the Gibbs energy of a multiphase system with the charge contribution. Without loss of generality, we ignore this contribution in this section for simplicity:

$$\begin{gathered} G = \sum_{\alpha=1}^{N_P} \sum_{i=1}^{N_C} n_i^\alpha \mu_i^\alpha \\ \text{s.t. } \mathbf{A} \sum_{\alpha=1}^{N_P} \mathbf{n}^\alpha = \mathbf{b} \end{gathered} \tag{96}$$

Apart from the satisfaction of the material balance, at the minimum:

$$\nabla_{\mathbf{n}^\alpha} G^\alpha = \mathbf{A}^{\mathrm{T}} \boldsymbol{\lambda}$$
$$\alpha = 1, ..., N_P \tag{97}$$

Any root-finding method can be used to solve Eq. (97), and if it converges successfully, the conditions at the minimum will be met. Given that the equations correspond to a minimum, if we use a method that satisfies the constraints at each iteration (feasible region), the procedure becomes much safer. Compared to direct root-finding, minimization methods allow the monitoring of the objective function. If the function increases in the current iteration, we can intervene to rectify ascent directions or simply avoid overstepping the solution.

The gradient of the Gibbs energy based on the thermodynamic definition is:

$$\left(\frac{\partial G}{\partial n_i^\alpha} \right)_{T,p,n_{j\neq i}^\alpha} = \mu_i^\alpha \tag{98}$$

and based on the direct differentiation of Eq. (96):

$$\left(\frac{\partial G}{\partial n_i^\alpha} \right)_{T,p,n_{j\neq i}^\alpha} = \mu_i^\alpha + \sum_{j=1}^{N_C} n_j^\alpha \left(\frac{\partial \mu_j^\alpha}{\partial n_i^\alpha} \right)_{T,p,n_{j\neq i}^\alpha} \tag{99}$$

According to the Gibbs-Duhem equation [Eq. (18)], the summation in Eq. (99) is zero and the gradient matches the one of Eq. (98). However, when the thermodynamic model does not satisfy the Gibbs-Duhem equation, the summation term persists. This creates the following problems:

1. If we want to satisfy the familiar equations of chemical and phase equilibrium, the gradients should be found from Eq. (98). The solution does not correspond to the minimum of Eq. (96), since we did not use the real gradients [Eq. (99)]. Consequently, the method becomes less safe, because we cannot expect a descent direction at every iteration.
2. If we want to minimize Eq. (96), the gradients should be found from Eq. (99). However, at the minimum we do not satisfy familiar thermodynamic conditions. In other words, phase equilibrium would not correspond to the equality of the chemical potentials, but the real gradients from Eq. (99).

Derivations in section 2.2 use the conditions of the symmetric fugacity coefficient derivatives and the Gibbs-Duhem equations. These allow the simplification of the working equations to the system of Eq. (57). A consequence of the Gibbs-Duhem is:

$$\sum_{i=1}^{N_C} M_{ij}^\alpha n_i^\alpha = 1 \Leftrightarrow \sum_{i=1}^{N_C} \left(M_{ij}^\alpha \right)^{-1} = n_j^\alpha$$
$$j = 1, ..., N_C \tag{100}$$

Similar considerations apply to stability analysis in section 2.5, which appears to be even more susceptible, given that the objective function combines two sets of chemical potentials [Eq. (75)]. In this work, we used the eNRTL model that was first published by Chen and Evans (1986) and is also implemented in the ASPEN Plus process simulator. Activity coefficients from this implementation of eNRTL violate the Gibbs-Duhem equation: both Pitzer-Debye-

Hückel and Born terms consider the solvent as a pseudo-pure component and no composition derivatives in density or dielectric constant are included. Different issues appear in the NRTL term as well. Equations and relevant comments are included in the Appendix. When our algorithm converges using these equations of eNRTL, the electrochemical potentials are equal in all phases and they satisfy chemical equilibrium. Unfortunately, strictly speaking, this is not the minimum of the objective function for the reasons mentioned above.

Finally, such modeling can create ambiguities in the analytical expression of the Gibbs energy. This is supposed to be given by:

$$G = \sum_{\alpha=1}^{N_P} \sum_{i=1}^{N_C} \left(\frac{\partial G}{\partial n_i^\alpha} \right)_{T,p,n_{j\neq i}^\alpha} n_i^\alpha \tag{101}$$

Differentiating Eq. (101) should yield back those derivative terms in the summations. As we have seen, this is not the case when the Gibbs-Duhem equation is not satisfied. No further analysis will be attempted in this work about such models. For more information about the violation of Gibbs-Duhem and eNRTL, we suggest the studies of Bollas et al. (2008), Chang and Lin (2020).

3 Results and discussion

3.1 System and parameters

To test the algorithm on the equilibrium of multiple electrolyte phases, we select the demixing amine system of water, DEEA, MAPA and carbon dioxide (Mouhoubi et al., 2020), described by the following set of reactions:

$$\begin{aligned}
2H_2O &\rightleftharpoons H_3O^+ + OH^- \\
2H_2O + CO_2 &\rightleftharpoons H_3O^+ + HCO_3^- \\
HCO_3^- + H_2O &\rightleftharpoons H_3O^+ + CO_3^{2-} \\
DEEAH^+ + H_2O &\rightleftharpoons DEEA + H_3O^+ \\
MAPAH^+ + H_2O &\rightleftharpoons MAPA + H_3O^+ \\
H^+MAPAH^+ + H_2O &\rightleftharpoons MAPAH^+ + H_3O^+ \\
MAPA + HCO_3^- &\rightleftharpoons MAPACOO^- + H_2O
\end{aligned} \tag{102}$$

Water, DEEA and MAPA are solvents, and the remaining components are solutes. Solvents follow the pure saturated liquid reference state, while solvents the infinite dilution reference state. In the current LLE calculations, vapor pressures and Henry's constants are not reported, as they eventually cancel out from the equations. The influence of the Poynting correction was ignored for all components.

Mouhoubi et al. (2020) modeled this system with eNRTL (as further detailed in the Appendix) and determined binary and ternary interaction parameters using VLE data. No LLE data were included in the regressions. In our work, the necessary thermodynamic properties to calculate equilibrium are:

- eNRTL parameters, dielectric constants for DEEA, MAPA (modification due to different reference temperature) (Mouhoubi et al., 2020)
- water dielectric constant (Khodakovskii and Dorofeeva, 1981)
- water density (Le Blanchon Bouhelec, 2006)
- DEEA, MAPA densities (Pinto et al., 2014a)
- formation properties (reference state chemical potentials) (Arshad et al., 2016)
- H_3O^+ formation properties were extracted from the value of K_w (Bandura and Lvov, 2005), while being consistent with the formation properties of water and OH^- reported in (Arshad et al., 2016)

Table 1: Constants for dielectric constant and density correlations for the solvents [Eq. (A 7)].

		Water	DEEA	MAPA
Dielectric constant	A	88.399	24.756	11.804
	B	33174.2	8992.68	4411.8
	T_{ref} (K)		273.15	
Density (mol/L)	A	4.9669	0.8050	2.0410
	B	0.27788	0.29387	0.41787
	C	647.13	592.0	599.0
	D	0.1874	0.28237952	0.37282388

Table 2: Formation properties of H_3O^+ (infinite dilution mole fraction-based), as extracted from K_w (Bandura and Lvov, 2005).

ΔG (kJ/mol)	ΔH (kJ/mol)
-216.996	-289.294

3.2 Apparent compositions

Experimental data in electrolyte systems are not always presented with speciation. Properties or phase splits can be reported with the apparent molecular compositions, despite the existence of ions at equilibrium. Apparent components take a similar meaning to the elements in a non-stoichiometric method: they are the reaction invariant independent entities which are sufficient to define the equilibrium state of the system. If the overall content of those apparent species is given, we have enough information to determine the compositions of the true species through chemical equilibrium. In our work, we specify through the feed composition the elemental amounts in vector **b** [Eq. (36)]. Although vector **b** does not represent the equilibrium composition, it carries sufficient information to eventually calculate it. In multiphase systems, **b** vectors can be found for every phase [Eq. (48)**Erreur ! Source du renvoi introuvable.**]. These only show us the partitioning of the elements between the phases. Consequently, to reveal the true compositions, we need to solve single-phase chemical equilibrium for each individual phase.

In contrast to our work, apparent compositions are not usually reported in terms of chemical elements, but preferably in terms of the few molecules that dissociate to produce the ions. Manually, it would be possible to calculate the apparent composition of e.g., carbon dioxide based on the carbon balance as:

$$\hat{n}_{CO_2} = n_{CO_2} + n_{HCO_3^-} + n_{CO_3^{2-}} + n_{MAPACOO^-} \tag{103}$$

where the symbol $\hat{n}$ corresponds to apparent mole numbers. Manual calculation is however tedious and error-prone. We can take advantage of the formula matrix to automate the calculation of the required apparent compositions. The steps to follow are:

1. Select N_E components in the system as the desired apparent components.
2. Modify the formula matrix **A** by moving the columns of the apparent components to the front. Columns of the formula matrix represent components, while rows represent elements.
3. Calculate the reduced row echelon form of the modified formula matrix as:

$$\hat{\mathbf{A}} = \begin{bmatrix} \mathbf{I} & \mathbf{A}' \end{bmatrix} \tag{104}$$

   This new formula matrix corresponds to an equivalent definition of the system (same equilibrium solution) where component 1 is element 1, component 2 is element 2, etc. The remaining part of new formula matrix is simply what remains after the row operations to obtain this form.

4. Calculate the apparent mole numbers as:

$$\hat{n}_i^{\alpha} = \sum_j^{N_C} \hat{A}_{ji} n_i^{\alpha} \qquad i = 1, ..., N_E \tag{105}$$

5. Normalize the apparent mole numbers to obtain system-size independent compositions.

It is worth mentioning that the concise statement "component 1 is element 1" is misleading. The mole numbers of the components change due to reaction, but this is not true for the elements. When a component is defined as an element, these two share only chemical formulas, not properties. The elements in non-stoichiometric methods are in general abstract entities that do not need to be tangible (e.g., actual chemical elements). Therefore, the apparent composition of water in a reactive system means the composition of the element "H_2O". Real water molecules in the system react and their mole numbers change.

For the current system, the transpose formula and modified formula matrices are presented:

$$\mathbf{A}^{T} = \begin{array}{cccccc} \text{C} & \text{H} & \text{O} & \text{N} & z & \\ \hline 0 & 2 & 1 & 0 & 0 & \text{H}_2\text{O} \\ 6 & 15 & 1 & 1 & 0 & \text{DEEA} \\ 4 & 12 & 0 & 2 & 0 & \text{MAPA} \\ 1 & 0 & 2 & 0 & 0 & \text{CO}_2 \\ 0 & 3 & 1 & 0 & 1 & \text{H}_3\text{O}^+ \\ 6 & 16 & 1 & 1 & 1 & \text{DEEAH}^+ \\ 4 & 13 & 0 & 2 & 1 & \text{MAPAH}^+ \\ 4 & 14 & 0 & 2 & 2 & \text{H}^+\text{MAPAH}^+ \\ 0 & 1 & 1 & 0 & -1 & \text{OH}^- \\ 1 & 1 & 3 & 0 & -1 & \text{HCO}_3^- \\ 1 & 0 & 3 & 0 & -2 & \text{CO}_3^{2-} \\ 5 & 11 & 2 & 2 & -1 & \text{MAPACOO}^- \end{array} \tag{106}$$

and:

$$\hat{\mathbf{A}}^{T} = \begin{array}{ccccccc} \text{H}_2\text{O} & \text{DEEA} & \text{MAPA} & \text{CO}_2 & \text{H}_3\text{O}^+ & & \\ \hline 1 & 0 & 0 & 0 & 0 & \text{H}_2\text{O} \\ 0 & 1 & 0 & 0 & 0 & \text{DEEA} \\ 0 & 0 & 1 & 0 & 0 & \text{MAPA} \\ 0 & 0 & 0 & 1 & 0 & \text{CO}_2 \\ 0 & 0 & 0 & 0 & 1 & \text{H}_3\text{O}^+ \\ -1 & 1 & 0 & 0 & 1 & \text{DEEAH}^+ \\ -1 & 0 & 1 & 0 & 1 & \text{MAPAH}^+ \\ -2 & 0 & 1 & 0 & 2 & \text{H}^+\text{MAPAH}^+ \\ 2 & 0 & 0 & 0 & -1 & \text{OH}^- \\ 2 & 0 & 0 & 1 & -1 & \text{HCO}_3^- \\ 3 & 0 & 0 & 1 & -2 & \text{CO}_3^{2-} \\ 1 & 0 & 1 & 1 & -1 & \text{MAPACOO}^- \end{array} \tag{107}$$

Note that the last column of the transpose formula and modified formula matrices are the same. As a result, element H_3O^+ in the modified formula matrix corresponds to the charge and its apparent composition will always be 0. Only the apparent compositions of water, DEEA, MAPA and carbon dioxide are presented in the following section.

3.3 Comparison with experimental data and convergence

LLE data were obtained in apparent compositions and compared to equilibrium calculations (Figure 1). Pinto et al. (2014b) reported the concentrations (mol/L) of the four molecules at different carbon dioxide partial pressures. For the feed of the reactive flash for each experimental point we calculated the average experimental composition of the two liquid phases

(midpoint of the experimental tie-line, Table 3) as the safest feed that could lead to an LLE split. The partial pressure of carbon dioxide in the original publication of Pinto et al. was not used. No vapor phase was identified by stability analysis, so no CO_2 partial pressure was calculated.

Table 3: Experimental mole fractions and feed of calculations at 313.15 K.

Exp. point number	Aqueous phase (Pinto et al., 2014b)				Organic phase (Pinto et al., 2014b)				Feed in calculations			
	H_2O	DEEA	MAPA	CO_2	H_2O	DEEA	MAPA	CO_2	H_2O	DEEA	MAPA	CO_2
1	0.591	0.023	0.197	0.189	0.257	0.728	0.011	0.005	0.424	0.376	0.104	0.097
2	0.526	0.031	0.222	0.221	0.281	0.699	0.011	0.010	0.403	0.365	0.116	0.116
3	0.554	0.041	0.197	0.208	0.295	0.683	0.010	0.012	0.425	0.362	0.103	0.110
4	0.564	0.041	0.191	0.204	0.308	0.667	0.012	0.013	0.436	0.354	0.101	0.109
5	0.567	0.051	0.181	0.200	0.290	0.676	0.016	0.018	0.429	0.364	0.098	0.109
6	0.503	0.086	0.188	0.223	0.279	0.692	0.010	0.019	0.391	0.389	0.099	0.121
7	0.552	0.073	0.172	0.204	0.304	0.653	0.016	0.026	0.428	0.363	0.094	0.115
8	0.558	0.078	0.164	0.201	0.330	0.615	0.022	0.034	0.444	0.346	0.093	0.117

The model (eNRTL) was parametrized in Mouhoubi et al. (2020) fitting only VLE experimental data. Using exactly the same set of parameters, our algorithm was able to identify a liquid-liquid split when applied directly at the experimental LLE conditions mentioned in Pinto et al. (2014b). In Figure 1, the biggest deviations are found for the apparent DEEA in the aqueous phase. Additionally, in the organic phase, the trend between the first two experimental points for water and DEEA disagrees with the trend of the calculations. It must be stressed that the accuracy of the model is not the purpose of this work. We intended to demonstrate the feasibility of electrolyte LLE calculations with a non-stoichiometric algorithm. Nevertheless, given that the parameters of Mouhoubi et al. (2020) came from VLE data regressions, the algorithm converged to a reasonable description of the two liquid phases. The VLE parameters seem to capture the experimental behavior to some extent.

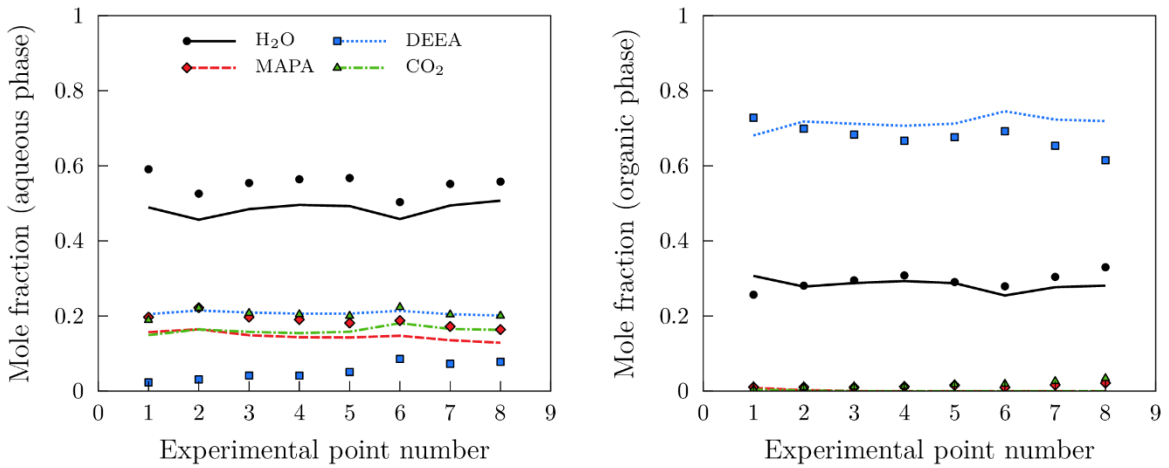
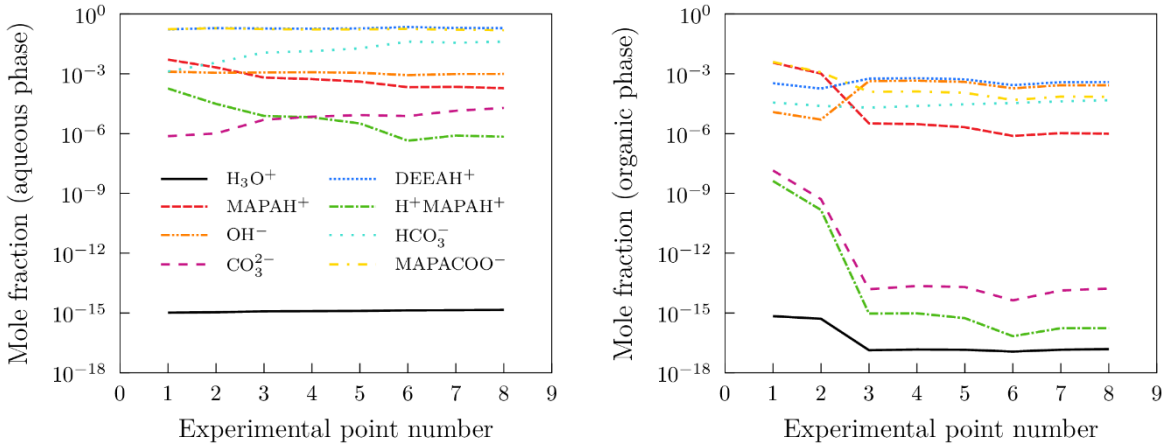


Figure 1: Comparison of experimental and calculated apparent compositions at 313.15 K and 1 bar (experimental data: points, calculations: lines).

In Figure 2 the true mole fractions of the ions in each phase are presented. It is evident that the aqueous phase has a much higher content of ions than the organic phase. The aqueous phase has a higher dielectric constant, and as a result dissociation is favored. Modeling the LLE of the demixing amine system is necessary to obtain more meaningful description of the speciation.



(a) (b)

Figure 2: Composition of ions at 313.15 K and 1 bar.

In Figure 3, the ionic strength, the total relative charge and the potential difference are shown for both liquid phases. Ionic strength is found as:

$$I_x^\alpha = \frac{1}{2}\sum_i^{N_C} z_i^2 x_i^\alpha \tag{108}$$

and the absolute value of the relative charge as:

$$\left|z_{\text{tot}}^\alpha\right| = \left|\sum_i^{N_C} z_i x_i^\alpha\right| \tag{109}$$

As shown in Figure 2, Figure 3(a) and (b) illustrate that both phases contain non-negligible amounts of charged species. The ionic strengths are above 0.1 for the aqueous phase and above 0.0001 for the organic phase. However, the total charge of both phases is close to machine precision. This is the most direct validation that the algorithm has converged to the expected set of phases: the two phases contain molecules and ions individually at equilibrium, but they remain electroneutral. Furthermore, potential differences between the phases are shown in Figure 3(c). Although we cannot directly compare our potentials with any experimental data (Denbigh, 1981; Guggenheim, 1986), we can find measured values of potentials in Haynes et al. (1991) for a different system: salt concentration up to 1 mM in PEG/Dextran solutions resulted in potentials up to 7-8 mV.

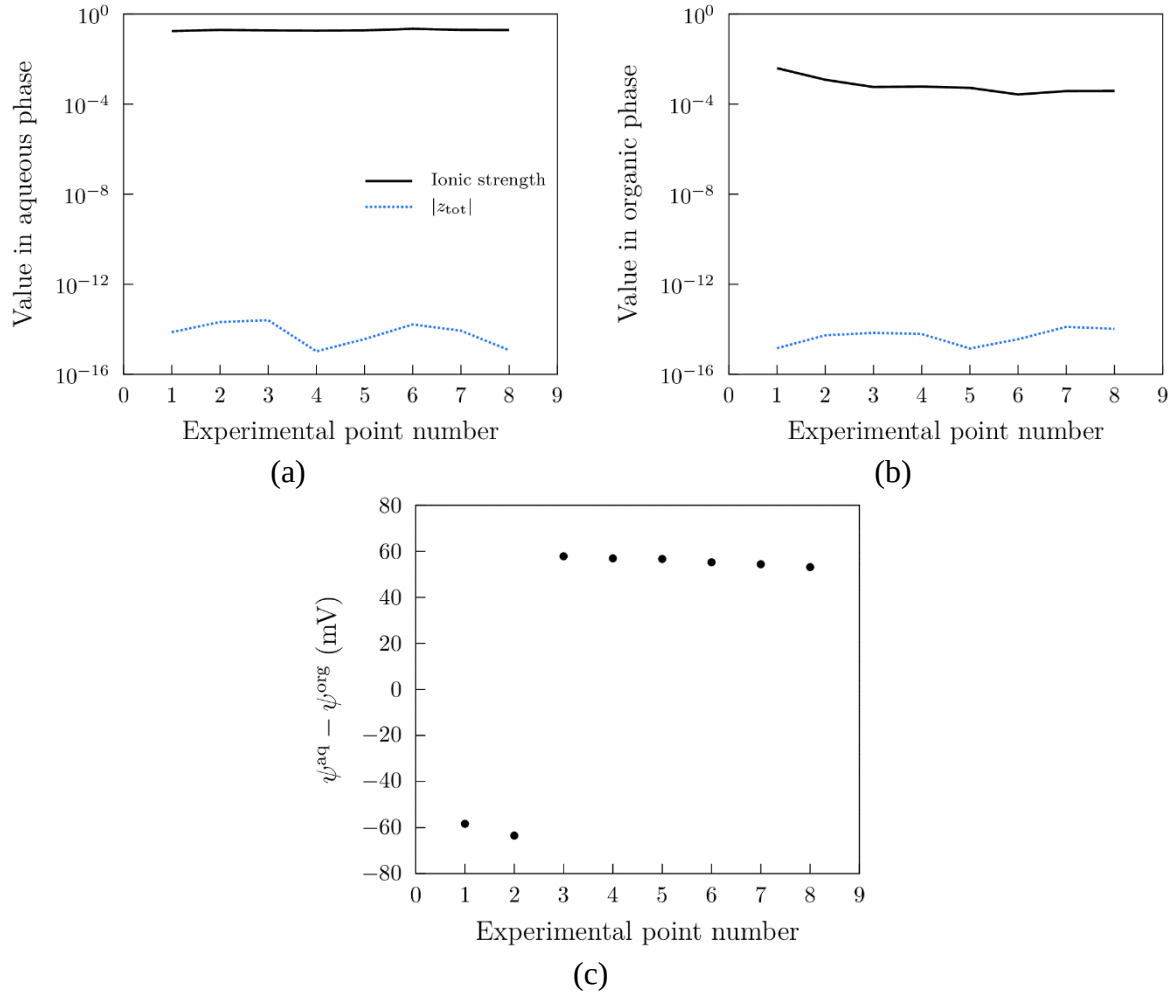


Figure 3: Calculated ionic strength, total relative charge and potential difference for the two liquid phases.

Finally, Figure 4 illustrates the convergence behavior of the algorithm. An initial liquid phase is assumed, converged, and then stability analysis introduces a second liquid phase. L and LL curves are shown for two convergence strategies: using composition derivatives of fugacity coefficients and ignoring them completely (partial Newton). Our method is similar to the modified RAND method, where quadratic convergence is expected (White et al., 1958; Tsanas et al., 2017a; Paterson et al., 2018; Medeiros et al., 2021). Figure 4 clearly demonstrates that including or excluding the derivatives does not greatly impact convergence. Moreover, the number of iterations seems quite high for a Newton's method and the convergence is linear close to the solution.

Although we did include composition derivatives of fugacity coefficients, we were not able to use the full derivatives from eNRTL. The derivatives of the Pitzer-Debye-Hückel and the Born terms had to be ignored because they are asymmetric and they violate the Gibbs-Duhem equation (see Appendix). However, this is an essential term in ionic systems, since it describes the Coulombic long-range interactions. Figure 4 shows that ignoring the long-range term, leads practically to the convergence of a partial Newton's method where the fugacity coefficient derivatives are completely ignored. Our general recommendation is to avoid using models that violate the Gibbs-Duhem with a minimization method. The main point of this publication was to show that LLE calculations with electrolytes are possible and the converged solution satisfies Eq. (42). The system of Mouhoubi et al. (2020) was simply selected because it was already modeled, it is adequately complex and experimental data suggested that it separates into two

immiscible phases. Additionally, the extent of dissociation of the components is not known beforehand (e.g., full dissociation of NaCl), but it is controlled by chemical equilibrium. A fugacity/activity coefficient model that satisfies the Gibbs-Duhem and its composition derivatives are symmetric is not expected to exhibit such behavior, because it's full derivatives are compatible with the framework of the algorithm.

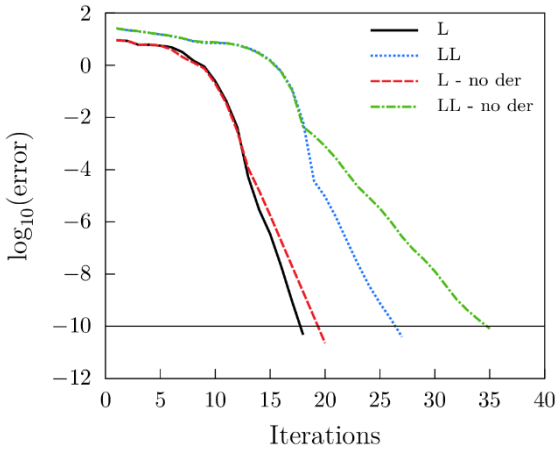


Figure 4: Convergence of the system at 313.15 K and 1 bar.

4 Conclusions

The method of Gautam, Seider and White (Gautam and Seider, 1979a, 1979b, 1979c; White and Seider, 1981) for simultaneous chemical and phase equilibrium was re-derived to include composition derivatives of fugacity coefficients and was further extended for application to multiphase electrolyte systems. This method is similar to the modified RAND (Tsanas et al., 2017a; Paterson et al., 2018; Medeiros et al., 2021). The algorithm minimizes an approximation to the reduced Gibbs energy with the charge/electric potential contribution, by solving at each iteration for the chemical potentials of chemical elements, the electric potentials and the phase amounts. The algorithm was applied to a demixing amine system modeled with eNRTL and the same set of parameters for both ion-containing phases. The system was chosen as it was complex enough for our purpose and model parameters were already available. Calculations start by establishing chemical equilibrium for a single liquid phase, then stability analysis identifies a second liquid phase, and finally the full system is solved. Stability analysis is expressed in terms of the electrochemical potential. This allows the search for an ion-containing trial phase whose composition respects electroneutrality. The algorithm convergences to two liquid electroneutral phases, where electrochemical potentials are equal for each individual component and chemical equilibrium is satisfied. The main difference with LLE calculations in the literature is that both molecules and ions are treated as individual components of the system without the limitation of full electrolyte dissociation (e.g., partitioning of NaCl). Instead of forcing phase equilibrium for salts (combination of ions), we allow the ions to partition individually in the different phases. Although the algorithm converges, we were not able to attain quadratic convergence rate as expected by the method. This is because the system was modeled by an implementation of eNRTL which does not satisfy the Gibbs-Duhem equation, and it was not possible to include the full derivatives of the fugacity coefficients (non-symmetric). Nevertheless, our priority was to demonstrate that the general equations of the algorithm can be applied to electrolyte LLE and converge to compositions that satisfy all the equilibrium constraints. However, to use the method to its full capacity and take advantage of its efficiency and reliability, we advise against the use of a model that violates the Gibbs-Duhem equation.

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Appendix: eNRTL equations

To model a mixed-solvent ion-containing phase, we use the eNRTL activity coefficient model (Chen and Evans, 1986). The activity coefficient of a solvent follows the symmetric convention:

$$\ln \gamma_i = \ln \gamma_i^{\mathrm{PDH}} + \ln \gamma_i^{\mathrm{NRTL}} \tag{A 1}$$

whereas for a solute, it follows the asymmetric mole fraction-based convention:

$$\ln \tilde{\gamma}_i = \ln \tilde{\gamma}_i^{\mathrm{PDH}} + \ln \tilde{\gamma}_i^{\mathrm{NRTL}} + \ln \tilde{\gamma}_i^{\mathrm{Born}} \tag{A 2}$$

An important point in the definition of the asymmetric activity coefficients in eNRTL is that they are defined with respect to infinite dilution in water:

$${}_{\mathrm{w}}^{\mathrm{s}}\tilde{\gamma}_i = \frac{\gamma_i}{{}_{\mathrm{w}}\gamma_i^{\infty}} \tag{A 3}$$

In Eq. (A 3), the following convention was used: a property X in a solution with mixed solvent "s" defined with respect to an aqueous reference state is ${}_{\mathrm{w}}^{\mathrm{s}}X$. The symbol ${}_{\mathrm{w}}\gamma_i^{\infty}$ refers to the symmetric infinite dilution activity coefficient of i in water. The Pitzer-Debye-Hückel contribution for the solvents is:

$$\ln \gamma_i^{\mathrm{PDH}} = 2A_{\varphi} \frac{I_x^{3/2}}{1+\rho I_x^{1/2}} \tag{A 4}$$

and for the solutes:

$$\ln \tilde{\gamma}_i^{\mathrm{PDH}} = -A_{\varphi}\left[\frac{2z_i^2}{\rho}\ln\left(1+\rho I_x^{1/2}\right) + \frac{z_i^2 I_x^{1/2} - 2I_x^{3/2}}{1+\rho I_x^{1/2}}\right] \tag{A 5}$$

where ρ is a parameter in the model and is equal to 14.9. The Debye-Hückel slope is calculated from:

$$A_{\varphi} = \frac{1}{3}\left(\frac{2\pi N_A \rho_{\mathrm{s}}}{1000}\right)^{1/2}\left(\frac{e^2}{\varepsilon_{\mathrm{s}} k_B T}\right)^{3/2} \tag{A 6}$$

Dielectric constants and densities are given for pure solvents as functions of temperature:

$$\varepsilon = A + B\left(\frac{1}{T} - \frac{1}{T_{ref}}\right) \qquad \rho = \frac{A}{B^{1+\left(1-\frac{T}{C}\right)^{D}}} \tag{A 7}$$

and the final mixture properties are found with the help of simple mixing rules, using only solvent components in the summations:

$$\varepsilon_{\mathrm{s}} = \frac{1}{M_{\mathrm{s}}}\sum_{i\in \mathrm{s}} x_i M_i \varepsilon_i \qquad \rho_{\mathrm{s}} = \left(\sum_{i\in s}\frac{x_i}{\rho_i}\right)^{-1} \tag{A 8}$$

The Born contribution for the solutes is given by (CGS units):

$$\ln \tilde{\gamma}_i^{\mathrm{Born}} = \frac{e^2}{2kT}\left(\frac{1}{\varepsilon_{\mathrm{s}}} - \frac{1}{\varepsilon_{\mathrm{w}}}\right)\frac{z_i^2}{r_i}10^{-2} \tag{A 9}$$

The NRTL contribution follows the symmetric convention for both solvents and solutes. The input parameters are energy interaction and non-randomness parameters between molecules (*m*, *m*'), cations (*c*, *c*') and anions (*a*, *a*'):

$$\begin{array}{cccccccc} \tau_{mm'} & \tau_{m'm} & \tau_{m,ca} & \tau_{ca,m} & \tau_{ca,ca} & \tau_{ca',ca} & \tau_{ca,c'a} & \tau_{c'a,ca} \\ \alpha_{mm'} = \alpha_{m'm} & & \alpha_{m,ca} = \alpha_{ca,m} & & \alpha_{ca,ca'} = \alpha_{ca',ca} & & \alpha_{ca,c'a} = \alpha_{c'a,ca} & \end{array}$$

Input parameters are calculated as functions of temperature:

$$\tau = \tau_0 + \frac{\tau_1}{T} \tag{A 10}$$

and

$$G = \exp\left(-\alpha\tau\right) \tag{A 11}$$

The equation for the activity coefficients is presented with the more straightforward formulas found in the documentation of ASPEN Plus, rather than the one in Chen and Evans (1986):

$$\ln \gamma_k^{\mathrm{NRTL}} = Z_k\left[R_k + \sum_j \frac{X_j G_{kj}\left(\tau_{kj} - R_j\right)}{S_j}\right] \tag{A 12}$$

To convert the symmetric to the asymmetric activity coefficient required by the solutes, we need to normalize them with their infinite dilution activity coefficient in water:

$$\ln {}_{\mathrm{w}}\gamma_k^{\infty,\mathrm{NRTL}} = Z_k\left(G_{\mathrm{kw}}\tau_{\mathrm{kw}} + \tau_{\mathrm{wk}}\right) \tag{A 13}$$

The auxiliary variables in the equations are:

- "charge" fraction

$$X_i = Z_i x_i \qquad Z_i = \begin{cases} 1, & i = m \\ z_i, & i = c \\ |z_i|, & i = a \end{cases} \qquad \text{(A 14)}$$

- ion-specific fractions:

$$Y_c = \frac{X_c}{\sum_{c'} X_{c'}} \qquad Y_a = \frac{X_a}{\sum_{a'} X_{a'}} \qquad \text{(A 15)}$$

- "mixing" parameters

$$\alpha_{cm} = \alpha_{mc} = \sum_a Y_a \alpha_{ca,m} \qquad \alpha_{am} = \alpha_{ma} = \sum_c Y_c \alpha_{ca,m} \qquad \text{(A 16)}$$

$$\alpha_{ca} = \sum_{c'} Y_{c'} \alpha_{ca,c'a} \qquad \alpha_{ac} = \sum_{a'} Y_{a'} \alpha_{ac,a'c} = \sum_{a'} Y_{a'} \alpha_{ca,ca'} \qquad \text{(A 17)}$$

$$G_{cm} = \sum_a Y_a G_{ca,m} \quad G_{mc} = \sum_a Y_a G_{m,ca} \quad G_{am} = \sum_c Y_c G_{ca,m} \quad G_{ma} = \sum_c Y_c G_{m,ca} \qquad \text{(A 18)}$$

$$G_{ca} = \sum_{c'} Y_{c'} G_{ca,c'a} \qquad G_{ac} = \sum_{a'} Y_{a'} G_{ac,a'c} = \sum_{a'} Y_{a'} G_{ca,ca'} \qquad \text{(A 19)}$$

$$\tau_{ij} = -\frac{\ln G_{ij}}{\alpha_{ij}} \qquad \text{(A 20)}$$

After all the parameters have been calculated from Eq. (A 16) to (A 20), we can write the model with the general form of Eq. (A 12), where:

$$S_j = \sum_i X_i G_{ij} \qquad U_j = \sum_i X_i G_{ij} \tau_{ij} \qquad R_j = \frac{U_j}{S_j} \qquad \text{(A 21)}$$

Finally, we do not account for *cc*' or *aa*' interactions:

$$G_{cc'} = 0 \qquad G_{cc'} \tau_{cc'} = 0 \qquad G_{aa'} = 0 \qquad G_{aa'} \tau_{aa'} = 0 \qquad \text{(A 22)}$$

Apart from the activity coefficients, the algorithm requires the derivatives of the activity coefficients with respect to composition. The expression of eNRTL is quite complex, therefore we adopt the following assumptions:

1. The derivation of the PDH and Born activity coefficients is performed by differentiating the corresponding excess Gibbs energy expressions. To obtain Eq. (A 4), (A 5) and (A 9), the differentiation assumes that the solvent properties are constant, although this is not

true for mixed solvents because the dielectric constant and the density depend on solvent composition. Following the same assumption, the derivatives of the Born activity coefficients are 0 for all solutes.

2. The PDH term given by Eq. (A 4) and (A 5), violates the Gibbs-Duhem equation at constant temperature and pressure (not thermodynamically consistent). Additionally, its derivatives are not symmetric. Therefore, the derivatives of the PDH activity coefficients are completely ignored for all components. For the reader's reference:

$$\frac{\partial \ln \tilde{\gamma}_k^{\mathrm{PDH}}}{\partial x_q} = -A_\varphi \left[\frac{0.75 z_k^2 z_q^2 I_x^{-1/2} - 1.5 z_q^2 I_x^{1/2} - \rho z_q^2 I_x + 0.5 \rho z_k^2 z_q^2}{\left(1 + \rho I_x^{1/2}\right)^2} \right] \tag{A 23}$$

3. The derivation of the NRTL contribution to the activity coefficient from the corresponding excess Gibbs energy expression assumes constant ion fractions Y_i, although this is not true for multiple cations and anions. Keeping the same assumption in the differentiation of the activity coefficient:

$$\begin{aligned} \frac{\partial \ln \gamma_k^{\mathrm{NRTL}}}{\partial x_q} = Z_q Z_k \frac{G_{qk}\left(\tau_{qk} - R_k\right)}{S_k} + \frac{G_{kq}\left(\tau_{kq} - R_q\right)}{S_q} \\ - Z_q Z_k \sum_j \frac{X_j G_{kj} G_{qj}\left(\tau_{kj} + \tau_{qj} - 2R_j\right)}{S_j^2} \end{aligned} \tag{A 24}$$

and:

$$\frac{\partial \ln \gamma_k^{\infty,\mathrm{NRTL}}}{\partial x_q} = 0 \tag{A 25}$$

Consequently, in this work, for all components, solvents or solutes:

$$\frac{\partial \ln \gamma_k}{\partial x_q} = \frac{\partial \ln \tilde{\gamma}_k}{\partial x_q} = \frac{\partial \ln \gamma_k^{\mathrm{NRTL}}}{\partial x_q} \tag{A 26}$$

Mole fractions are considered independent in the model and the derivatives with respect to mole numbers can be found as:

$$\frac{\partial \ln \gamma_i}{\partial n_j} = \frac{1}{\sum_{k=1}^{N_C} n_k} \frac{\partial \ln \gamma_i}{\partial x_j} \tag{A 27}$$

The sum of the mole numbers equal to one is not forced by the model, but externally.