An Algorithm for Phase Determination in Multiphase Equilibrium

Alberto Posada, Andrés F. Merchán, Jorge A. Velásquez.
Facultad de Ingeniería Química, Universidad Pontificia Bolivariana, Circular 1 #70-01, Medellín, Colombia

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Abstract

Efficient and robust methods for phase determination in multiphase-multicomponent equilibrium are key tools for chemical processes simulation. The most widely used methods for equilibrium calculations are generally based on Gibbs free energy minimization or on simultaneous solving of the material balance and equilibrium equations. Both techniques exhibit numerical challenges due to the involvement of highly nonlinear functions/equations and their efficiencies depend on initialization procedures since the number and type of phases present are not known a priori.

In this work, an equation-solving algorithm is proposed for determination of the number and type of phases, and their corresponding fractions and compositions, in vapor-liquid equilibrium, for given temperature, pressure and overall composition. The algorithm follows a decision flowchart that, based on actual pressure and the system's phase change pressure values at fixed temperature and overall compositions, determines the number and type of equilibrium phases present and the corresponding set of equations describing material balances and phase equilibria. Assumption on a bound for the number of equilibrium phases only need to be done for the calculation of the bubble point pressure. A solution is first exhaustively searched for the case of two liquid phases; if no solution is found, then a single liquid phase is considered for bubble point calculation. The robustness of the algorithm is based on the facts that the two-phase (vapor-liquid and liquid-liquid) and three-phase (vapor-liquid-liquid) isothermal flash calculations are performed only when a physically meaningful solution is guaranteed to exist, and good initial guesses for their corresponding solutions are obtained from a previous calculation of a phase change pressure.

The algorithm was implemented using the Patel-Teja Equation of State and the Wong-Sandler mixing rules for calculation of thermodynamic properties; and numerical solutions of the resulting nonlinear equation sets were obtained using homotopy-based methods. Applications of the algorithm to typical examples for two-phase and three-phase equilibrium calculations are presented along with comparisons against other calculation and initialization methods in the literature.

Description of the algorithm

The proposed algorithm follows the decision flowchart shown in Fig. 1., that based on actual pressure (P) and the system's phase change pressure values (dew pressure (P_d), bubble pressure (P_b), and secondary dew pressure (P_{ds})) at fixed temperature (T) and overall compositions ($z_i \ \forall i = 1,\ldots, N$), determines the number and type of equilibrium phases present and the corresponding set of equations describing material balances and phase equilibria. The main equations used by the algorithm are summarized below. The description of the notation is given in a separate section at the end. The fugacity coefficients can be calculated using the Patel-Teja Equation of State (Patel and Teja, 1982) and the Wong-Sandler mixing rules (Wong and Sandler, 1992).
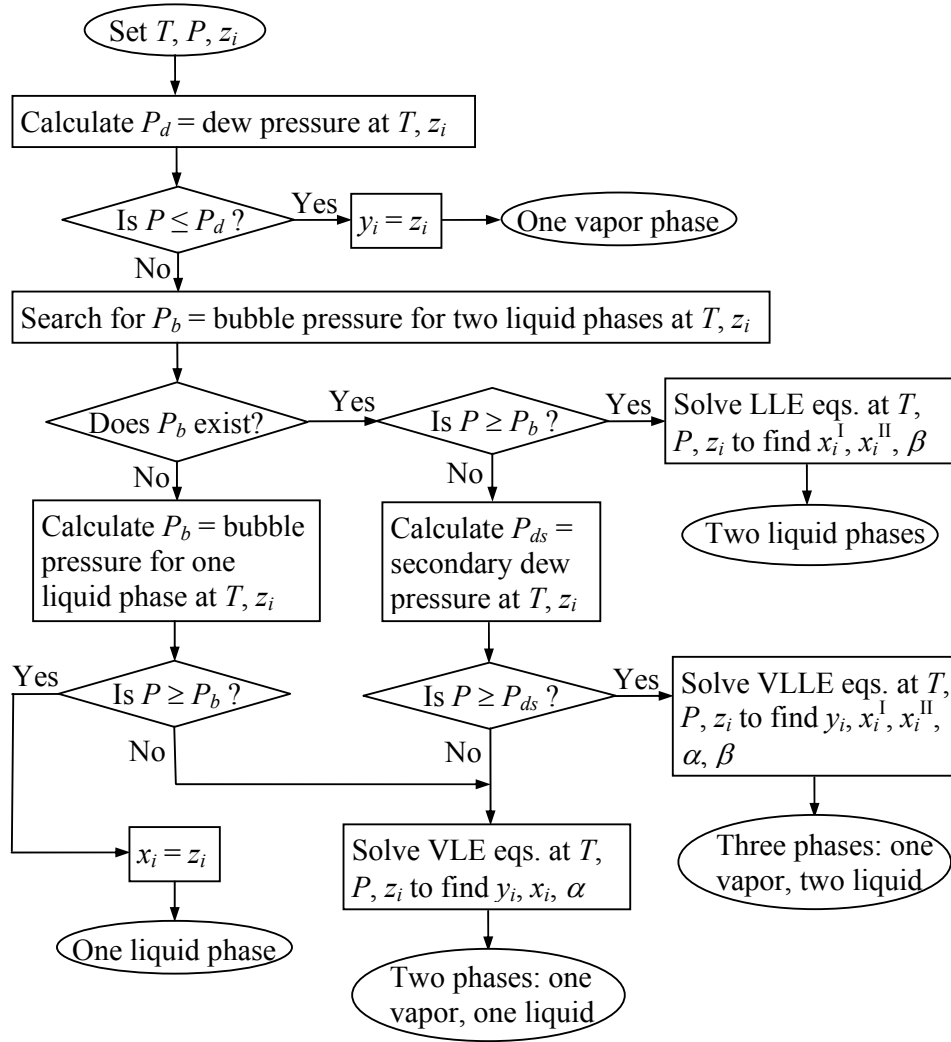
Fig 1. Algorithm's flowchart.

VLLE equations:

$$z_i = v_i + l_i^I + l_i^{II} \quad \forall i = 1,...,N \tag{1}$$

$$\hat{\phi}_i^V \frac{v_i}{\sum\limits_{j=1}^{N} v_j} = \hat{\phi}_i^I \frac{l_i^I}{\sum\limits_{j=1}^{N} l_j^I} \quad \forall i = 1,...,N \tag{2}$$

$$\hat{\phi}_i^V \frac{v_i}{\sum\limits_{j=1}^{N} v_j} = \hat{\phi}_i^{II} \frac{l_i^{II}}{\sum\limits_{j=1}^{N} l_j^{II}} \quad \forall i = 1,...,N \tag{3}$$

VLE equations:

$$z_i = v_i + l_i \quad \forall i = 1,...,N \tag{4}$$

$$\hat{\phi}_i^V \frac{v_i}{\sum\limits_{j=1}^{N} v_j} = \hat{\phi}_i^L \frac{l_i}{\sum\limits_{j=1}^{N} l_j} \quad \forall i = 1,...,N \tag{5}$$

LLE equations:

$$z_i = l_i^I + l_i^{II} \quad \forall i = 1,...,N \tag{6}$$

$$\hat{\phi}_i^I \frac{l_i^I}{\sum\limits_{j=1}^{N} l_j^I} = \hat{\phi}_i^{II} \frac{l_i^{II}}{\sum\limits_{j=1}^{N} l_j^{II}} \quad \forall i = 1,...,N \tag{7}$$

Equations for calculation of compositions in mole fractions in each phase:

$$y_i = \frac{v_i}{\sum\limits_{j=1}^{N} v_j} \quad \forall i = 1,...,N \tag{8}$$

$$x_i = \frac{l_i}{\sum\limits_{j=1}^{N} l_j} \quad \forall i = 1,...,N \tag{9}$$

$$x_i^I = \frac{l_i^I}{\sum\limits_{j=1}^{N} l_j^I} \quad \forall i = 1,...,N \tag{10}$$

$$x_i^{II} = \frac{l_i^{II}}{\sum\limits_{j=1}^{N} l_j^{II}} \quad \forall i = 1,...,N \tag{11}$$

Equations for calculation of phase fractions:

$$\alpha = \sum\limits_{i=1}^{N} v_i \tag{12}$$

$$\beta = \frac{\sum\limits_{i=1}^{N} l_i^I}{\sum\limits_{i=1}^{N} l_i^I + \sum\limits_{i=1}^{N} l_i^{II}} \tag{13}$$

Calculation of dew pressure

The dew pressure (P_d) is calculated by solving for P, v_i, and l_i, for given T and z_i, from the system of VLE equations (Eqs. (4) and (5)) subject to restriction (14), i.e. an infinitesimal liquid droplet containing the total mass present in the liquid phase:

$$\sum\limits_{i=1}^{N} l_i = 1 \times 10^{-10} \tag{14}$$

The solution of this system can be obtained using homotopy continuation methods (Wayburn and Seader, 1987). The following initial values are proposed: $P = 1/\sum_{i=1}^{N} \dfrac{z_i}{P_i^{sat}}$ (applying Raoult's law); $v_i = z_i \; \forall i = 1,\dots, N$; $l_i = 0.01z_i \; \forall i = 1,\dots, N$. The solution obtained for P is P_d; and the corresponding values of v_i and l_i are substituted in Eqs. (8) and (9), respectively, to calculate the composition of the vapor phase (y_i; $y_i \approx v_i \approx z_i$), and the composition of the first liquid droplet (x_i), respectively.

Calculation of bubble pressure for two liquid phases

The bubble pressure (P_b) for two liquid phases is calculated by solving for P, v_i, l_i^{I}, and l_i^{II}, for given T and z_i, from the system of VLLE equations (Eqs. (1)–(3)) subject to restriction (15), i.e. an infinitesimal vapor bubble containing the total mass present in the vapor phase:

$$\sum_{i=1}^{N} v_i = 1 \times 10^{-10} \tag{15}$$

The solution of this system can be obtained using homotopy continuation methods. The following initial values are proposed: $P = 1.2P_d$; $v_i = 0.01z_i$. Liquid phase I is assumed to be richer in the component with the highest critical pressure (usually the aqueous phase). Liquid phase II is assumed to be richer in the component with the lowest critical pressure. If component j has the highest critical pressure, and component k has the lowest critical pressure, then the initial values are the following: $l_j^{I} = 0.9z_j$; $l_k^{I} = 0.1z_k$; $l_i^{I} = l_i^{II} = 0.5z_i \; \forall i \neq j,\ i \neq k$; $l_j^{II} = 0.1z_j$; $l_k^{II} = 0.9z_k$. The solution obtained for P is P_b, and the corresponding values of v_i, l_i^{I}, and l_i^{II} are substituted in Eqs. (8), (10), (11), and (13), to calculate the composition of the first vapor bubble (y_i), the compositions of the liquid phases I and II (x_i^{I} and x_i^{II}), and the fraction of the liquid that corresponds to phase I (β), respectively. The search for a solution is exhaustive, so that if no solution is found, it can be concluded that the probability of existence of the vapor-liquid-liquid equilibrium is too low, and the algorithm assumes it does not exist.

Calculation of bubble pressure for one liquid phase

The bubble pressure (P_b) for one liquid phase is calculated by solving for P, v_i, and l_i, for given T and z_i, from the system of VLE equations (Eqs. (4) and (5)) subject to restriction (15). The solution of this system can be obtained using homotopy continuation methods. The following initial values are proposed: $P = \sum_{i=1}^{N} z_i P_i^{sat}$ (applying Raoult's law); $v_i = 0.01z_i \; \forall i = 1,\dots, N$; $l_i = z_i \; \forall i = 1,\dots, N$. The solution obtained for P is P_b; and the corresponding values of v_i and l_i are substituted in Eqs. (8) and (9), respectively, to calculate the composition of the first vapor bubble (y_i) and the composition of the liquid phase (x_i; $x_i \approx l_i \approx z_i$), respectively.

Calculation of secondary dew pressure

The secondary dew pressure (P_{ds}) is calculated by solving for P, v_i, l_i^{I}, and l_i^{II}, for given T and z_i, from the system of VLLE equations (Eqs. (1)–(3)) subject to restriction (16), i.e. an infinitesimal liquid droplet containing the total mass of either liquid phase I or liquid phase II:

$$L^I \triangleq \sum_{i=1}^{N} l_i^I = 1 \times 10^{-10} \quad \text{or} \quad L^{II} \triangleq \sum_{i=1}^{N} l_i^{II} = 1 \times 10^{-10} \tag{16}$$

The solution of this system can be obtained using Newton´s method with mapping into the subspace of nonnegative real numbers, however its success is highly dependent on good initial values. The solution obtained from the previous calculation of the bubble pressure for two phases, i.e. the solution to (1)–(3) at P_b, is a good initial value if P_{ds} is close to P_b. Since this is not always the case, the following methodology is proposed: using the values from the solution at P_b, determine the minimum between L^I and L^{II}, and assign the corresponding value to L_{min}. If for example the minimum is L^I, then replace constraint (16) with the following constraint for L^I, depending on the magnitude of L_{min}: $L^I = 0.1 L_{min}$ if $L_{min} \leq 0.1$; or $L^I = L_{min} - 0.1$ if $L_{min} > 0.1$. If the minimum is L^{II}, then the constraint is defined for L^{II} instead. Employing Newton´s method with mapping into nonnegative numbers, solve the resulting system, using the solution at P_b as initial value. The new solution is used to recalculate L^I and L^{II}, determine the new value of L_{min} (that will be lower than the previous one), and redefine the constraint used to replace constraint (16), as explained above. Solve the new system using the previous solution as initial value. This way the system is solved each time using a constraint with a lower value of L_{min}, and the process is repeated until $L_{min} \leq 1 \times 10^{-10}$ is reached. The solution obtained for P is P_{ds}, and the corresponding values of v_i, l_i^I, and l_i^{II} are substituted in Eqs. (8) and (10)–(12), to calculate the composition of the vapor phase (y_i), the compositions of the liquid phases I and II (x_i^I and x_i^{II}), and the fraction of the system that corresponds to the vapor phase (α), respectively.

VLE calculation

The system of VLE equations (Eqs. (4) and (5)) is solved to find v_i and l_i, for given T, P, and z_i. The solution of this system can be obtained using Netwon´s method with mapping into the subspace of nonnegative real numbers. The initial values proposed are those corresponding to the dew point previously calculated (see calculation of dew pressure). The values obtained for v_i and l_i are substituted in Eqs. (8), (9), and (12), to calculate the composition of the vapor phase (y_i), the composition of the liquid phase (x_i), and the fraction of the system that corresponds to the vapor phase (α), respectively.

VLLE calculation

The system of VLLE equations (Eqs. (1)–(3)) is solved to find v_i, l_i^I, and l_i^{II}, for given T, P, and z_i. The solution of this system can be obtained using Netwon´s method with mapping into the subspace of nonnegative real numbers, however its success is highly dependent on good initial values. The solution obtained from the previous calculation of the bubble pressure for two phases, i.e. the solution to (1)–(3) at P_b, is a good initial value if P is close to P_b. Since this is not always the case, the following methodology is proposed: employing Newton´s method with mapping into nonnegative numbers, the system is solved first at a pressure P_1, where P_1 is close to P_b, and $P_1 < P_b$ (e.g. $P_1 = P_b - 0.05$ kPa), using the solution at P_b (from bubble pressure calculation for two liquid phases) as initial value. Then the pressure is set to a lower value, below and close to P_1, and the system is solved using the solution at P_1 as the new initial value. This way the system is solved each time at a lower pressure, and the process is repeated until given P is reached. The solution values obtained for v_i, l_i^I, and l_i^{II} are substituted in Eqs. (8) and (10)–(13), to calculate the composition of the vapor phase (y_i), the compositions of the liquid phases I and II (x_i^I and x_i^{II}), the fraction of the system that corresponds to the vapor phase (α), and the fraction of the liquid that corresponds to phase I (β), respectively.

LLE calculation

The system of LLE equations (Eqs. (6)–(7)) is solved to find l_i^I and l_i^{II}, for given T, P, and z_i. Based on the arguments discussed for the VLLE calculation, the following methodology is proposed: using Newton´s method with mapping into nonnegative numbers, the system is solved first at a pressure P_1, where P_1 is close to P_b, and $P_1 > P_b$ (e.g. $P_1 = P_b + 0.05$ kPa), using the solution at P_b (from bubble pressure calculation for two liquid phases) as initial value. Then the pressure is set to a higher value, above and close to P_1, and the system is solved using the solution at P_1 as the new initial value. This way the system is solved each time at a higher pressure, and the process is repeated until given P is reached. The solution values obtained for l_i^I and l_i^{II} are substituted in Eqs. (10), (11), and (13), to calculate the compositions of the liquid phases I and II (x_i^I and x_i^{II}), and the fraction of the liquid that corresponds to phase I (β), respectively.

Notation

l_i : fraction of the moles of component i ($\forall i = 1,\ldots, N$) in the system that are in the liquid phase
l_i^I : fraction of the moles of component i ($\forall i = 1,\ldots, N$) in the system that are in liquid phase I
l_i^{II} : fraction of the moles of component i ($\forall i = 1,\ldots, N$) in the system that are in liquid phase II
L^I : fraction of the moles in the system that are in liquid phase I
L^{II} : fraction of the moles in the system that are in liquid phase II
L_{min}: minimum between L^I and L^{II}
N : total number of components
P : pressure
P_b : bubble pressure
P_d : dew pressure
P_{ds} : secondary dew pressure
P_i^{sat} : vapor pressure of pure component i.
T : temperature
v_i : fraction of the moles of component i ($\forall i = 1,\ldots, N$) in the system that are in the vapor phase
x_i : mole fraction of component i ($\forall i = 1,\ldots, N$) in the liquid phase
x_i^I : mole fraction of component i ($\forall i = 1,\ldots, N$) in liquid phase I
x_i^{II} : mole fraction of component i ($\forall i = 1,\ldots, N$) in liquid phase II
y_i: mole fraction of component i ($\forall i = 1,\ldots, N$) in the vapor phase
z_i: mole fraction of component i ($\forall i = 1,\ldots, N$) in the system

Greek symbols

α : fraction of the moles in the system that are in the vapor phase
β : fraction of the moles in the liquid that are in liquid phase I
$\hat{\phi}_i^I$: fugacity coefficient of component i in the liquid phase I mixture.
$\hat{\phi}_i^{II}$: fugacity coefficient of component i in the liquid phase II mixture
$\hat{\phi}_i^L$: fugacity coefficient of component i in the liquid phase mixture
$\hat{\phi}_i^V$: fugacity coefficient of component i in the vapor phase mixture

References

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