



# Dynamic method for computation of chemical and phase equilibria



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## ABSTRACT

A generalized approach for the calculation of complex chemical and phase equilibria is presented that is based on the simulation of the dynamic evolution of a mixture from non-equilibrium initial composition towards the final equilibrium composition. The proposed method is able to solve pure chemical or phase equilibria as well as simultaneous chemical/phase equilibria. The advantage of our approach compared to conventional equilibrium calculations is the fact that the approach is physically motivated and can handle chemical and phase equilibria as well as simultaneous chemical and phase equilibria.

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## 1. Introduction

In process simulation a variety of thermodynamic equilibria such as reaction equilibria and phase equilibria between two or more phases have to be solved in various process units, e.g. for reaction as well as separation. It is common that for different types of equilibria diverse mathematical approaches are applied. For reaction equilibria, the most common approach is the direct Gibbs energy minimization which formulates the equilibrium condition in terms of an optimization problem (Lwin, 2000; Gmehling et al., 2012). In the case of phase equilibria such as vapour–liquid equilibria (VLE) or liquid–liquid equilibria (LLE) a set of algorithms is available that solve the thermodynamic conditions to be fulfilled at the equilibrium state namely the equality of the chemical potentials of all species in the coexisting phases at constant pressure and temperature (Lucia et al., 2000; Poling et al., 2007).

The approach of reformulating algebraic models as differential equations and solve them up to their steady state in chemical engineering dates back to Ketchum (1979). In this contribution, we propose a general approach based on the solution of a set of ordinary differential equations (ODE) that is able to handle chemical as well as phase equilibria. This solution strategy is physically motivated by the mass fluxes between phases or as a consequence of chemical reactions. The proposed approach is able to handle chemical and phase equilibria as well as simultaneous chemical and phase

equilibria, and therefore it is also suitable for the simultaneous solution of an overall process flowsheet.

In the next section we introduce the mathematical formulation of the dynamic method. After that we apply it to several examples and show that it is able to solve equilibrium problems of different complexity.

A brief overview of the proposed method was published in a previous work (Zinser et al., 2015). In this contribution, we give a more comprehensive summary and exemplify the applicability with several case studies. Additionally, we compare our dynamic method with the conventional Gibbs energy minimization technique. An approach for the reduction of the resulting set of evolution equations in multiphase systems is presented as well.

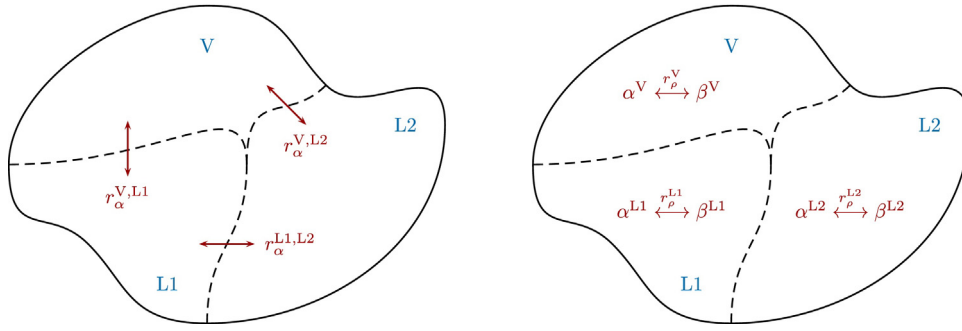
## 2. Method formulation

We assume a set of phases  $\mathcal{P}$  that may occur in the considered system. For example,  $\mathcal{P} = \{V, L1, L2\}$ , refers to a VLL-system with one vapour phase (V) and two liquid phases (L1 and L2). Additionally, in each phase  $\pi \in \mathcal{P}$  a set  $\mathcal{S}^\pi$  of species may occur. In many systems, every species is allowed to occur in every phase, i.e.  $S = \mathcal{S}^\pi \forall \pi \in \mathcal{P}$ . In some systems, it is not possible to compute the fugacities for every component in every phase such as systems including non-condensable gases, molecular salts, and ions.

For computing the thermodynamic phase equilibrium of a  $p$ -phase system with  $s$  species, up to  $sp(p-1)/2$  rate expressions  $r_\alpha^{\pi, \pi'}$  are required that describe the molar fluxes of all species  $\alpha \in S$  between the phases  $\pi$  and  $\pi'$  with  $\pi, \pi' \in \mathcal{P}$  and  $\pi \neq \pi'$ , see also Fig. 1 (left).

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**Fig. 1.** General VLL system with the fluxes  $r_{\alpha}^{\pi,\pi'}$  between the three phases (left) and the fluxes  $r_{\rho}^{\pi}$  due to chemical reactions (right).

Additionally, in each phase  $\pi \in \mathcal{P}$  may occur a set of chemical reactions  $\rho \in \mathcal{R}^{\pi}$  as shown in Fig. 1 (right).

The proposed methodological approach for solving chemical as well as phase equilibria is formulated as a set of ordinary differential equations

$$\frac{d\mathbf{n}}{d\tau} = \mathbf{A}\mathbf{r} \quad (1)$$

that describes the evolution of the molar compositions in each phase

$$\mathbf{n} = [\mathbf{n}^{\pi}]_{\pi \in \mathcal{P}} \quad \text{with} \quad \mathbf{n}^{\pi} = [n_{\alpha}^{\pi}]_{\alpha \in \mathcal{S}^{\pi}} \quad (2)$$

w. r. t. time  $\tau$ . Here,  $\mathbf{A}$  is the stoichiometric matrix and  $\mathbf{r}$  is a vector of rate expressions that describes the fluxes between the phases as well as the fluxes due to chemical reactions. The stoichiometric matrix

$$\mathbf{A} = [\mathbf{A}_p \quad \mathbf{A}_r] \quad (3)$$

consists of a part  $\mathbf{A}_p$  that models the interactions between the phases and a part  $\mathbf{A}_r$  that models the stoichiometry of the chemical reactions in each phase. In the same way the vector of rate expressions

$$\mathbf{r} = \begin{bmatrix} \mathbf{r}_p \\ \mathbf{r}_r \end{bmatrix} \quad (4)$$

consists of two parts: one for the rates of the phase transitions  $\mathbf{r}_p$ , i.e. the mass fluxes between the phases, and one for the chemical reaction rates  $\mathbf{r}_r$ .

All the above rate expressions are constructed in a thermodynamic consistent way so that the steady state of the ODE system (1) corresponds to the molar composition of the system in thermodynamic equilibrium.

### 2.1. Phase transitions

This section assumes that the set of species  $\mathcal{S}$  applies to all phases  $\pi \in \mathcal{P}$ , i.e. every component may exist in every phase. The case that each phase defines its own set of allowable species  $\mathcal{S}^{\pi}$  is discussed in the next section. The rate expressions for mass transfer of the species between the phases are

$$\mathbf{r}_p = [\mathbf{r}^{\pi,\pi'}]_{\substack{\pi,\pi' \in \mathcal{P} \\ \pi \neq \pi'}} \quad \text{with} \quad \mathbf{r}^{\pi,\pi'} = [r_{\alpha}^{\pi,\pi'}]_{\alpha \in \mathcal{S}}. \quad (5)$$

They are directly derived from the thermodynamic equilibrium condition, i.e. equal fugacities, between the two phases  $\pi$  and  $\pi'$

$$f_{\alpha}^{\pi} = f_{\alpha}^{\pi'}. \quad (6)$$

This leads to the rate expression

$$r_{\alpha}^{\pi,\pi'} = k_{\alpha}^{\pi,\pi'} (f_{\alpha}^{\pi} - f_{\alpha}^{\pi'}) \quad (7)$$

**Table 1**

Number of dynamic states  $n_s$  and the number of rate expressions  $n_r$  as function of the number of phases  $p$  and the number of species  $s$  in a system.

Phases $p$	1	2	3	4	$p$
States $n_s$	$s$	$2s$	$3s$	$4s$	$ps$
Rates $n_r$	0	$s$	$3s$	$6s$	$\frac{1}{2}p(p-1)s$

which describes a measure for the distance between equilibrium and non-equilibrium state. This rate becomes  $r_{\alpha}^{\pi,\pi'} = 0$  if the thermodynamic phase equilibrium is reached. The rate constant  $k_{\alpha}^{\pi,\pi'}$  describes the rate of mass transfer. Due to the fact, that we are interested in the steady state of the ODE system (1), this constant has no physical meaning and can be set to an arbitrary value, e.g.  $k_{\alpha}^{\pi,\pi'} = 1$ , or, it can be used as a parameter to adjust the numerical performance of the ODE solver. With the definitions of the fugacity coefficients  $\varphi_{\alpha}^{\pi}$  and activity coefficients  $\gamma_{\alpha}^{\pi}$  the fugacities  $f_{\alpha}^{\pi}$  can be written as

$$f_{\alpha}^{\pi} = x_{\alpha}^{\pi} \varphi_{\alpha}^{\pi} P \quad (8a)$$

or

$$f_{\alpha}^{\pi} = x_{\alpha}^{\pi} \gamma_{\alpha}^{\pi} f_{\alpha}^{\circ\pi} \quad (8b)$$

where the standard fugacity  $f_{\alpha}^{\circ\pi}$  can be set to the standard pressure  $f_{\alpha}^{\circ\pi} = P^{\circ} = 101,325 \text{ Pa}$ .

Eq. (8a) can be applied to gaseous as well as liquid phases. The fugacity coefficients  $\varphi_{\alpha}^{\pi}$  can be obtained from an Equation of State (EoS). In this work, we use the predictive Soave–Redlich–Kwong (PSRK) EoS (Holderbaum and Gmehling, 1991; Gmehling et al., 2012, p. 312).

Eq. (8b) is applied to liquid phases and the activity coefficient  $\gamma_{\alpha}^{\pi}$  can be computed from an activity coefficient model, such as NRTL or UNIQUAC. In this work we use the group contribution method UNIFAC (Gmehling et al., 2012).

In the case of a two-phase system, e.g. a VL or LL system, the stoichiometric matrix  $\mathbf{A}_p$  as well as the corresponding vector of rate expressions  $\mathbf{r}_p$  is given by

$$\mathbf{A}_p = \begin{bmatrix} -\mathbf{I} \\ \mathbf{I} \end{bmatrix}, \quad \mathbf{r}_p = [\mathbf{r}^{\pi_1,\pi_2}]. \quad (9a)$$

and for a three-phase system such as a VLL system  $\mathbf{A}_p$  and  $\mathbf{r}_p$  are given by

$$\mathbf{A}_p = \begin{bmatrix} -\mathbf{I} & -\mathbf{I} & 0 \\ \mathbf{I} & 0 & -\mathbf{I} \\ 0 & \mathbf{I} & \mathbf{I} \end{bmatrix}, \quad \mathbf{r}_p = \begin{bmatrix} \mathbf{r}^{\pi_1,\pi_2} \\ \mathbf{r}^{\pi_1,\pi_3} \\ \mathbf{r}^{\pi_2,\pi_3} \end{bmatrix}. \quad (9b)$$

The overall number of dynamic states  $n_s$  as well as the number of rate expressions  $n_r$  that are required are given in Table 1.

If in a three phase system one phase  $\pi$  is in equilibrium with the other phases  $\pi'$  and  $\pi''$ , the phase  $\pi'$  is also in equilibrium with

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