

Report on OLI Engine's phase identification

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SUBJECT: OLI Engine's phase identification

Introduction

The story of how the Engine decides what phases need to be included and how the species are distributed starts in the Engine's initializer. The phases of interest are liquid-1(aqueous), liquid-2 (organic), vapor and solids. In this report, focus is on the liquid-1, liquid-2 and vapor phases. For the MSE model [1], the activity coefficients for liquid-1 and liquid-2 phases are obtained using the liquid phase activity coefficient model [1] and vapor phase fugacity coefficients are obtained using the Soave-Redlich-Kwong (SRK) equation of state [2]. On the other hand, the AQ model uses the liquid phase activity coefficient model [3] only for liquid-1 phase and the SRK equation of state for both vapor and liquid-2 fugacity coefficients. The initializer sets the phases that must be present which is ultimately used by the solver for the final equilibrium calculation.

SRK equation of state and the vapor phase

The Engine uses the SRK equation of state to predict the vapor phase fugacity coefficients (MSE model) and both vapor and liquid-2 fugacity coefficients in the AQ model. It is a cubic equation of state and has up to three roots, the largest of the roots being the vapor root and the smallest being the liquid root. Depending on system conditions, there might be one real root (single phase), three equal real roots (critical point) or three distinct real roots (a possible multiphase system).

For the MSE model, the role of SRK equation is to calculate the vapor fugacity coefficients in the iteration step as required. For the AQ model, in addition to the vapor phase, the liquid-2 phase fugacity coefficients are also calculated. *Solving the SRK equation of state and obtaining valid vapor/liquid-2 roots does not guarantee the phases are present in the final system.* In both models, it is the total convergence and careful analysis of phase amounts in each 'test' phase that ultimately determines phase equilibrium. The idea of a 'test' phase will be made clear in the next section.

The initializer in a nutshell

Prior to generating the final set of phase equilibrium equations, the initializer predicts the probable valid phases and guesses for species concentrations in each phase, and some properties i.e. enthalpy, pH etc. depending on the type of calculation. The AQ and MSE models use different approaches for initialization. For the MSE model, the initializer starts by assuming only liquid-1 and liquid-2 phases being present. It then proceeds to partition the inflows to the liquid phases (liquid-1 and liquid-2) and performs the equilibrium convergence routine while continually calculating the liquid phase activity coefficients. If the convergence occurred within allowable tolerance, the initializer proceeds to add the vapor phase. This is initiated by calculating the vapor phase fugacity coefficients (SRK equation of state) and obtaining species concentration guesses in the vapor phase. The decision to add vapor

is done by checking if the sum of mole fractions in the vapor phase is greater than unity i.e. $\sum y_i > 1.0$. If yes, then the current species concentration in the vapor phase is used in the next iteration step, otherwise vapor is not added. Hence vapor is tested to be present or absent in the phase equilibrium calculation depending on its tendency to form, hence it is a 'test' phase in this part of the calculation. The cycle continues by trying to converge all the added phases, if all phases converge the initializer tests for the total amounts in liquid-2 phase and if it is below tolerance, the phase is excluded and the case is re-converged. Finally if all liquid-2 and vapor phase totals are within tolerance, the phases are included. Liquid-1 phase cannot be excluded as all the equilibrium calculations depend on it. The initializer treats pure component inflows differently; it will not be discussed here. Below is a highly simplified block diagram of the initializer.

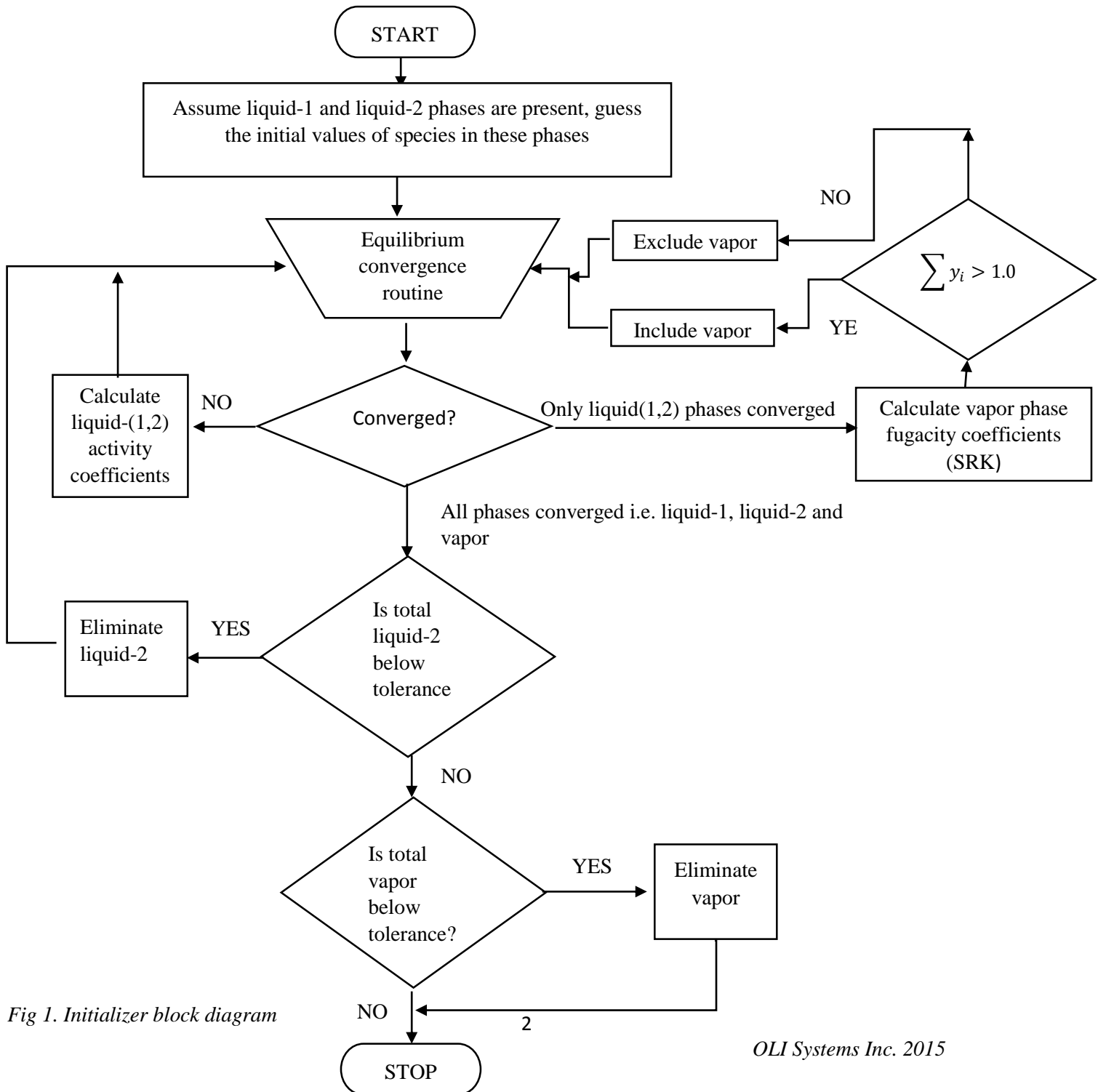


Fig 1. Initializer block diagram

In the AQ model, if there is no water, it proceeds to exclude the aqueous phase and tries to find vapor and liquid-2 compositions. It essentially tries to converge the vapor-organic equilibrium using SRK derived fugacity coefficients. Based on these results, vapor and organic initial guesses are stored or one or both phases are excluded. This completes the initialization for no water type of condition. If water is present, the initializer proceeds to compute the aqueous-vapor equilibrium using a simplified flash calculation. If organic phase has been enabled, the initializer computes the organic-vapor liquid equilibrium using the SRK equation of state just as if the aqueous phase was absent, as explained at the beginning. Organic and vapor phases might be excluded depending on the results of this step. The AQ model finally performs the same initialization procedure as described above in the MSE model to get final species concentration guesses. Phases that have been excluded in the previous steps will not be a part of this initialization.

Engine treatment and the supercritical phase

Apart from the four obvious phases (liquid-1, liquid-2, vapor and solids), the supercritical phase cannot be predicted at a given condition for multicomponent systems, short of analyzing the complete topology of the phase diagram in wide P-T ranges and even then there would be a degree of arbitrariness in defining it. A supercritical phase is devoid of a clear demarcation between a liquid or a gas and in essence inherits properties from both types depending on system state variables. This means that there might be a smooth transition of density between two phases. As far as the Engine is concerned, a phase could be supercritical and be classified as liquid-1, liquid-2 or vapor phase depending on the phase equation system convergence i.e. whether that phase is tending towards being a vapor or a liquid.

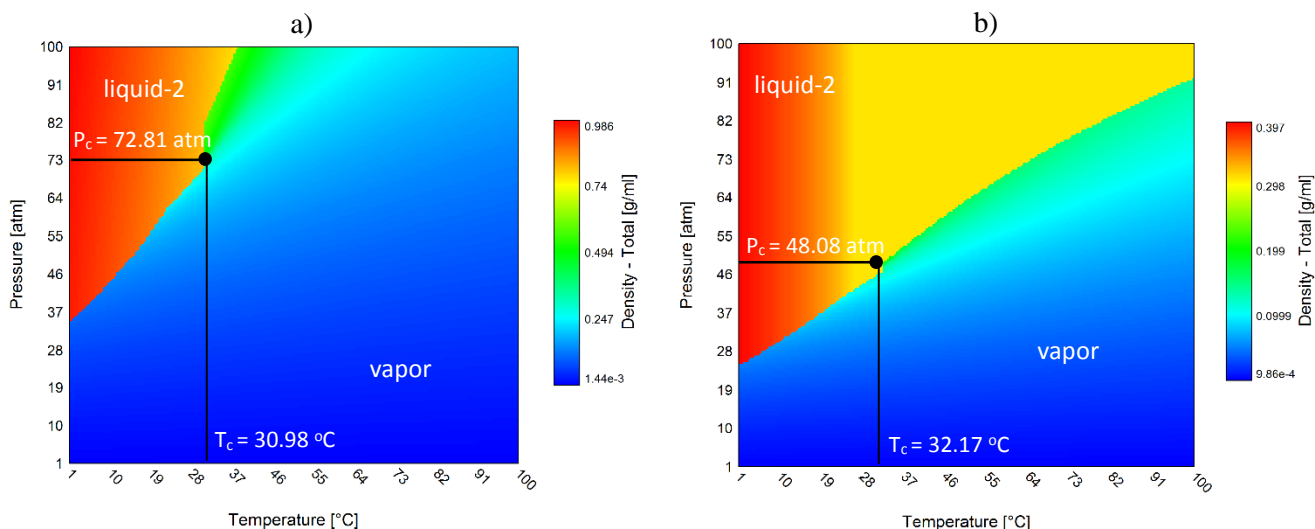


Fig 2. a) Density VS. [P,T] for carbon dioxide b) Density VS. [P,T] for ethane

From Fig 2., a clear demarcation between the calculated liquid-2 and vapor phases can be observed. In the subcritical region the difference in densities is clear between the two phases, however, in the supercritical region this becomes less apparent. In any case density cannot be an indicator for phase assignment in any region, the determinant factor is the phase equilibrium calculation convergence.

Concluding remarks

The engine does not make a strong connection to actual physical meanings of a phase (aqueous, organic and vapor) and the variables it solves for in a “phase” other than the argument that these phases tends to appear liquid like or vapor like. For the engine there are three physically distinct types of phases which is phase-1, phase-2 and phase-3. This is because the classification of phases is unavoidably arbitrary at some conditions. From the earlier discussion, it was also inferred that density was found to be a poor indicator of phase type.

References

- [1] P. Wang, A. Anderko, *Fluid Phase Equilib.* 141-176 (2002) 203
- [2] G. Soave, *Chemical Engineering Science*, 1197-1203 (1972) 27
- [3] J.F. Zemaitis, Jr., “Thermodynamics of Aqueous Systems with Industrial Applications.” *Predicting Vapor-Liquid-Solid Equilibria in Multicomponent Aqueous Solutions of Electrolytes*. Ed. S.A. Newman, H.E. Barner, M. Klein, S.I. Sandler, 1979. 227-246. Print.