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Generalized Phase Boundary Determination Algorithm for Multicomponent Mixtures

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An improved method to determine phase boundaries for multicomponent mixtures is described. This technique uses procedures based upon Gibbs minimization that lead to a more efficient algorithm that can also converge closer to the mixtures' critical points than other algorithms (e.g., *K*-value method). Moreover, all the curves reported correspond to stable points according to the stability analysis suggested by Michelsen that implies minimization of the tangent plane distance function. Several examples compare the efficiency of this technique to commercial programs that often fail at certain conditions around the critical point, cricondenbar, and/or cricondentherm.

1. Introduction

Phase boundary calculations play an important role in phase equilibrium calculations in industrial applications, such as process design and studies of hydrocarbon systems. Currently, most of the commercial programs that determine phase boundaries use the *K*-value method, which solves a set of material balances and thermodynamic equations (equality of chemical potentials). Despite its fast computational performance, this method often predicts trivial solutions corresponding to local Gibbs energy minima; hence, many of these solutions do not satisfy the stability criterion proposed by Michelsen.^{1,2} In addition, the choice of inappropriate initial estimates can cause the programs to fail.

This work proposes a generalized algorithm to determine phase boundaries based upon a method described by Iglesias-Silva et al.³ Following the equal area method proposed by Eubank and Hall⁴ and developed further in a series of papers involving their students,^{5–10} the procedure generates a system of nonlinear algebraic equations whose solution results in Gibbs minimization.³ For construction of the phase envelope, the method sets the composition of one of the phases equal to the overall composition depending upon the type of calculations considered: for bubble point calculations, it is the composition of the liquid phase, and for dew point calculations, it is the vapor phase composition. The last unknown to fulfill the set of equations is either the pressure or the temperature, the choice of which depends upon the dimensionless slope of the phase envelope. Ziervogel and Poling¹⁰ propose a simple technique to determine the use of *P* or *T*.

Other key issues are the initial estimates and the numerical method. Resolution of the first issue results from calculating stationary points that are approximations to the actual solution. Moreover, initial guesses can be the calculated variables from the previous iteration. Regarding the numerical solution of the nonlinear system of equations, a combination of optimization procedures and a globally convergent gradient method leads to fast convergence in most cases.

Finally, a stability analysis of each converged solution assures that all points reported correspond to stable and correct solutions.¹ The results indicate that this procedure works even in regions close to the critical point, the cricondenbar, and the cricondentherm. This paper compares difficult systems using the current method to commercial predictions, which usually fail in different regions of the curve. This work uses the Peng–Robinson (PR)¹² and Soave–Redlich–Kwong (SRK)¹³ equations of state.

2. Phase Equilibrium Model

Iglesias-Silva et al.³ proposed a Gibbs minimization technique that requires only the solution of a set of algebraic equations to determine phase boundaries. The technique applies to any number of phases and any number of components, *C*. The generalized equations resolve into one set that represents equality of the chemical potentials (or fugacities) and an equation that provides a tangent plane expression. The chemical potential set is

$$\left(\frac{\partial g}{\partial x_i}\right)^v_{TP_{x_{k \neq i}}} = \left(\frac{\partial g}{\partial x_i}\right)^l_{TP_{x_{k \neq i}}} = \dots = \left(\frac{\partial g}{\partial x_i}\right)^\pi_{TP_{x_{k \neq i}}} \quad \text{for } i = 1, 2, \dots, C - 1 \quad (1)$$

in which *T* is temperature, *P* is pressure, *x* is composition, the superscripts represent phases (*v* is vapor, *l* is liquid and *π* represents number of phases); and *g* is the reduced Gibbs energy of mixing. It is necessary to use either the total Gibbs energy (*nG*) or the Gibbs energy of mixing in phase equilibrium problems. Either of these properties may be used because their derivatives with respect to composition are directly proportional. The Gibbs energy of mixing is

$$\frac{\Delta_m G}{RT} = g(x_1, x_2, \dots, x_{C-1}) = \frac{G - G_C^0}{RT} - \sum_{j=1}^{C-1} x_j \frac{G_j^0 - G_C^0}{RT} \quad (2)$$

in which the superscript 0 indicates pure fluid. Assuming *π* is 2 (where *π* is the number of phases), it is necessary to solve *C* – 1 equations at equilibrium. Shyu et al.⁵ provide an expression

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to calculate the derivative g with respect to composition from an equation of state:

$$\left(\frac{\partial g}{\partial x_i}\right)_{TP_{k \neq i}} = \ln\left(\frac{\hat{f}_i^n}{\hat{f}_i^f}\right) \quad (3)$$

Equation 1 can be evaluated if one knows the fugacities of the pure components, f_i , at the mixture conditions, and the partial fugacities, \hat{f}_i , in both phases. In this equation, the subscript n represents a reference component, which could be any of the C components.

The tangent plane equation references an equilibrium point in a phase α . Generalizing over all equilibrium points, in any phase i

$$(g^i - g^\alpha) - \sum_{j=1}^{C-1} (x_j^i - x_j^\alpha) \left(\frac{\partial g}{\partial x_j}\right)_{TP_{k \neq j}}^\alpha = 0 \quad \text{for } i = \beta, \gamma, \dots, \pi - 1 \quad (4)$$

Equation 4 takes into account the tangent plane criterion and provides additional equations that accompany the set of equations from eq 1. Upon convergence, the C equations formed from combining eqs 1 and 4 reduce identically to the equality of chemical potentials. However, at convergence this set of equations also guarantees global Gibbs minimization of the system.

One might ask why not simply use the equal fugacities criterion that leads to the K -value method. Many authors have developed phase equilibrium calculations based upon this technique;¹⁹ however, the method has many drawbacks for systems more complex than two components with two phases. Anything other than excellent initial guesses to start the calculations can lead to local Gibbs minima (incorrect solutions) or to no solution at all. The K -value method also has problems as the calculations approach the cricondentherm, the cricondenbar, and the critical point.

3. Algorithm

This work tests the algorithm with two equations of state: Peng–Robinson (PR)¹² and Soave–Redlich–Kwong (SRK).¹³ The binary interaction parameters used, determined at Texas A&M University, currently remain unpublished. The principle underlying this algorithm is that, for dew points, the composition of the vapor phase is the overall composition, and for bubble points, the overall composition is the composition of the liquid phase. It is convenient to perform the first iteration at low pressure, where Raoult's law provides a reasonable estimate for the initial temperature and composition in the unknown phase (vapor if it is a bubble point calculation or liquid if it is a dew point). The Antoine equation can model vapor pressures for pure components. Afterward, improving the initial estimates result from finding stationary points. These are compositions that minimize the tangent plane distance function:^{3,19}

$$F(x) = \sum_{i=1}^C x_i (\mu_i^l - \mu_i^z) \quad (5)$$

where μ_i is the chemical potential. Michelsen et al.¹⁹ propose that the stationary points for the tangent plane distance in a binary mixture exist where the tangent to the Gibbs energy curve is parallel to the tangent at z (the overall composition). In the same way, this statement applies to multicomponent mixtures by solving

$$\left(\frac{\partial g}{\partial x_i}\right)_{TP_{k \neq i}} \Big|_x - \left(\frac{\partial g}{\partial y_i}\right)_{TP_{k \neq i}} \Big|_{y=z} = 0 \quad \text{for } i = 1, 2, \dots, C - 1 \quad (6)$$

$$\left(\frac{\partial g}{\partial y_i}\right)_{TP_{k \neq i}} \Big|_y - \left(\frac{\partial g}{\partial x_i}\right)_{TP_{k \neq i}} \Big|_{x=z} = 0 \quad \text{for } i = 1, 2, \dots, C - 1 \quad (7)$$

Equation 6 applies to dew points and eq 7 to bubble points, while y and x represent the compositions in the vapor and liquid phases, respectively. The Levenberg–Marquardt^{14–16} algorithm together with a line search method provides the solution of eqs 6 and 7.

It is important to decide whether the pressure or the temperature is the proper variable at any calculation stage (except the first iteration where the low pressure is the parameter and the temperature is variable). This work uses the dimensionless criterion suggested by Ziervogel and Poling.¹¹ They suggest a temperature or pressure calculation depending upon the value of $\beta = d(\ln P)/d(\ln T)$. They suggest a pressure calculation when $\beta < 2$ and a temperature calculation when $\beta > 20$. If the β values lie between 2 and 20, either calculation converges. This work uses $\beta < 20$ for pressure calculations and $\beta > 20$ for temperature calculations. This paper also uses only one switching criterion instead of two as originally proposed. This is possible because this paper has different equilibrium equations compared to the K -value method used by Ziervogel and Poling.¹¹

The stationary compositions provide the initial guesses for pressure or temperature. After finding the stationary compositions, the next step is to solve eqs 4 and 6. For the latter equation, any phase may serve as reference. The first step is to perform an optimization procedure similar to that in the stationary points subroutine. Then, these numbers become initial values for a globally convergent method that combines the rapid convergence of the Newton method with line-search and backtracking strategies using a safeguarded mixed quadratic and cubic polynomial interpolation and extrapolation. In both, finding stationary points and equilibrium solutions, the number of iterations lies between 8 and 20, depending upon the tightness of the tolerance criteria and the proximity to the critical point; for normal tolerances, the number of iterations is roughly 12. Also, it is important to note that when the number of components increases, convergence near the critical region becomes more difficult. Hence, it is normal to expect a small gap near the critical point (where the solution fails) in mixtures with many components.

Subsequently, it is necessary to ensure the stability of each point.^{1,2} Non-negative values for the tangent plane distance function, eq 5, satisfy this criterion (eq 5 is zero at a stationary point). Finally, each point uses the last calculated value as its initial guess and the process continues. This proceeds up to the critical point, where both the bubble and dew point routines fail. The program also stops when encountering an azeotrope, because one of the criteria to stop is the equality of compositions. Figure 1 is a flow diagram for the algorithm.

4. Results and Discussion

Figure 2 compares the current algorithm to two well-known commercial programs for the calculation of phase envelopes: PhasePro¹⁷ and REFPROP;¹⁸ the latter is an offering from the National Institute of Standards and Technology. The Peng–Robinson equation of state (EOS) is used to calculate the phase boundary of a binary mixture consisting of 90 mol % methane

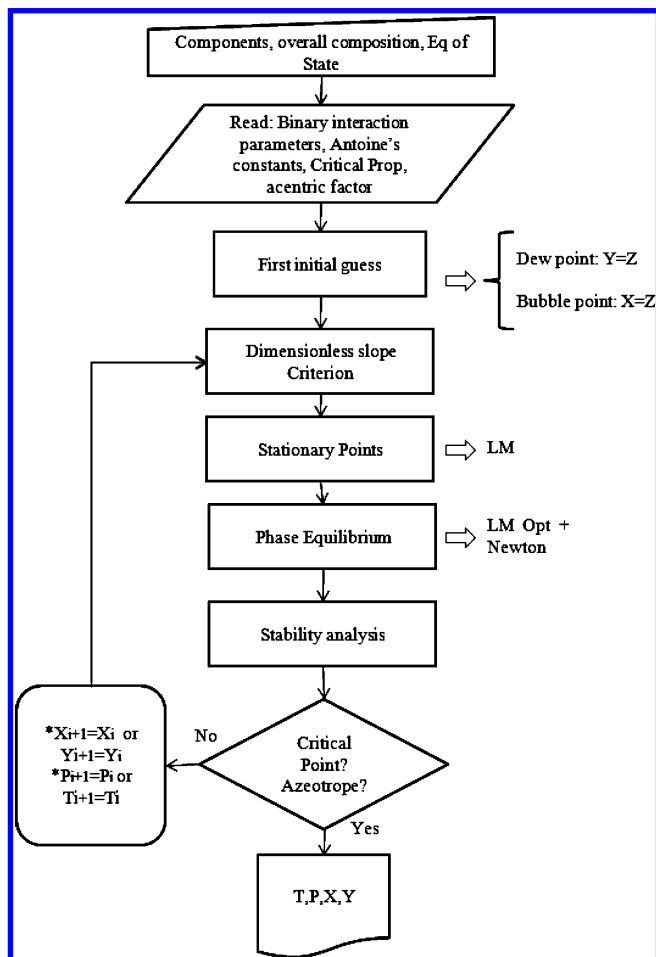


Figure 1. General flowchart of the algorithm; LM, Levenberg–Marquardt; Opt, optimization.

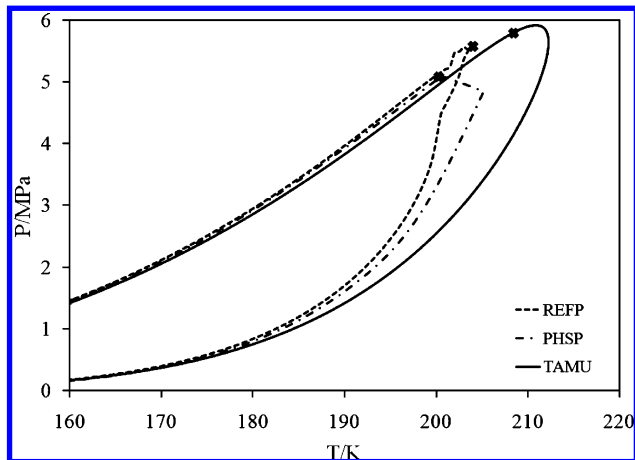


Figure 2. Phase envelope for methane (90%)–carbon dioxide (10%) using the Peng–Robinson (PR) equation of state. Tested with REFPROP (REFP), PhasePro (PHSP), and the current algorithm (TAMU).

and 10 mol % carbon dioxide. The differences among these curves at the cricondentherm, cricondenbar, and critical point result from the uncertainties in the binary interaction parameters (BIP) used in the EOS because the current algorithm, REFPROP, and PhasePro use different sets of BIP. However, the anomalies in the shape of the phase reflect the algorithm and convergence criteria. The current method to predict phase boundaries converges closer to the critical point. Other programs insert a straight line when convergence fails.

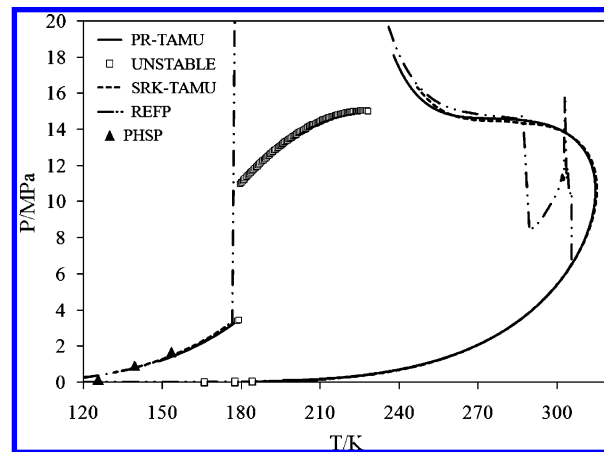


Figure 3. Phase envelope for methane (50%)–hydrogen sulfide (50%). Tested with PR in REFPROP (REFP), PR in PhasePro (PHSP), PR with the current algorithm (PR-TAMU), and SRK with the current algorithm (SRK-TAMU).

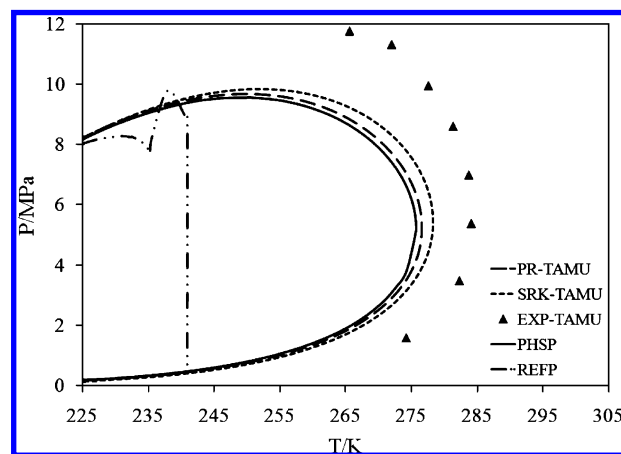


Figure 4. Phase envelope for SNG1. Tested with PR in REFPROP (REFP), PR in PhasePro (PHSP), PR with the current algorithm (PR-TAMU), and SRK with the current algorithm (SRK-TAMU), with comparison to experimental values (EXP).

Figure 3 presents a phase envelope for a hydrogen sulfide + methane mixture. This mixture has phase envelopes with more than two inflection points and discontinuous shapes at very high pressures.⁹ This specific case is known as a difficult system; however, while no specific rule of thumb exists to predetermine the difficult systems, polar/nonpolar mixtures are highly likely to present problems. As shown in the figure, the SRK is essentially identical to the PR. This mixture demonstrates the robustness of the current algorithm, because it converges regardless of the choice of EOS. However, the problems associated with commercial programs become obvious and probably result from the complexity of the phase equilibrium model used in their formulations. A single equation might be the difference between converging successfully or not; for instance, PhasePro only calculates three points in the bubble point region, and three phases might exist there. In this case, the stability criterion is essential. Although the points marked with squares correspond to converged values, they are unstable, and the curve is false.

Figures 4 and 5 illustrate the performance of the current algorithm with multicomponent mixtures. The figures represent the phase behavior of two synthetic natural gas mixtures. Figure 4 shows the phase envelope of a mixture with only hydrocarbon components (SNG1) while Figure 5 shows one with hydrocarbons mixed with nitrogen and carbon dioxide (SNG2). Table 1

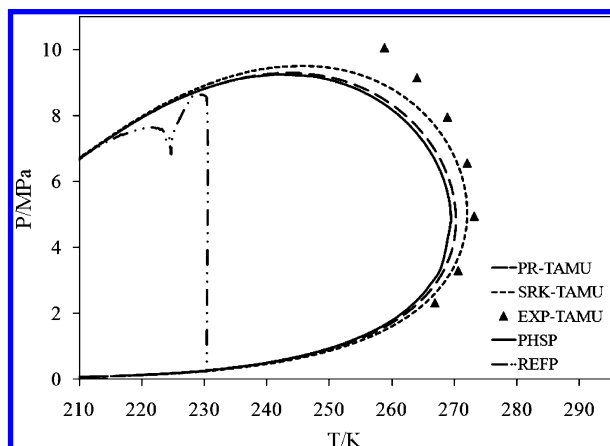


Figure 5. Phase envelope for SNG2. Tested with PR in REFPROP (REFP), PR in PhasePro (PHSP), PR with the current algorithm (PR-TAMU), and SRK with the current algorithm (SRK-TAMU), with comparison to experimental values (EXP).

Table 1. Molar Composition of SNG1 and SNG2

component	SNG1	SNG2
methane	0.90001	0.89975
ethane	0.04565	0.02855
propane	0.02243	0.01427
isobutane	0.01140	0.00709
<i>n</i> -butane	0.01151	0.00722
isopentane	0.00450	0.00450
<i>n</i> -pentane	0.00450	0.00450
nitrogen	—	0.01713
carbon dioxide	—	0.01699

contains the molar compositions for the mixtures. The experimental data come from the Thermodynamic Research Laboratory at Texas A&M University.

In Figure 4, both PhasePro and REFPROP have anomalies near the cricondentherm. This is apparent from the straight line between 1 and 8 MPa for REFPROP and between 3 and 5 MPa for PhasePro. These curves come from PR. The curves predicted by the algorithm suggested in this paper are smooth over this pressure and temperature range. The deviations from the experimental values result from the EOS and not from the algorithm.

In Figure 5, some difficulties arise when calculating the phase boundary near the cricondenbar. These problems occur when attempting to calculate the dew point pressure when dT/dP approaches zero. In such a region, the calculation should switch to the dew/bubble temperature. Analogously, in the cricondenbar region, the calculation must change to the dew/bubble pressure because dT/dP approaches infinity.

Figure 6 shows several ethane–carbon dioxide mixtures along with their critical loci using the PR. Although the dew and bubble curves are very close, the algorithm can produce the narrow phase envelopes. The most remarkable case takes place at the azeotropic composition ($\sim 70\%$ CO_2), where the phase envelope is so narrow that it appears to be a line.

In the light of the difficulties associated with REFPROP and PhasePro, it should be noted that these packages use more complex equations of state that have multiple roots resulting in nonconvergence in some regions. Additionally, these packages do not use previous calculations as initial guesses for generating phase boundaries. Version 8.1 of REFPROP will include the algorithms presented here to improve the phase boundary calculations.

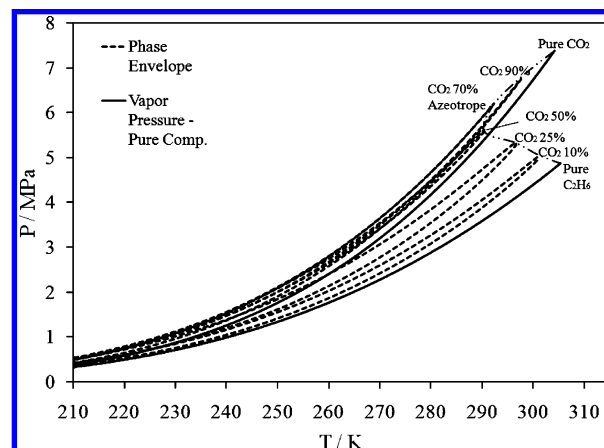


Figure 6. Phase envelope for ethane–carbon dioxide mixtures, PR with the current algorithm.

5. Conclusions

This paper presents a new algorithm to construct phase boundaries using Gibbs minimization. This algorithm can provide smooth phase envelopes for mixtures for which some commercial programs using the conventional K -value method have difficulty describing. The initial guesses for the current algorithm are stationary points that improve convergence of the method. Use of the stability analysis criterion assures that all the curves reported are thermodynamically stable. Future work can extend this procedure to several phases and more equations of state.

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List of Symbols

- C = number of components
- f_i = fugacity of pure i
- \hat{f}_i = partial fugacity of component i
- G = Gibbs energy
- $\Delta_m G$ = Gibbs energy of mixing
- g = reduced Gibbs energy of mixing
- l = liquid phase
- P = pressure
- R = gas constant
- T = temperature
- v = vapor phase
- x_i = mole fraction of component i
- x = composition of the liquid phase
- y = composition of the vapor phase
- z = overall composition

Greek Letters

- α, β = phases
- μ_i = chemical potential of component i
- π = number of phases

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