

An efficient flash procedure using cubic equations of state

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Abstract

A robust and highly efficient procedure to solve the isothermal two-phase flash problem at critical and sub-critical conditions is proposed in this work. From a calculated initialization, an accelerated successive substitution method is applied until either the solution is achieved or the change in the Gibbs free energy becomes positive, i.e. the Gibbs energy increases. From this point, an unconstrained optimization method is applied where the Hessian is kept positive definite and a line search method is implemented to guarantee a decrease in the Gibbs function. Using cubic equations of state to calculate the required thermodynamic properties has broadly tested the approach. Three hydrocarbon binary systems and a five-component mixture are used in this work to show the robustness of this procedure. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Prediction of two-phase equilibrium is of great importance in chemical processes and petroleum related industries. Knowledge of the equilibrium composition of each phase is essential in design and simulation of vaporization, condensation, and multistage separation processes. Computation of the amount and composition of each phase into which a given mixture splits is fundamentally based on satisfying the second law of thermodynamics. For a specified pressure, temperature, and the overall mass of each chemical species, the total Gibbs free energy is minimum with respect to all possible mass distribution. The problem can be formulated as a constrained optimization problem by inclusion of the mass balance equation. Alternatively, the mass balance can be incorporated into the objective function to formulate the problem as a purely unconstrained optimization case. The optimum clearly requires the equality of the chemical potential that leads to the equality of fugacities.

Iterative solution of the flash represents a computational problem that may range from slow rate of convergence to no convergence, particularly in the critical point neighborhood or near phase boundaries. Convergence may fail when the initial estimate of the iteration variables is not sufficiently

accurate or may require a substantial number of iterations to achieve a solution. In addition, there may exist trivial values, which satisfy the necessary fugacity conditions and the mass conservation in the system, but do not correspond to the minimum in the Gibbs function [1–3].

Using cubic equations of state has proved to be an effective approach to estimate the required fugacities from given pressure, temperature and overall molar fractions even at critical conditions. However, applications of cubic equations of state may introduce computational problems because of the existence of spurious roots and undefined derivatives [4].

In this work, the isothermal two-phase flash problem is addressed and solved at critical and sub-critical conditions. The problem has been briefly established in this section and the following reviews the current methods. Then, the proposed procedure is presented. Relevant improvements have been achieved as shown with the numerical evidence in the following section. Finally, the conclusions are established.

2. Current methods

Current frameworks to solve the flash problem can be divided into two main types: indirect and direct minimization.

Indirect minimization methods apply numerical techniques to solve the equality of fugacities. They are largely based on the *K*-value concept and it is hoped that the result

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will correspond to the minimum Gibbs energy. A K -value is defined as an equilibrium ratio of mole fractions of a species in two phases in equilibrium, see for instance [5,25]. Experience shows that derivative dependent numerical methods may fail at high pressure and temperature where fugacities become highly dependent on composition. Successive substitution (SS) is the most popular method that has proved to converge to the optimal in most practical cases [5,25]. However, a good initial estimation is required to avoid undesired solutions and enhance convergence [6,7]. Various attempts have been reported to enhance the rate of SS convergence [8–10].

Direct minimization methods apply numerical methods for optimization to determine those compositions that satisfy sufficient conditions to a local optimum. Conditions for a global minimum and their geometric interpretation for phase equilibrium have been established, for instance, in [11]. The first Gibbs minimization approach reported used a steepest descent combined with a linear programming technique [12]. Both steepest descent and Newton methods were used in reservoir compositional simulation [8]. The pure vapor–liquid equilibrium problem is dealt in [13]. Global optimization techniques have been successfully applied using solution models [14,15]. Pan and Firoozabadi [16] used simulated annealing and concluded that it is a very reliable technique but costly in computational time.

Notwithstanding, the solution to the flash problem may correspond to either a trivial or a false solution. A trivial solution typically occurs when the equation of state ends up in predicting the same composition in both phases. A false solution occurs when the solution corresponds to a local minimum. Trivial solution points are false numerical solutions when the Hessian matrix is nonnegative since they are also local minima. The main difficulty is that desired solutions are close to the trivial solutions as the critical point is approached. The best attempt to avoid undesired solutions has been to provide good initial guesses [17].

3. Proposed procedure

After analyzing the current methods to solve the flash problem, the following algorithm has been developed. It combines both direct and indirect minimization methods.

Algorithm: Flash

1. Select an initial set of K -values.
2. Using an indirect Gibbs minimization procedure, repeat n times:
 - Calculate the molar composition in each phase.
 - If a switching condition has been achieved, go to 3.
 - If the convergence criterion has been achieved, go to 4.
 - Calculate a new set of K -values.
3. Until convergence, apply a direct method to minimize the Gibbs free energy.

4. Perform a stability analysis. Stop if all phases are stable, otherwise select a new set of mole fractions or K -values and repeat from 2.

The initialization step is carried out using Mollerup's correlation [7] that is based on reduced properties,

$$K_j = P_r \exp[5.42(1 - T_r)] \quad (1)$$

where P_r and T_r are reduced pressure and reduced temperature, respectively. This initialization has been successful not only for vapor–liquid mixtures but also for liquid–liquid systems.

In Step 2, the molar distribution for each phase is calculated with a Rachford–Rice type of procedure [18]. An accelerated SS method is suggested to calculate the new K -values. The acceleration technique described by Obut et al. [10] was found to be the simplest and the most efficient to enhance the rate of convergence of SS. The K -values are accelerated after one iteration using the following expression:

$$K_{j,k+1} = K_{j,k} r_{j,k}^{1/(1-K_{j,k})} \quad (2)$$

where $K_{j,k}$ is the K -value of species j during iteration k . The acceleration factor r is defined as

$$r_{j,k} = \frac{f_{j,k-1}^I (f_{j,k}^{II} - f_{j,k}^I)}{f_{j,k}^I (f_{j,k-1}^{II} - f_{j,k-1}^I)} \quad (3)$$

where $f_{j,k}^I$ is the fugacity of species j in the mixture during iteration k at phase I.

The above acceleration method improves substantially the rate of convergence. However, a common weakness of all acceleration methods is that the function may increase during the iteration and eventually converge to a false or trivial solution; hence the need for stopping the procedure when sufficient progress has been achieved [19]. The proposed switch occurs as soon as the Gibbs function increases during the current iterate. This is equivalent to the standard Newton-like convergence criteria based on the gradient of the objective function to be small enough.

The Newton method has been implemented for the last part of the proposed scheme since it is normally well behaved and has order two or quadratic convergence when the starting point is close enough to the solution. It is also unaffected by the scale of the variables so that scaling is unnecessary. Newton step is guaranteed to be a descent direction if the Hessian is positive definite. Hence, a Levenberg–Marquardt method is used where, in particular, the Hessian is maintained symmetric and positive definite [20]. Finally, a line search backtracking framework is also implemented to safeguard that the Gibbs function decreases in each iteration [21].

Thus, the proposed scheme takes advantages of the best characteristics of two methods: derivative independence from SS and quadratic convergence from Newton. Computational results demonstrate that the method has the same reliability and nearly the same efficiency in the critical and

away from the critical point. However, a phase stability analysis is required to verify if the produced result corresponds to the global optimum. A procedure to carry out the phase stability analysis has been developed by Michelsen [2]. If a phase is considered unstable then the phase stability procedure detects the composition of the new phase that decreases the Gibbs function.

4. Examples and discussion

Four examples are considered in this section to demonstrate the robustness and efficiency of the proposed procedure. The equilibrium state at sub-critical and critical conditions have been computed to show that the procedure works even for difficult problems.

4.1. Ethane-*n*-heptane system

The first example is a binary case, which has been outlined in [22]. A 26.54 mol% ethane and 73.46 mol% heptane mixture has been flashed at various pressures and temperatures to reproduce the phase envelope. The Soave equation of state [23] with a zero binary interaction coefficient is also used for the sake of consistency with the original reference. Table 1 shows some of the results. The molar fraction y refers to the lightest phase since two liquid phases coexist at supercritical conditions. The number of iterations to achieve convergence using both pure SS and the proposed approach is also indicated. Values inside parenthesis indicate iterations used during direct optimization whereas values outside parenthesis are iterations in either the pure or the accelerated SS method. A typical pattern is obtained around the critical point where difficulty normally increases substantially. Successive substitution converges to the trivial solution though it behaves well for this particular mixture when conditions are

Table 1
Flash results for a 26.54 mol% ethane and 73.46% *n*-heptane mixture at several temperatures and pressures

P (bar)	T (K)	Mole fraction ethane		Iterations	
		y	x	Pure SS	This work ^a
15	430	0.656051	0.102353	12	15(0)
20	430	0.725057	0.148399	7	2(6)
25	430	0.765639	0.193213	6	14(0)
30	430	0.791737	0.236876	7	14(0)
35	450	0.723836	0.247011	Trivial	12(0)
40	500	0.443432	0.215711	Trivial	4(30)
41	500	0.449201	0.224778	Trivial	4(84)
42	500	0.454530	0.233948	Trivial	6(83)
43	500	0.459387	0.243151	Trivial	8(0)
44	500	0.463799	0.252462	Trivial	7(0)
45	500	0.467773	0.261877	Trivial	7(0)

^a Values inside parenthesis indicate iterations used during direct optimization whereas values outside parenthesis are iterations in the accelerated SS method.

far from the critical point. The proposed approach achieves convergence in the whole set of conditions.

4.2. Methane-*n*-heptane system

A mixture containing 65 mol% methane and 35 mol% *n*-heptane is used here at 151 bar and 450 K. The Soave equation of state [23] with a zero binary interaction coefficient is also used for the sake of simplicity. The algorithm proposed in this work saves several iterations that would be required by a pure SS method. However, the main purpose of this example is to show that bounding the acceleration factor has advantages. Fig. 1 illustrates the behavior of the pure accelerated method in terms of the fraction vaporized and the Gibbs function. Results in Gibbs function during the first two iterations are not presented to magnify the typical observed effect: the method behaves well until the Gibbs function starts increasing. When the Gibbs function increases, the method takes several iterations to converge and it may end up in false or trivial solutions. It was also observed here that accelerating factors became very different to unity. Bounding these factors to [0.9,1.1] makes the accelerated method converge in 17 iterations without activating the switch (see Fig. 2). Using the switch, the method converges in 4(8) iterations.

4.3. Hydrogen sulfide–methane system

An equimolar mixture of H₂S–CH₄ is used as a third example. The flash is carried out using the Soave equation of state [23] with an interaction coefficient equal to 0.08 [4]. Without phase stability analysis, the flash calculation converges, when the conditions are 40.53 bar and 190 K, using two iterations with the indirect minimization method and 21 iterations with the direct minimization method. However, this solution corresponds to false liquid–vapor equilibrium as detected by the phase stability analysis. A second attempt using the vapor phase and the new composition obtained from phase stability gets the appropriate solution in 25 iterations. The results of both the false and the true solutions are given in Table 2.

4.4. Five-component mixture

The five-component mixture in the critical region given in [8] is used here. The mole fraction of each species in the system is shown in Table 3. The Peng–Robinson equation

Table 2
Flash results for an equimolar mixture of hydrogen sulfide and methane at 40.53 bar and 190 K

Solution	Vapor fraction	Calculated mole fractions	
		y (H ₂ S)	x (CH ₄)
Real	0.477674	0.0920857	0.873043
False	0.436051	0.0207171	0.979283

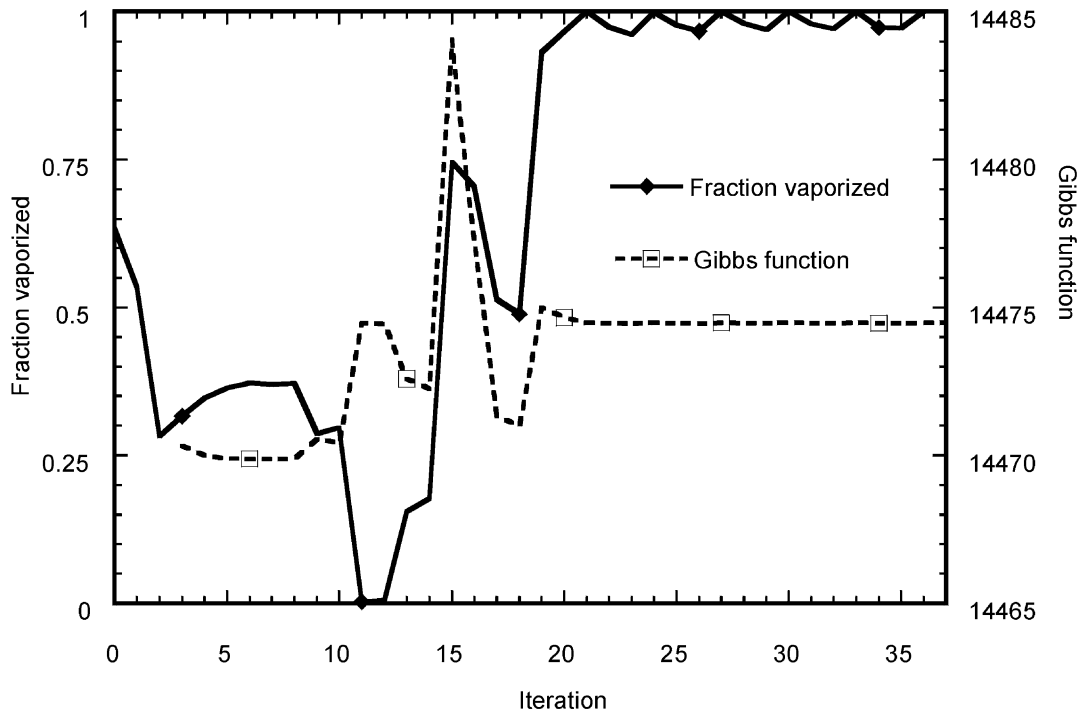


Fig. 1. Accelerated method without bounds for a mixture containing 65 mol% methane and 35 mol% *n*-heptane at 151 bar and 450 K.

of state [24] with the alpha correction is used to perform flash calculations at various pressures and a temperature of 388.92 K, which is the calculated critical temperature. All interaction parameters were assumed to be zero since no

further information is provided about them in the original reference. Table 4 shows the vapor fraction obtained here as well as the number of iterations required for achieving the solution in each flash calculation. The iterations inside

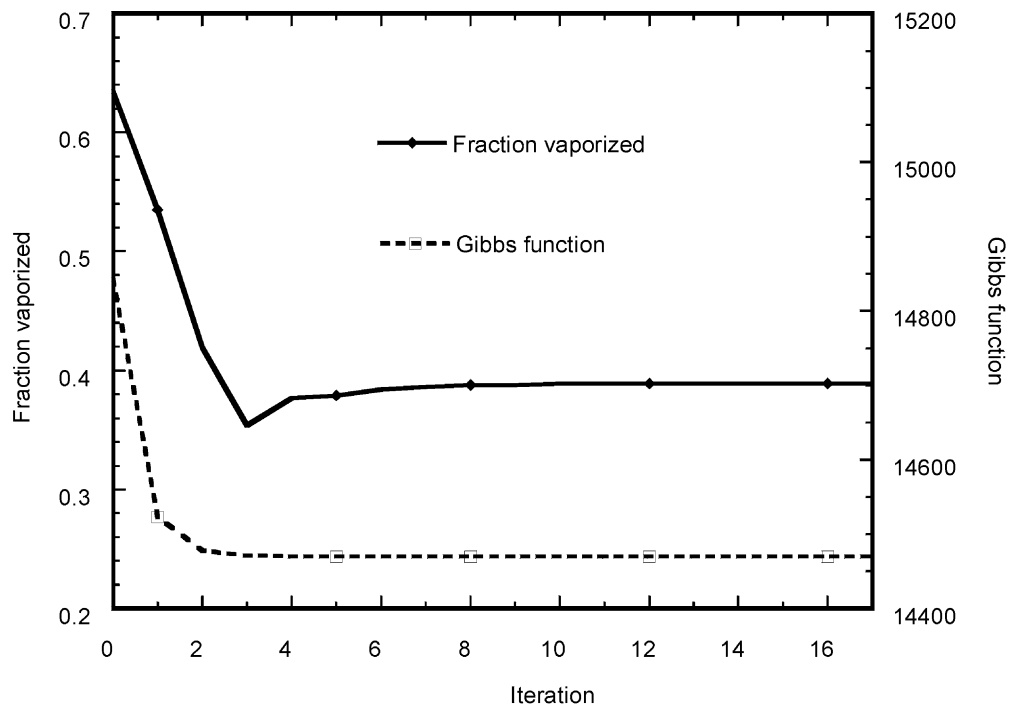


Fig. 2. Bounded accelerated method for a mixture containing 65 mol% methane and 35 mol% *n*-heptane at 151 bar and 450 K.

Table 3
Composition of the five-component mixture

Component	Mole fraction
Ethane	0.39842
Propane	0.29313
<i>n</i> -Butane	0.20006
<i>n</i> -Pentane	0.07143
<i>n</i> -Hexane	0.03696

Table 4
Flash results for a five-component mixture at 388.92 K

<i>P</i> (bar)	Vapor fraction	Iterations	
		Pure SS	This work ^a
41.3685	1.0	9	4(0)
43.0922	0.981459	11	4(14)
44.8159	0.948306	12	4(14)
46.5396	0.912191	13	4(14)
48.2633	0.872244	14	4(14)
49.9869	0.827138	16	4(14)
51.7106	0.0	22	4(14)
53.4343	0.708418	32	4(14)
55.1580	1.0	102	4(14)

^a Values inside parenthesis indicate iterations used during direct optimization whereas values outside parenthesis are iterations in the accelerated SS method.

parenthesis indicate those used during direct optimization whereas the values outside are the iterations in either the pure or the accelerated SS method. The proposed approach saves several iterations that the pure SS method would take to solve those mixtures whose conditions are close enough to the critical point.

5. Conclusions

A procedure that combines direct and indirect minimization techniques for the Gibbs free energy has been proposed in this work to solve the flash problem. Keeping consistency with the mass balance in each iteration, the SS method is accelerated to either produce the solution or to approximate it so that the Newton, a second order method, ends up in an optimal answer. The phase stability analysis is used as a means to produce the global solution. Nevertheless, Newton method can be very expensive because of the Hessian

calculation. However, this is preferred and found necessary to achieve the solution when false solutions become strong attractors for SS. Modifying Newton method to guarantee a decrease in the Gibbs function resulted in a computationally efficient and robust procedure.

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