

Comparison of Computational Methods for Reaction Equilibrium

Sanoja A. Jayarathna¹, Bernt Lie¹, Morten C. Melaaen^{1,2}

¹Telemark University College, Norway; ²Tel-Tek, Norway

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Specie concentrations for chemical equilibrium can be found in various ways such as solving a system of algebraic equations or solving a dynamic model to steady state. The algebraic equation system for reacting systems consists of multivariate polynomials with multiple solutions. Some traditional and modern methods for solving such systems are discussed together with their advantages and disadvantages. The dynamic model results from ordinary differential equations (ODEs) based on dynamic material balances. It is shown how the ODE system contains all the information in the algebraic equation system. Based on the comparison of methods, it is suggested that solving the dynamic model to steady state in many ways is the simplest way for computing speciation data at the equilibrium of a reacting system.

Introduction

Reactive systems are widely used in the process industry, including the CO_2 capturing field. Equilibrium concentrations of the species available in the reactive systems are considered as an important source of information regarding the reaction kinetics. Computation of the equilibrium concentrations with known equilibrium coefficients is important for checking the equilibrium with the experimental data. Equilibrium concentrations are important also for the modelling of the systems.

In chemical engineering, the values of the equilibrium concentrations are often found by solving a set of algebraic equations, [1]. The algebraic equation set consists of the relations from setting the reaction rates to zero in tandem with the atom or charge balances; the latter ensure mass conservation. Alternatively, a method like minimization of Gibbs free energy ([2], [3], [4] & [5]) can be used. Usually such methods also result a set of equations to solve for the equilibrium compositions. The set of equations to be solved is usually a set of non-linear polynomials in several variables. A number of methods are applicable for solving such systems of non-linear polynomials with their own advantages and disadvantages. The use of some of these methods for solving for the equilibrium concentrations are discussed in this paper.

Alternatively, the dynamic mole balances (ODEs) can be solved until the steady state is reached. This gives the equilibrium concentrations.

The relationship between the algebraic equation system and the ODEs is discussed, including advantages and disadvantages of the two approaches.

The paper is organized as follows: first, the algebraic equations for chemical equilibrium are discussed, together with the possibility of multiple solutions. Methods for solving such algebraic equations are then briefly covered. Next, it is shown how dynamic models for concentrations are related to the algebraic equations, with examples. The methods are illustrated through computing a speciation curve which is relevant for post combustion CO_2 capturing. Finally, some conclusions are drawn and further work is discussed.

Nomenclature

c	Concentration	$[mol/m^3]$
MEA	Monoethanolamine	$[-]$
$MEACOO^-$	Protonated MEA	$[-]$
r	Rate of reaction	$[mol/s \cdot m^3]$
t	Time	$[s]$
ν	Stoichiometric matrix	$[-]$

1 Equilibrium Concentrations with Algebraic Equations

In chemical engineering, the equilibrium concentrations are often specified as the solution of

$$r(c) = 0 \quad (1)$$

$$Vc = b \quad (2)$$

where Vc indicates a linear combination of the elements of c . Here, $r(c) = 0$ is a nonlinear set of equations, while the linear equations $Vc = b$ typically are based on the idea of conservation of mass.

The use of minimization of Gibbs free energy is one of the alternative methods to find the equilibrium compositions in a reactive mixture. The numerical value of the standard state Gibbs energy of reaction (ΔG_T^0) is used to determine the reaction coordinate (ξ) at equilibrium [3]. The Eq. 3 provides the relation between the equilibrium coefficient, the ΔG_T^0 term and the component fugacities

$$K_a = \exp \left[\frac{-\Delta G_T^0}{RT} \right] = \prod \left[\frac{\hat{f}_i}{f_i^0} \right]^{v_i} \quad (3)$$

The reaction coordinates can be found by representing the component fugacities in terms of the mole fractions. With use of the known K_a 's and simplifications to the Eq. 3 a set of polynomials as presented by Eq. 4 will be resulted

$$a\xi^k = 0 \quad (4)$$

where $a\xi^k$ is a non-linear combination of the reaction coordinates when $k \neq 1$. Ultimately, the Gibbs free energy method can also result a set of non-linear polynomials to solve for the equilibrium compositions.

In either case, numerical methods should be used if the situation is complicated for normal hand calculations. Only the $r(c) = 0 \wedge Vc = b$ case will be used for the analysis in the rest of the paper while stating that the facts are common for all the similar cases.

Use of an iterative method like Newton's method is an option for solving a system of algebraic equations, [6]. A drawback of this method is that it gives only one possible solution among all possible solutions satisfying $r(c) = 0 \wedge Vc = b$ or $a\xi^k = 0$. The solution is dependent on the initial guess used to start the iterations.

Having a good guess will not always guarantee the expected results as systems of polynomials can have both stable and unstable solutions, as well as physically unrealistic solutions (negative concentrations or complex roots).

Sup-pose the reaction is a third order polynomial in the concentration of specie A , leading to the ODE

$$\frac{dc_A}{dt} = -kc_A^3 + c_A \quad (5)$$

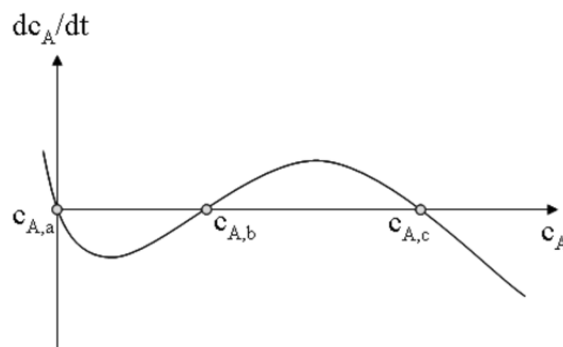


Figure 1. Possible solutions of the polynomial given by Eq. 5:

The possible solutions are $c_{A,a}$, $c_{A,b}$ and $c_{A,c}$ for c_A , which can be depicted as in Figure 1. Since dc_A/dt is negative between $c_{A,a}$ and $c_{A,b}$ the value of the concentration should decrease providing that any initial guesses between $c_{A,a}$ and $c_{A,b}$ will converge to $c_{A,a}$.

All the initial guesses between $c_{A,b}$ and $c_{A,c}$ will settle $c_{A,c}$ due to the positive values of dc_A/dt , leaving $c_{A,b}$ as an unstable solution. In general it is viable that the steady state solution of a dynamic model with polynomial reaction rate $r(c_A)$,

$$\frac{dc_A}{dt} = r(c_A)$$

is either complex (not physical), real and negative (not physically realizable), or real and positive. In the latter case, the solution may be stable or unstable. Only stable solutions are of interest.

Alternatively to Newton's method, a method such as Buchberger's algorithm for the Gröbner basis [7] can be used to solve the algebraic equation system. The Gröbner basis forms a "triangular" set of polynomial "bases" similar to triangular result of Gaussian elimination. As an illustrative example, consider the ammonia synthesis reaction, Eq. 6



The equilibrium coefficient ($K = 17.653$) is found in [3].

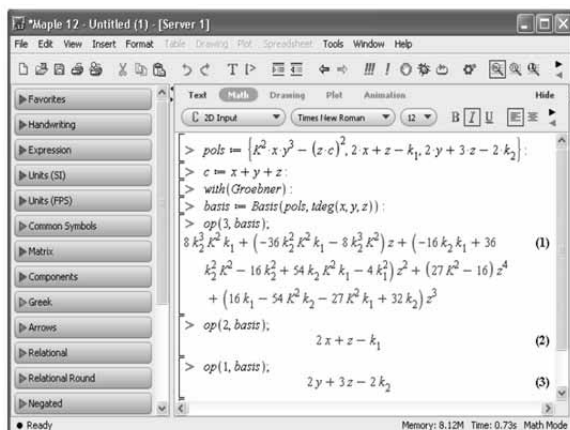


Figure 2. Calculation of Gröbner basis using Maple.

The initial N_2 and H_2 concentrations in the reactor are taken as k_1 and k_2 . The system of algebraic equations to solve for the equilibrium concentrations is given below, where Eq. 7 gives the equilibrium coefficient relating the concentrations. Nitrogen and hydrogen atom balances are given in Eqs. 8 and 9

$$K c_{N_2}^{1/2} + c_{N_2}^{3/2} + c_{NH_3} c_T = 0 \quad (7)$$

$$2c_{NT} + c_{NH_3} - 2c_{N_{2,in}} = 0 \quad (8)$$

$$2c_{H_2} + 3c_{NH_3} - 2c_{N_{2,in}} = 0 \quad (9)$$

where c_T is the total concentration given by Eq. 10

$$c_T = c_{N_2} + c_{H_2} + c_{NH_3} \quad (10)$$

The Gröbner bases can be found using Maple [8]; Figure 2 shows the steps in Maple when $c_{N_{2,n}}$ and $2c_{N_{2,in}}$ are denoted k_1 and k_{12} , respectively. In Figure 2, concentrations of N_2 , H_2 and NH_3 are represented by the symbols x , y and z , respectively.

The resulting equations imply that

$$\begin{aligned} 0 = & 8c_{N_{2,in}}c_{H_{2,in}}^3K^2 \\ & + (-36c_{N_{2,in}}c_{H_{2,in}}^2K^2 - 8c_{H_{2,in}}^3K^2)c_{NH_3} \\ & + (-16c_{N_{2,in}}c_{N_{2,in}} + 36c_{H_{2,in}}^2K^2 - 16c_{H_{2,in}}^2) \\ & + 54c_{N_{2,in}}c_{H_{2,in}}K^2 - 4c_{N_{2,in}}^2c_{NH_3}^2 \\ & + (16c_{N_{2,in}} - 54c_{H_{2,in}}K^2 - 27c_{N_{2,in}}K^2 \\ & + 32c_{H_{2,in}})c_{NH_3}^3 + (27K^2 - 16)c_{NH_3}^4 \end{aligned}$$

$$c_{N_2} = \frac{1}{2}(c_{N_{2,in}} - c_{NH_3})$$

$$c_{H_2} = c_{H_{2,in}} - \frac{3}{2}c_{NH_3}$$

From the equations above, c_{NH_3} is found by solving a fourth order polynomial in c_{NH_3} , which yields 4 solutions in the complex field; the solutions may be real positive or negative, or complex. The two subsequent equations give c_{N_2} and c_{H_2} directly from c_{NH_3} .

In conclusion, there are 4 triples $(c_{N_2}, c_{H_2}, c_{NH_3})$ of solutions. In order to be a physically realistic solution, every element in a triple must be real and positive. Furthermore, it is necessary to check whether the remaining physically realistic solutions are stable or unstable.

Finally, it must be determined which of the physically realistic and stable solutions belong to realistic initial concentrations $c(t=0)$.

The disadvantages of the Gröbner basis method are: (i) much computer memory is required, (ii) the computational time is high, (iii) the method is numerically ill-posed with current algorithms, and (iv) some post treatment is required to select the physically correct solution. The advantage is that all solutions are found, and it is not necessary to “guess” any initial value in an iteration procedure.

In [9], it is recommended to instead use ideas from continuation/homotopy to find all solutions; continuation has better numerical properties than current implementations of the Gröbner basis method.

2 ODEs for Generating Equilibrium Concentrations

Solving an ODE system until steady state is reached, is an alternative to solving a set of polynomials to get the equilibrium compositions. Additional information such as forward and backward reaction rates are required, but as long as their ratio equals the equilibrium constant, the steady state equation should be correct.

As long as only the steady state solution is required, exists, and is unique, and ODE solver can be looked upon as a special kind of root finder.

Many other such methods exist, in addition to standard solvers such as the Newton method, see e.g. [10].

Batch reactors with perfect mixing and a constant volume have concentrations given by

$$\frac{dc}{dt} = v^T r \quad (11)$$

where $c \in \mathbb{R}^n$ is a vector of concentrations with elements c_j , $r(c) \in \mathbb{R}^m$ is a vector of overall reaction rates for the m reactions with elements r_i , and $v \in \mathbb{R}^{m \times n}$ is the stoichiometric matrix.

With a given initial condition $c(t_0)$, and assuming the existence of a steady state, the steady state can be found by solving this set of ODEs until $t \rightarrow \infty$, or for a sufficiently large time. The concentrations at the steady state gives the equilibrium concentrations and is easily found with known realistic initial conditions.

It is simple to show that these ODEs contain the same information as in the system of algebraic equations being discussed earlier.

2.1 Partitioning into Reaction Invariants and Reaction Variants

The following partitioning into reaction invariants and variants is discussed in [11]. Let us introduce fictitious species with concentration s_j which are linear combinations of the real species with concentration c_j . Stacking the concentrations s_j into vector s , s can then be written as

$$s = M c$$

We can then formulate the dynamic model for s as

$$\frac{ds}{dt} = M v^T r$$

As long as M is invertible, this differential equation for s holds exactly the same information as the differential equation for c in the previous subsection.

Let us now choose matrix M in a particular way: let M be composed of submatrices M_N and M_C ,

$$M = \begin{pmatrix} M_N^T \\ M_C^T \end{pmatrix}$$

where the columns of M_N lie in the nullspace $\mathcal{N}(v)$ of v , while the columns of M_C lie in the column space $\mathcal{C}(v^T)$ of v^T ; the nullspace $\mathcal{N}(v)$ of v consists of all possible vectors n such that $v \cdot n = 0$.

The the column space of v^T contains all the linear combinations of the columns of v^T [12].

Linear algebra tells us that it is possible to choose columns in M_N and M_C such that M is invertible [12]. With this structure of M , the differential equation for s becomes

$$\begin{aligned} \frac{ds}{dt} &= M v^T r = \begin{pmatrix} M_N^T \\ M_C^T \end{pmatrix} v^T r \\ &\Downarrow \\ \frac{ds_j}{dt} &= M_N^T v^T r \\ \frac{ds_v}{dt} &= M_C^T v^T r \end{aligned}$$

Here, s_j are the reaction invariant fictitious concentrations, while s_v are the reaction variant fictitious concentrations.

Since the columns of M_N , $m_N \in \mathcal{N}(v) \Leftrightarrow v \cdot m_{N,i} = 0$, we have

$$M_N^T v^T r = (v M_N)^T r = 0 \cdot r = 0$$

Thus,

$$\frac{ds_j}{dt} = 0 \Rightarrow s_j = \text{constant}$$

Furthermore

$$M_C^T v^T = (v M_C)^T \in \mathbb{R}^{\rho \times \rho}$$

is square and invertible with $\rho = \text{rank} v$ when v is of full rank; when v is not of full rank, superfluous reactions can be removed to ensure full rank of v . Since $M_C^T v^T$ is invertible, it follows that in steady state

$$\frac{ds_v}{dt} = M_C^T v^T r = 0 \Rightarrow r = 0$$

In conclusion, this shows that the steady state solution of the differential equation Eq. 11 for c is equivalent to the solution found by simultaneously setting

$$r(c) = 0$$

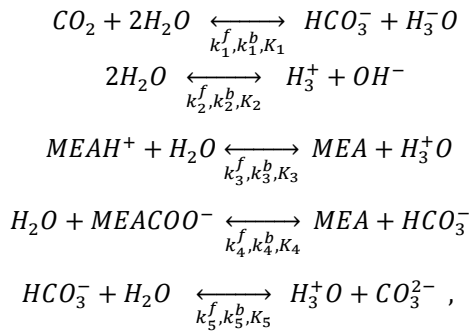
$$s_j = M_C^T = \text{constant}$$

Here, M_N^T corresponds to V in Eq. 2, while the constant corresponds to b .

Using linear algebra software such as Matlab, Maple, etc., M_N can easily be computed, while the constant is given from the initial conditions $c(t_0)$. But finding the solutions of this set of equations can be difficult as already explained.

2.2 Case Study

This example will illustrate how the ODEs are related with the algebraic equations using an example found in CO_2 capturing systems [13]:



where

$$K_i \triangleq \frac{k_i^f}{k_i^b}$$

Here K_i ; k_i^f and k_i^b are the equilibrium coefficient, forward reaction coefficient and backward reaction coefficient of reaction i , respectively. For the set of reactions considered, the stoichiometric matrix ν is

$$\nu = \begin{bmatrix} -1 & 0 & 0 & 0 & 1 & 0 & 1 & 0 & -2 \\ 0 & 0 & 0 & 0 & 0 & 1 & 1 & 0 & -2 \\ 0 & 1 & -1 & 0 & 0 & 0 & 1 & 0 & -1 \\ 0 & 1 & 0 & -1 & 1 & 0 & 0 & 0 & -1 \\ 0 & 0 & 0 & 0 & -1 & 0 & 1 & 1 & -1 \end{bmatrix}$$

when the species are considered in the order CO_2 , MEA , $MEAH^+$, $MEACOO^-$, HCO_3^- , OH^- , HCO_3^+ , CO_3^{2-} and H_2O . The overall reaction rates r_i of the system are given as

$$r_1 = k_1^f \cdot c_{CO_2} \cdot (c_{H_2O})^2 - k_1^b \cdot c_{HCO_3^-} \cdot c_{H_3O^+}$$

$$r_2 = k_2^f \cdot (c_{H_2O})^2 - k_2^b \cdot c_{OH^-} \cdot c_{H_3O^+}$$

$$r_3 = k_3^f \cdot c_{MEAH^+} \cdot c_{H_2O} - k_3^b \cdot c_{MEA} \cdot c_{HCO_3^-}$$

$$r_4 = k_4^f \cdot c_{MEACOO^-} \cdot c_{H_2O} - k_4^b \cdot c_{MEA} \cdot c_{HCO_3^-}$$

$$r_5 = k_5^f \cdot c_{HCO_3^-} \cdot c_{H_2O} - k_5^b \cdot c_{H_3O^+} \cdot c_{CO_3^{2-}}$$

In order to solve the dynamic model based on the mole balances, the forward and backward reaction coefficients are required. The values of the forward reaction coefficients can either be found in the literature (e.g. in [14]), or fixed at some chosen value.

With given forward rates, the backward reaction coefficients are chosen in such a way that the equilibrium coefficients are correct. The mass conservation of each specie contributes with an ODE to be solved in time. Since the reactor contains nine species, the ODE system consists of nine equations which can be stacked into a vector-matrix formulation as in Eq. 11.

The nullspace $\mathcal{N}(\nu)$ of ν and the column space $\mathcal{C}(\nu^T)$ of ν^T are found using the computer algebra system MuPAD within the word processor Scientific Workplace, and are given by the following basis vectors $b_{N,i}$ and $b_{C,i}$ respectively:

$$\mathcal{N}(\nu) = \left\{ \begin{bmatrix} 0 \\ 1 \\ 1 \\ 1 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \end{bmatrix}, \begin{bmatrix} 2 \\ -1 \\ 0 \\ 0 \\ 1 \\ -1 \\ 1 \\ 0 \\ 0 \end{bmatrix}, \begin{bmatrix} 1 \\ -1 \\ -1 \\ 0 \\ 1 \\ 0 \\ 0 \\ 1 \\ 0 \end{bmatrix}, \begin{bmatrix} -3 \\ 2 \\ 1 \\ 0 \\ -1 \\ 2 \\ 0 \\ 0 \\ 1 \end{bmatrix} \right\}$$

$$\mathcal{C}(\nu^T) = \left\{ \begin{bmatrix} -1 \\ 0 \\ 0 \\ 0 \\ 1 \\ 0 \\ 1 \\ 0 \\ -2 \end{bmatrix}, \begin{bmatrix} 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 1 \\ 1 \\ 0 \\ -2 \end{bmatrix}, \begin{bmatrix} 0 \\ 1 \\ -1 \\ 0 \\ 0 \\ 0 \\ 1 \\ 0 \\ -1 \end{bmatrix}, \begin{bmatrix} 0 \\ 1 \\ 0 \\ -1 \\ 1 \\ 0 \\ 0 \\ 0 \\ -1 \end{bmatrix}, \begin{bmatrix} 0 \\ 0 \\ 0 \\ 0 \\ -1 \\ 0 \\ 1 \\ 0 \\ -1 \end{bmatrix} \right\}$$

Using the linear combinations of basis vectors in the nullspace $\mathcal{N}(\nu)$ of ν the columns in M_N can be chosen.

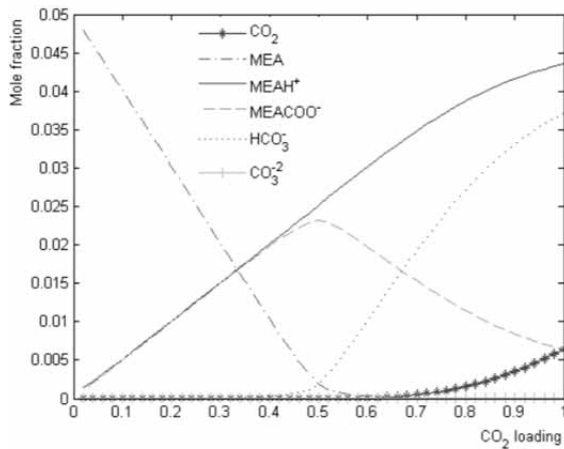
The following column vectors of M_N are used here:

$$m_{N,1} = b_{N,2} - b_{N,1},$$

$$m_{N,2} = b_{N,1} - b_{N,3},$$

$$m_{N,3} = b_{N,3} - b_{N,1}$$

$$m_{N,4} = 2b_{N,1} + b_{N,2} + 3b_{N,3} + b_{N,4}.$$


Figure 3. Speciation curves at 40 °C

Hence,

$$M_{\mathcal{N}} = \begin{bmatrix} 0 & 1 & 0 & 2 \\ 0 & 0 & 1 & 0 \\ 1 & 0 & 1 & 0 \\ -1 & 1 & 1 & 2 \\ -1 & 1 & 0 & 3 \\ -1 & 0 & 0 & 1 \\ 1 & 0 & 0 & 1 \\ -2 & 1 & 0 & 3 \\ 0 & 0 & 0 & 1 \end{bmatrix}$$

The columns of $M_{\mathcal{C}}$ are chosen to be the basis vectors of $\mathcal{C}(v^T)$, i.e. $m_{e,i} = 2b_{c,i}$.

$$M_{\mathcal{C}} = \begin{bmatrix} -1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 1 & 0 \\ 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & -1 & 0 \\ 1 & 0 & 0 & 1 & -1 \\ 0 & 1 & 0 & 0 & 0 \\ 1 & 1 & 1 & 0 & 1 \\ 0 & 0 & 0 & 0 & 1 \\ -2 & 2 & -1 & -1 & -1 \end{bmatrix}$$

The reaction invariant set of equations is found for the fictitious species s_j

$$\begin{aligned} \frac{ds_j}{dt} &= M_{\mathcal{N}}^T v^T r \\ \Downarrow M_{\mathcal{N}}^T v^T r &= 0 \in \mathbb{R}^{4 \times 5} \\ \frac{ds_j}{dt} &= 0 \end{aligned}$$

Since $ds_j/dt = 0$, this shows that $s_j = \text{constant}$, or $V_c = b$.

The reaction variant equation set is found for the fictitious species s_v :

$$\frac{ds_v}{dt} = M_{\mathcal{C}}^T v^T r$$

where matrix $M_{\mathcal{C}}^T v^T$ is an invertible matrix, hence in steady state the condition $r(c) = 0$ is also satisfied.

This example shows that the ODEs, $\frac{dc}{dt} = v^T r$ contains all the information available from the system the system of algebraic equations, $r(c) = 0 \wedge Vc = b$.

3 Results of the ODEs

A dynamic model of the case study is simulated to steady state to find the equilibrium concentrations. The equilibrium coefficients for this reacting system can be found in e.g. [13], [15], and [16].

The dynamic model is simulated for a sufficiently long time and the steady state solution is taken as the equilibrium concentrations.

It can be shown that the equilibrium results depend on the initial concentrations of CO_2 and MEA , $c_{CO_2,in}$ and $c_{MEA,in}$, respectively. It is of interest to construct a so called speciation diagram, see Figure 3.

The speciation diagram shows the equilibrium mole fractions of the various species, as a function of the so called CO_2 loading, i.e. as a function of the fraction $c_{CO_2,in}/c_{MEA,in}$.

In the speciation diagram of Figure 3, a temperature of 40° C is assumed, and the results are in good agreement with the reference work [13].

4 Conclusions

The equilibrium concentrations of a reactor can be found by solving a set of algebraic equations satisfying Eqs. 1 and 2. In the case of polynomial algebraic equations, the roots lie in the complex field. However, only real and positive roots are physically realistic.

Furthermore, among the real and positive roots, some solutions represent unstable steady states, and the stable steady state roots are thus the only acceptable equilibrium concentrations.

A basic method for solving algebraic equations is Newton's method; this method only finds one root, and the root that is found depends on the chosen initial guess c^0 . There is no guarantee that the chosen c^0 leads to the most physically realistic solution. To study all solutions using Newton's method, it is necessary to use the method repeatedly, each time using a different value of c^0 .

When the algebraic equations are polynomials in several variables, the algebraic equations can be transformed to Gröbner bases using Buchberger's algorithm. Thereafter, all possible sets of solutions can be found using a standard solver for single variable polynomials.

Finally, it is necessary to postprocess the solutions in order to find the physically acceptable equilibrium concentrations. However, Buchberger's algorithm is quite demanding when it comes to computer memory and computation time. Thus, it may be better to use continuation/homotopy methods to find all solutions.

Another alternative is to solve the dynamic model of a batch reactor to steady state. Comparing the dynamic model $\frac{dc}{dt} = v^T r$ with the algebraic equations, it is easily shown that the dynamic model contains all the information from the algebraic equation system $r(c) = 0 \wedge Vc = b$. Additionally, dynamics of the reaction system is included in the dynamic model.

Clearly, simulating an ODE to steady state where we do not care about the transient behavior, is similar to using e.g. Newton's method; the ODE solver can be considered as just another root solver. Ensuring that steady state is reached with the ODE solver, is comparable to ensuring that the Newton solver has converged to the root. In both cases, we iterate on $v^T r(c^0)$ such that $v^T r(c^0) \rightarrow 0$.

The advantage of using a physically realistic dynamic model with an ODE solver, is that we know that the dynamic model has the equilibrium solution as the steady state solution, and that we can choose a realistic initial value for the ODEs such that the equilibrium solution is found.

Clearly, ODEs exist with complex dynamics such as limit cycle behavior where no steady state solution exist, or with bifurcations where the steady state solution is extremely sensitive to the chosen initial value or numerical inaccuracies. But these complex dynamic cases will also be difficult to solve with alternative methods.

The above factors indicate that both solving the algebraic equations using Newton's method, and solving the ODEs using an ODE solver should be equally accurate in steady state.

Since it is just as simple to formulate the ODEs as formulating the algebraic equations, since it is simpler to suggest physically reasonable initial values than guessing an initial iterate for the Newton solver, and since the ODE solver automatically will lead to a stable steady state, we suggest that using an ODE solver is favorable.

Using an ODE solver to find the equilibrium concentrations has been illustrated through computing the speciation diagram relevant for post combustion CO₂ capturing using MEA.

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Corresponding author: Berndt Lie,
Telemark University College, Postboks 203,
3901 Porsgrunn, Norway
Bernt.Lie@hit.no

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