Simultaneous Chemical and Phase Equilibrium Calculations with Non-Stoichiometric Method - DTU Orbit (09/10/2019)

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Simultaneous chemical and phase equilibrium (CPE) calculations constitute a major class of challenging equilibrium problems, with applications in diverse scientific disciplines and engineering fields, such as the chemical industry, oil and gas production, and geochemistry. Robustness and efficiency of computational procedures are essential for demanding simulations of industrial processes, such as reactive distillation, heterogeneous organic synthesis, and fuel synthesis from renewable feedstocks. Most association equations of state, such as the popular SAFT family models, are essentially special cases of physical models incorporating chemical (association) equilibrium. Solution and further improvement of these association models can benefit from the advance in CPE calculations. Over 70 years of research on CPE computation have resulted in a long list of algorithms with many variants but there seems to be no clear consensus on the most adequate methods. The deterministic algorithms can be roughly divided into stoichiometric and nonstoichiometric methods. The stoichiometric methods are more intuitive but less efficient for systems with many reactions. They are usually implemented with inefficient nested loops, whereas quadratic formulation can involve quite a cumbersome implementation for multiple phases. The non-stoichiometric methods are less common but suitable to systems with many reactions. However, most applications of non-stoichiometric methods are for ideal single-phase mixtures to lightly non-ideal two-phase systems and the reported algorithms are mostly non-quadratic for non-ideal systems. The primary aim of this work is to develop a general and systematic non-stoichiometric approach which can determine the equilibrium state of multicomponent multiphase systems with multiple reactions at specified temperature and pressure. Two methods based on Gibbs energy minimization under material balance constraints are derived and presented in their extended form for non-ideal multi-phase reaction systems. Both can be classified under the same category of using the Lagrange multipliers (and the phase molar amounts) as variables. For distinction, they are called the Lagrange multipliers method and the modified RAND method, respectively. In the Lagrange multipliers method, successive substitution is employed to solve a modified set of equations originating from the Lagrangian conditions at the minimum. Convergence is quadratic for ideal systems (ideal gas/ideal solution) and linear for non-ideal systems. In the modified RAND method, one of the Lagrangian conditions is linearized around the current estimate of mole numbers. Composition derivatives of fugacity or activity coefficients are utilized to achieve quadratic convergence. The methods can be combined to form a robust and efficient approach: the Lagrange multipliers method is used for the first iterations of successive substitution and the modified RAND method for the second-order convergence. The resulting algorithm is called the combined algorithm in this thesis. For comparison, a successive substitution based algorithm using only the first-order Lagrange multipliers method is also investigated in this study. Both algorithms incorporate a reliable initialization procedure, where initial estimates are provided by the minimization of a convex function, and stability analysis to introduce additional phases when needed. The combined algorithm, as the recommended approach for CPE problems, has several advantages including a smaller system of equations (fewer variables), less sensitivity to initial estimates, the same treatment for all components and all phases, and the ability to monitor the decrease in Gibbs energy in the modified RAND steps to guide convergence. The algorithms were applied to vapor-liquid (VLE), liquid-liquid (LLE) and vapor-liquid-liquid (VLLE) equilibrium of ideal as well as non-ideal systems that are commonly tested in the literature, including acid/alcohol esterifications, alkene/alcohol ethersifications, hydration, hydrogenation and isomer separation. Additionally, predictions were made for the more complex transesterification of two individual triglycerides with methanol, which entails five chemical reactions and can result in one-, two- or even three-phase equilibrium. Finally, CPE calculations were attempted for electrolyte systems. The electroneutrality equation is satisfied by the material balance constraints, therefore there is no need to change the working equations of the algorithms. The equilibrium solution was obtained for aqueous mixtures of electrolytes in contact with a vapor and a solid phase. Consideration of the solid phase did not affect the convergence of the initial procedure or the CPE calculations. This makes the algorithms potentially applicable to more complicated geological systems with an electrolyte aqueous phase and multiple solids. From the simple one-reaction ideal systems to the highly non-ideal electrolyte mixtures with speciation reactions and solids, both algorithms could converge without problems to the electrolyte solution. The CPU time and the reasonable number of iterations, allowed us to conclude that the methods presented are efficient and robust for the equilibrium determination of reaction systems. The thesis also involves a small study on the dimethyl ether (DME) phase equilibrium modeling. DME is a slightly polar compound able to dissolve in both water/brine and hydrocarbon phases. It has been considered as a novel solvent in enhanced oil recovery, and more specifically in DME enhanced waterflooding (DEW) process. DME is dissolved in water/brine and injected into the reservoir. It partitions preferably into the oil phase to improve the mobility of the oil by swelling it and reducing its viscosity. DME itself is first-contact miscible with the oil. Accurate phase equilibrium modeling is necessary in DEW simulations. Parameters for CPA and PR/SRK EoS with Huron-Vidal mixing rules are regressed from experimental data of DME binary systems with water, hydrocarbons and inert gases. With satisfactory phase equilibrium modeling, predictions are made focusing on the K-value of DME between oil and aqueous phases in DME/water/oil mixtures (oil modeled as a mixture of methane, n-butane and n-decane). Different oil compositions appear to slightly affect the partitioning of DME, which could possibly simplify simulations of the DEW process. Finally, sensitivity of the K-value is investigated with respect to temperature, pressure and salinity of the aqueous phase. K-values increase with temperature and salinity but slightly decrease with pressure. Dependence on temperature is larger, while high salinity in the aqueous phase favors markedly the DME partitioning into the oil phase.

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