Reliable Computation of Mixture Critical Points

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Abstract

The determination of critical points of mixtures is important for both practical and theoretical reasons in the modeling of phase behavior, especially at high pressure. We present here the first *completely reliable* method for locating *all* the critical points of a given mixture. The method also verifies the nonexistence of a critical point if a mixture of a given composition does not have one. The methodology used is based on interval analysis, in particular an interval Newton/generalized bisection algorithm that provides a mathematical and computational guarantee that all mixture critical points are located. The procedure is initialization-independent, and thus requires no *a priori* knowledge of the number of mixture critical points or their approximate locations. The technique is illustrated using several example problems involving cubic equation of state models; however, the technique is general purpose and can be applied in connection with other thermodynamic models.

Introduction

As reviewed in more detail by Sadus (1994), the determination of critical points of mixtures is important for a variety of both practical and theoretical reasons, and thus has been widely studied (e.g., Deiters and Schneider, 1976; Boberg and White, 1962; Hurle *et al*., 1977a,b; Nagarajan *et al*., 1991a,b; Stockfleth and Dohrn, 1998; Spear *et al*., 1971; Enick *et al*., 1985; Grieves and Thodos, 1962; Munoz and Chimowitz, 1993; Teja and Kropholler, 1975; Teja and Rowlinson, 1973), especially in the context of hydrocarbon production and processing (e.g., Heidemann, 1975, 1983; Baker and Luks, 1980; Luks *et al*., 1987; Boshkov and Yelash, 1967; Rochocz *et al*., 1997). For example, knowledge of vapor-liquid critical points is useful in determining whether retrograde condensation or evaporation is possible. Knowledge of critical states can also be used in schemes for classifying the overall phase behavior of mixtures, as exemplified by the well-known scheme of van Konynenburg and Scott (1980).

Measurement of critical phenomena is often expensive, thus critical points are frequently calculated from models, typically equation-of-state (EOS) models. A mixture of a given composition may have one, more than one, or no critical points. Clearly it is desirable that methods used to compute critical points be capable of reliably finding *all* critical points, or verifying with certainty that there are none in the domain of interest. This task is made particularly difficult by the complex nonlinear form of the criticality conditions, especially since there is generally no knowledge *a priori* concerning the number of critical points to be found, or indeed if there are any.

Perhaps the most reliable and widely used techniques currently used for computation of critical points are the methods of Hicks and Young (1977) and Heidemann and Khalil (1980). The approach used by Hicks and Young (1977), which is based on searching for sign changes in the criticality conditions, can be very reliable, is capable of finding multiple critical points, and requires no initialization, only the specification of intervals of temperature and volume over which to search. However, as noted by Hicks and Young (1977), it may miss solutions to the criticality conditions and thus provides no guarantee that all critical points will be found. The method of Heidemann and Khalil (1980), which employs two nested single-variable iteration loops using a local equation solver (Newton-Raphson), is very reliable for locating a single high-temperature vapor-liquid critical point, requiring essentially no initialization (since any sufficiently high guesses of temperature and volume will suffice, and such guesses can easily be generated automatically). However, if there are other critical points to be found, this must be done by “choosing as the initial guess a volume near the desired root” (Heidemann and Khalil, 1980). Thus, some *a priori* knowledge of the number and approximate location of the mixture critical points is needed, without which there is no guarantee that all critical points will be found. For example, if it is known that there are exactly three critical points, then one can try as many different initial guesses as needed to find all three, stopping when the third has been found. However, if it is not known in advance how many critical points to look for, then one would not be able to tell when to stop trying different initial guesses, as the next one tried could converge to a critical point that had not been found before. To estimate the number and location of critical points, Heidemann and Khalil (1980) and others suggest using an approach based on looking for sign changes in the criticality conditions; however, as noted by Hicks and Young (1977), this type of approach may fail to identify all critical points. An excellent implementation of the method of Heidemann and Khalil (for finding a single high-temperature vapor-liquid critical point only) is available in the routine CRITPT that is a part of the IVC-SEP simulation package (Hytoft and Gani, 1996; Michelsen, 1984; Michelsen and Heidemann, 1981).

We describe here the first *completely reliable* approach for locating *all* critical points of mixtures, and for verifying when none exist. The technique is *mathematically and* *computationally guaranteed* to find (or, more precisely, to enclose within a very narrow interval) any and all solutions of the criticality conditions. Like the method of Hicks and Young (1977), and unlike the method of Heidemann and Khalil (1980), the new method requires no initialization and no *a priori* knowledge of the number of critical points to be found, requiring only the specification of intervals of temperature and volume over which to search. Unlike the method of Hicks and Young (1977), however, the new method described here provides a *guarantee* that no solutions to the criticality conditions will be missed. We will demonstrate the technique here using a generalized cubic EOS model. However, the methodology is general purpose and can be applied in connection with other models of phase behavior.

Problem Formulation

The criticality conditions can be stated in terms of the Gibbs free energy G or the Helmholtz free energy A. However, for a pressure-explicit EOS, a formulation based on A, with temperature and volume as independent variables, is generally preferred. Based on a Taylor series expansion of A, and considering the second and third order terms, Heidemann and Khalil (1980) formulated the criticality conditions for a mixture of C components as

$$Q\,\Delta\mathbf{n} = \mathbf{0} \tag{1}$$

$$\sum_{i=1}^{C}\sum_{j=1}^{C}\sum_{k=1}^{C} A_{ijk}\Delta n_i \Delta n_j \Delta n_k = 0\,. \tag{2}$$

In Eq. (1), the $C \times C$ matrix Q has elements

$$Q_{ij} = A_{ij} = \left(\frac{\partial^2 A}{\partial n_i \partial n_j}\right)_{T,V}$$

where n_i and n_j indicate component mole numbers, and $\Delta\mathbf{n} = (\Delta n_1, \Delta n_2, \ldots, \Delta n_C)^{\mathrm{T}}$ represents a nonzero perturbation in the component mole numbers, and in Eq. (2),

$$A_{ijk} = \left(\frac{\partial^3 A}{\partial n_i \partial n_j \partial n_k} \right)_{T,V} .$$

To assure that it is nonzero, the perturbation vector $\Delta\mathbf{n}$ is normalized

$$\Delta\mathbf{n}^{\mathrm{T}} \Delta\mathbf{n} - 1 = 0 . \tag{3}$$

The derivatives A_{ij} and A_{ijk} are evaluated at the given mixture composition $\mathbf{n}_0 = (n_{1,0}, n_{2,0}, \ldots, n_{C,0})^{\mathrm{T}}$. Thus, Eqs. (1)-(3) represent a system of C+2 equations in the C+2 variables T, V, and $\Delta\mathbf{n}$, the solution of which gives the critical temperature T_c, critical volume V_c and a corresponding $\Delta\mathbf{n}$. The critical pressure P_c can then be computed directly from the pressure-explicit EOS.

The Heidemann-Khalil formulation of the criticality conditions, as summarized above, is entirely equivalent to the often seen determinant-based formulations. It has been widely used due to its clear theoretical foundation and because it is relatively simple to implement computationally, and is the formulation we will use here for the computation of mixture critical points. It should be noted that the criticality conditions solved, whether in their determinant form or in the Heidemann-Khalil form, may yield points that are stable, unstable or metastable. Thus, computed solutions of the criticality conditions should be checked for phase stability. A completely reliable method for phase stability analysis using cubic EOS models, also based on interval analysis, has been presented and demonstrated by Hua *et al.* (1996,1998).

The EOS model used here is a generalized cubic EOS

$$P = \frac{RT}{v-b} - \frac{a}{(v + D_1 b)(v + D_2 b)}$$

and standard van der Waals mixing rules with a binary interaction parameter k_{ij} are used (see Appendix for notational details). Of course, a cubic EOS is analytic and cannot give the theoretically correct behavior at the critical point. The region immediately around a critical point can be accurately described by scaling laws that include critical exponents (e.g., Levelt Sengers, 1991). Nevertheless, EOS models are useful in providing a general description of high pressure phase behavior, and critical points computed from EOS models are useful in identifying appropriate operating conditions in a variety of process applications.

For the case of the generalized cubic EOS given above, Eqs. (1) and (2) can be expressed using the expressions of Michelsen and Heidemann (1981). Eq. (1) becomes

$$\sum_{j=1}^{C} A_{ij}\Delta n_j =$$

$$\frac{RT}{n}\left(\frac{\Delta n_i}{y_i}+F_1\left(\beta_i\overline{N}+\overline{\beta}\right)+\beta_i F_1^{2}\overline{\beta}\right)+\frac{a}{bn}\left(\beta_i\overline{\beta}F_3-\frac{F_5}{a}\sum_{j=1}^{C}a_{ij}\Delta n_j+F_6\left(\beta_i\overline{\beta}-\alpha_i\overline{\beta}-\overline{\alpha}\beta_i\right)\right)=0$$

$$i=1\ldots C \tag{4}$$

and Eq. (2) becomes

$$\sum_{i=1}^{C}\sum_{j=1}^{C}\sum_{k=1}^{C} A_{ijk}\Delta n_i\Delta n_j\Delta n_k =$$

$$\frac{RT}{n^2}\left(-\frac{\sum_{i=1}^{C}\Delta n_i^3}{y_i^2}+3\overline{N}(\overline{\beta}F_1)^2+2(\overline{\beta}F_1)^3\right)+\frac{a}{n^2 b}(3\overline{\beta}^2(2\overline{\alpha}-\overline{\beta})(F_3+F_6)-2\overline{\beta}^3F_4-3\overline{\beta}\overline{a}F_6)=0 \tag{5}$$

The notation used in these equations is explained in detail in the Appendix. We note that Eq. (5) is a corrected form of the equation given by Michelsen and Heidemann (1981), which contains an error in the last term.

Methodology

We apply here interval mathematics, in particular an interval Newton/generalized bisection (IN/GB) technique, to find, or, more precisely, to find very narrow enclosures of, all solutions of a nonlinear equation system, or to demonstrate that there are none. Recent monographs which introduce interval computations include those of Neumaier (1990), Hansen (1992) and Kearfott (1996). The algorithm used here has been described by Hua et al. (1998), and given in more detail by Schnepper and Stadtherr (1996). Properly implemented, this technique provides the power to find, *with mathematical and computational certainty,* enclosures of *all* solutions of a system of nonlinear equations or to determine with certainty that there are none, provided that initial upper and lower bounds are available for all variables (Neumaier, 1990; Hansen, 1992, Kearfott, 1996). This is made possible through the use of the powerful existence and uniqueness test provided by the interval Newton method. Our current implementation of the IN/GB method for the critical point problem is based on appropriately modified routines from the FORTRAN-77 packages INTBIS (Kearfott and Novoa, 1990) and INTLIB (Kearfott *et al.*, 1994). The key ideas of the methodology used are summarized very briefly here.

Consider the solution of a nonlinear equation system $\mathbf{f}(\mathbf{x}) = \mathbf{0}$, where $\mathbf{x} \in \mathbf{X}^{(0)}$ (interval quantities are indicated in upper case, point quantities in lower case). The solution algorithm is applied to a sequence of intervals, beginning with the initial interval vector $\mathbf{X}^{(0)}$ specified by the user. This initial interval can be chosen to be sufficiently large to enclose all physically feasible behavior. For an interval $\mathbf{X}^{(k)}$ in the sequence, the first step in the solution algorithm is the *function range test*. Here an *interval extension* $\mathbf{F}(\mathbf{X}^{(k)})$ of the function $\mathbf{f}(\mathbf{x})$ is calculated. An interval extension provides upper and lower bounds on the range of values that a function may have in a given interval. It is often computed by substituting the given interval into the function and then evaluating the function using interval arithmetic; this is the approach used here, with interval arithmetic implemented using the INTLIB package (Kearfott *et al.*, 1994). If there is any component of the interval extension $\mathbf{F}(\mathbf{X}^{(k)})$ that does not contain zero, then we may discard the current interval $\mathbf{X}^{(k)}$, since the range of the function does not include zero anywhere in this interval, and thus no solution of $\mathbf{f}(\mathbf{x}) = \mathbf{0}$ exists in this interval. Otherwise, if zero is contained in $\mathbf{F}(\mathbf{X}^{(k)})$, then processing of $\mathbf{X}^{(k)}$ continues.

The next step is to apply the *interval Newton test* to the current interval $\mathbf{F}(\mathbf{X}^{(k)})$. This requires solving the system of linear interval equations $F'(\mathbf{X}^{(k)})(\mathbf{N}^{(k)} - \mathbf{x}^{(k)}) = -\mathbf{f}(\mathbf{x}^{(k)})$ for a new interval, the *image* $\mathbf{N}^{(k)}$. Here $F'(\mathbf{X}^{(k)})$ is an interval extension of the Jacobian of $\mathbf{f}(\mathbf{x})$ over $\mathbf{X}^{(k)}$, and $\mathbf{x}^{(k)}$ is a point in $\mathbf{X}^{(k)}$, usually taken to be the midpoint. Comparison of the current interval and the image provides a powerful existence and uniqueness test (Neumaier, 1990; Kearfott, 1996). If $\mathbf{N}^{(k)}$ and $\mathbf{X}^{(k)}$ have a null intersection, this is mathematical proof that there is no solution of $\mathbf{f}(\mathbf{x}) = \mathbf{0}$ in $\mathbf{X}^{(k)}$. If $\mathbf{N}^{(k)}$ is a proper subset of $\mathbf{X}^{(k)}$, then this is mathematical proof that there is a *unique* solution of $\mathbf{f}(\mathbf{x}) = \mathbf{0}$ in $\mathbf{X}^{(k)}$. If neither of these two conditions is true, then no conclusions can be made about the number of solutions in the current interval. However, it is known (Kearfott, 1996) that any solutions that do exist must lie in the intersection of $\mathbf{N}^{(k)}$ and $\mathbf{X}^{(k)}$. If this intersection is sufficiently smaller than the current interval, one can proceed by reapplying the interval Newton test to the intersection. Otherwise, the intersection is bisected, and the resulting two intervals added to the sequence of intervals to be tested. These are the basic ideas of an interval Newton/generalized bisection (IN/GB) method.

When machine computations with interval arithmetic operations are done, as in the procedures outlined above, the endpoints of an interval are computed with a directed outward rounding. That is, the lower endpoint is rounded down to the next machine-representable number and the upper endpoint is rounded up to the next machine-representable number. In this way, through the use of interval, as opposed to floating point, arithmetic any potential rounding error problems are eliminated. Overall, the IN/GB method described above provides a procedure that is mathematically *and* computationally guaranteed to enclose all solutions to the nonlinear equation system or to determine with certainty that there are none.

It should be emphasized that the enclosure, existence, and uniqueness properties discussed above, which are the basis of the IN/GB method, can be derived without making any strong assumptions about the function $\mathbf{f}(\mathbf{x})$ for which roots (zeros) are sought. The function must have a *finite* number of roots over the search interval of interest; however, no special properties such as convexity or monotonicity are required. It is assumed that $\mathbf{f}(\mathbf{x})$ is continuous; however, it need not be continuously differentiable. Instead, as shown by Neumaier (1990), $\mathbf{f}(\mathbf{x})$ need only be Lipschitz continuous over the interval of interest; thus, functions with slope discontinuities can be handled. In order to apply the method, it must be possible to determine an interval extension of the Jacobian matrix (or of the "Lipschitz matrix" if $\mathbf{f}(\mathbf{x})$ is not continuously differentiable). In general, this requires having a analytic expression for $\mathbf{f}(\mathbf{x})$; thus, the interval approach is not suitable if $\mathbf{f}(\mathbf{x})$ is some kind of "black box" function. One difficulty with the interval Newton approach is that if a solution occurs at a singular point (i.e., where the Jacobian of $\mathbf{f}(\mathbf{x})$ is singular), then it is not possible to obtain the result that identifies a unique solution. For such a case, the eventual result from the IN/GB algorithm will be a very narrow interval for which all that can be concluded is that it *may* contain one or more solutions. In other words, the algorithm will not miss the solution (so the guarantee to enclose all solutions remains), but rather, will enclose it within a narrow interval which can then be examined using an alternative methodology (e.g., Kearfott et al., 2000).

Results and Discussion

To solve the criticality conditions, Eqs. (3)-(5), for a generalized cubic EOS, the IN/GB method, as outlined above, was used. Use of scaled volume and temperature variables was found to be both convenient and effective. The volume was scaled using the van der Waals volume parameter b in the EOS, and the initial interval used was $v/b \in [1.1, 4.0]$. The temperature was scaled by a factor of 200 K, and the initial interval used was $T/200 \in [0.55, 4.0]$. These initial intervals were considered reasonable for the range of example systems considered (Heidemann and Khalil, 1980). For the mole number perturbation variables, the initial intervals used were $\Delta n_1 \in [0, 1]$ and $\Delta n_{i\neq 1} \in [-1, 1]$. Restricting Δn_1 to be positive eliminates a duplicate set of roots which differ only in that the mole number perturbations are opposite in sign (this occurs since both $\Delta\mathbf{n}$ and $-\Delta\mathbf{n}$ satisfy the criticality conditions). Because $\Delta\mathbf{n}$ is normalized to a length of one by Eq. (3), the range of the mole number perturbation variables can be safely restricted to values of magnitude less than one.

For each of the example problems considered below, all of the solutions to the criticality conditions were found for mixtures of specified composition. The pure component properties (critical temperatures, critical pressures and acentric factors) required in the EOS models were taken from Reid *et al.* (1987). In the tables of results, we present the computed mixture critical states (T_c, v_c, P_c) and the corresponding mole number perturbation variables. The critical pressures are computed from the EOS after the criticality conditions have been solved for the critical volumes and temperatures. It should be noted that while point approximations of T_c, v_c, and $\Delta\mathbf{n}$ are given in the tables here, we have actually determined verified enclosures of each root. Each such enclosure is an extremely narrow interval known to contain a *unique* root, based on the interval Newton uniqueness test described above. For example, the first critical temperature reported in Table 1 is given as T_c = 190.82 K, but is actually computed as $T_c/200 \in [0.954123569210884, 0.954123569210885]$ K, and this interval is known to enclose a unique critical temperature root. While this level of precision is certainly not needed in this application, because the EOS parameters are known only to much lower precision, it is indicative of the potential power of this problem-solving tool. The degree of precision desired in the final results has little impact on the overall computational effort.

Several of the critical points found occur at negative pressures. A condensed phase at negative pressure is metastable and can be thought of as occurring when the material is in tension (i.e., stretched). Though metastable, these states can be observed experimentally, and, in fact occur in nature (e.g., the flow of sap in plants). Critical points at negative pressure correspond to the demixing of a liquid in tension into two other liquid phases in tension. Good discussions of the thermodynamics of negative pressures have been provided recently by Imre *et al*. (1998) and Debenedetti (1996). All of the critical points at positive pressures were checked for phase stability using the method of Hua *et al.* (1998) and are stable unless indicated otherwise.

Also presented in the tables is the CPU time required to solve each problem, given in seconds on a Sun Ultra 30 workstation. The computation times seen here are much higher than what is required by local methods such as the method of Heidemann and Khalil (1980) and Michelsen and Heidemann (1981). However, such local methods do not reliably find *all* critical points. Thus, there is a choice between faster methods that are not fully reliable, or this completely reliable but slower method that is guaranteed to give the correct answer, finding *all* critical points.

Example 1: Methane and Hydrogen Sulfide

In this first example problem we consider mixtures of methane (1) and hydrogen sulfide (2). The Soave-Redlich-Kwong (SRK) EOS model was used with a binary interaction parameter of $k_{ij} = 0.08$. This example problem, as well as Examples 2 and 3, are also used by Heidemann and Khalil (1980). However, direct comparison of computed results is not meaningful since Heidemann and Khalil do not provide the model parameters used in their computations. In our experience, the location of low temperature (liquid-liquid) critical points may be extremely sensitive to small changes in model parameters such as the k_{ij} used.

The critical states computed using the interval approach are shown in Table 1. Note that at some compositions there is one critical point, at some there are two critical points, at some there are three critical points, and at some there are no critical points. In order to verify that we correctly implemented the Heidemann-Khalil criticality conditions we used the routine CRITPT, a part of the IVC-SEP simulation package (Hytoft and Gani, 1996; Michelsen, 1984). CRITPT uses the same problem formulation as used here, but the solution method is the local method of Heidemann and Khalil (1980). This method is based on a automatic initialization that is suitable for finding high-temperature critical points. In order to use CRITPT to find other critical points, we modified the code to disable the automatic initialization and to allow the user to provide the initialization. Using this modified code, with the same model parameters as used in the IN/GB code, and with initializations that were carefully selected (guided by the results obtained with the interval approach), we were able to find the same critical points given in Table 1, as well as those given as results in other examples that follow. Of course, since CRITPT is a local, initialization-dependent solver, when it is used, even in this modified form, there are no guarantees that all critical points will be found. When the interval approach described here is used, such a guarantee is provided.

For the mixtures that have no critical point, the interval method provides mathematical proof that this is the case. This is important, since with local solvers, such as CRITPT, much effort could be wasted by trying a very large number of different initializations searching for a solution that does not exist, and one could never be sure that there was not really a solution.

Example 2: Carbon Dioxide and *n*-Octane

In this example we consider mixtures of carbon dioxide (1) and *n*-octane (2), a classic CO_2/alkane system. The SRK EOS model was used with a binary interaction parameter of $k_{ij} = 0$. The critical states determined, and computation times required, using the IN/GB method and the Heidemann-Khalil criticality conditions are given in Table 2 for several different mixture compositions. The behavior seen is different from that of the previous example (methane/hydrogen sulfide) in that the computed high temperature (vapor-liquid) critical locus is continuous between the critical points of carbon dioxide and *n*-octane.

For this example, a determinant-based form of the criticality conditions (Reid and Beegle, 1977) was also used, in addition to the Heidemann-Khalil formulation. The IN/GB approach was used to solve the determinant-based criticality conditions, yielding the same critical states as the Heidemann-Khalil formulation. However, using the Heidemann-Khalil formulation was significantly more efficient computationally, even though it involves four (C + 2) independent variables, versus only two when the determinant-based formulation is used. The is indicative of the fact that, while counterintuitive, reducing the dimensionality of nonlinear equation solving problems may in fact make them more, not less, difficult to solve.

Example 3: Carbon Dioxide and *n*-Hexadecane

The final binary system considered involves mixtures of carbon dioxide (1) and *n*-hexadecane (2). The SRK EOS model was used with a binary interaction parameter of $k_{ij} = 0$.

The critical states computed using the IN/GB method are given in Table 3 for several different mixture compositions.

The computation times reported here and in the other examples are actually quite good for a general-purpose approach offering a verified solution. To see this we also solved the problems in this example using the commercial package Numerica (ILOG), which also offers a verified solution. This code (van Hentenryck *et al.*, 1997) combines ideas from interval analysis, such as used here, with techniques from constraint satisfaction programming (CSP). On the first mixture in Table 3 ($n_1 = 0.97$), Numerica required 3947 s to find just the first critical point ($T_c =$ 386K), and to allow this critical point to be found within this amount of time, it was necessary to start with a narrow initial interval of width only 10 K and 10 cm^3 containing the critical point. The approach used here required only about 85 s to find all three critical points when starting with the wide initial interval indicated at the beginning of this section.

Example 4: Ternary Mixtures (SRK)

Ternary mixtures are often used as models to represent more complex mixtures in the petroleum industry. The first two ternary systems considered here, methane(1)/nitrogen(2)/hexane(3) and methane(1)/CO_2(2)/hexane(3), involve compounds that serve to model mixtures found in the cryogenic processing of liquefied natural gas (Merrill, 1983). The third system considered is the same as the second except that hexane is replaced by hydrogen sulfide. The SRK EOS was used to model these mixtures using the binary interaction parameters shown in Table 4.

The computed critical states for mixtures with various compositions are given in Table 5. For two cases, the critical points were also computed using the Peng-Robinson (PR) EOS. It is interesting to note that for the third system (involving H_2S), while there are relatively small differences between the two models in predicting the higher of the two critical points, there is a very large difference in the prediction of the lower temperature critical point. Not only is the location of low temperature critical points sometimes very sensitive to the form of the model, but, as noted above, it may also be very sensitive to the model parameters used. This is an indication that models should be validated carefully before use for specific applications.

We observe here, as well as in previous examples, that computing the critical points of mixtures for which one or more critical points has negative pressure often requires much more computing time compared to other cases. If finding critical states with negative pressure is not of interest, then it would be easy to modify the algorithm to limit the search by eliminating regions over which the pressure is negative. This could be done as a part of the function range test by computing the interval extension $P(\mathbf{X}^{(k)})$ from the EOS, and then discarding $\mathbf{X}^{(k)}$ if the upper bound of the interval $P(\mathbf{X}^{(k)})$ is negative.

Example 5: Ternary Mixtures (PR)

This second set of ternary systems consists of problems considered previously by Peng and Robinson (1977). These are representative of model systems studied in hydrocarbon processing. The PR EOS was used to model these mixtures using the binary interaction parameters shown in Table 6. The systems used are methane(1)/CO_2(2)/H_2S(3), ethane(1)/*n*-butane(2)/*n*-heptane(3), ethane(1)/*n*-pentane(2)/*n*-heptane(3), and methane(1)/propane(2)/nitrogen(3).

The critical points computed using the interval approach are shown in Table 7. These results are in excellent agreement with those computed by Peng and Robinson (1977), though in the problems solved here we have likely used slightly different k_{ij} parameters. In addition, we found a critical point for the first ternary mixture that had not been reported before, though Peng and Robinson (1977) may not have been looking for critical points with $P < 0$. This demonstrates the ability of the interval approach to find all solutions of the criticality conditions.

Concluding Remarks

We have described here the first *completely reliable* method locating *all* critical points of mixtures, and for verifying the nonexistence of critical points if none are present. As seen in several example problems, the method requires no point initialization and no *a priori* knowledge of the number of critical points, and can find both high and low temperature critical points. The technique is based on interval analysis, in particular an interval Newton/generalized bisection algorithm, which provides a *mathematical and computational guarantee* that all critical points are located. This guarantee comes at the expense of a significant CPU requirement. Thus, there is a choice between fast local methods that are not completely reliable, or this method that is guaranteed to give the complete and correct answer, finding *all* critical points of a mixture. The modeler must make a decision concerning how important it is to get the correct answer. Recent experiments in improving the IN/GB algorithm (Gau *et al.*, 1999) have shown significant promise in reducing the computation time requirements of the method on a variety of modeling problems, and we believe these techniques will also be applicable to the computational of critical points.

In the work presented here, the mixtures were modeled using cubic equations of state, with standard mixing rules. However, the problem solving technique used is general purpose and can be applied in connection with other thermodynamic models. In addition to the solution of critical point problems, the methodology used here can also be applied to a wide variety of other problems in the modeling of phase behavior (e.g., Stadtherr *et al.*, 1995; Hua *et al.*, 1998;

Maier *et al.*, 1998; Tessier *et al.*, 2000; Gau and Stadtherr, 1999, Xu *et al.*, 2000), and in the solution of process modeling problems (Schnepper and Stadtherr, 1996).

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References

Baker, L. E. and K. D. Luks, “Critical Points and Saturation Pressure Calculations for Multicomponent Systems,” *Soc. Pet. Eng. J.,* **20**, 15 (1980).

Boberg, T. C. and R. R. White, “Prediction of Critical Mixtures,” *Ind. Eng. Chem. Fundam*., **1**, 40 (1962).

Boshkov, L. Z. and L. V. Yelash, “Closed-loops of Liquid-Liquid Immiscibility in Binary Mixtures Predicted from the Redlich-Kwong Equation of State,” *Fluid Phase Equilib.*, **141**, 105 (1967).

Debenedetti, P. G., *Metastable Liquids: Concepts and Principles*, Princeton University Press, Princeton, New Jersey (1996).

Deiters, U. and G. M. Schneider, “Fluid Mixtures at High Pressures. Computer Calculations of the Phase Equilibria and the Critical Phenomena in Fluid Binary Mixtures from the Redlich-Kwong Equation of State,” *Ber. Bunsenges. Physik. Chem.*, **80**, 1316 (1976).

Enick, R., G. D. Holder and B. I. Morsi, “Critical and Three Phase Behavior in the Carbon Dioxide/Tridecane System,” *Fluid Phase Equilib.*, **22**, 209 (1985).

Gau, C-Y., R. W. Maier and M. A. Stadtherr, “New Interval Methodologies for Reliable Process Modeling,” presented at AIChE Annual Meeting, Dallas, TX, Oct. 31–Nov. 5, 1999.

Gau, C.-Y. and M. A. Stadtherr, “Nonlinear Parameter Estimation Using Interval Analysis,” *AIChE Symp. Ser*., **94**(320), 445 (1999).

Grieves, R. B. and G. Thodos, “The Critical Temperature of Ternary Hydrocarbon Systems,” *Ind. Eng. Chem. Fundam.*, **1**, 45 (1962).

Hansen E., *Global Optimization using Interval Analysis*, Marcel-Dekker, New York (1992).

Heidemann, R. A., “The Criteria for Thermodynamic Stability,” *AIChE J*., **21**, 824 (1975).

Heidemann, R. A and A. M. Khalil, “The Calculation of Critical Points,” *AIChE J*., **5**, 769 (1980).

Heidemann, R. A., “Computation of High Pressure Phase Equilibria,” *Fluid Phase Equilib.*, **14**, 55 (1983).

Hicks, C. P. and C. L. Young, “Theoretical Prediction of Phase Behavior at High Temperatures and Pressures for Non-Polar Mixtures: I. Computer Solution Techniques and Stability Tests,” *J. Chem. Soc. Faraday II*, **73**, 597 (1977).

Hua, Z., J. F. Brennecke and M. A. Stadtherr, “Reliable Prediction of Phase Stability Using an Interval-Newton Method,” *Fluid Phase Equilib.*, **116**, 52 (1996).

Hua, J. Z., J. F. Brennecke and M. A. Stadtherr, “Enhanced Interval Analysis for Phase Stability: Cubic Equation of State Models,” *Ind. Eng. Chem. Res*., **37**, 1519 (1998).

Hurle, R. L., F. Jones and C. L. Young, “Theoretical Prediction of Phase Behavior at High Temperatures and Pressures for Non-polar Mixtures,” *J. Chem. Soc. Faraday II*, **73**, 613 (1977a).

Hurle, R. L., L. Toczylkin and C. L. Young, “Theoretical Prediction of Phase Behavior at High Temperatures and Pressures for Non-polar Mixtures,” *J. Chem. Soc. Faraday II*, **73**, 618 (1977b).

Hytoft, G. and R. Gani, *IVC-SEP Program Package*, Danmarks Tekniske Universitet, Lyngby, Denmark (1996).

Imre, A., K Martinas and L. P. N. Rebelo, “Thermodynamics of Negative Pressures in Liquids,” *J. Non-Equilib. Thermodyn.*, **23**, 351 (1998).

Kearfott, R. B. and M. Novoa, “Algorithm 681: INTBIS. A Portable Newton/Bisection Package,” *ACM Trans. Math. Software* **16**, 152 (1990).

Kearfott, R. B., M. Dawande, K.-S. Du and C.-Y. Hu, “Algorithm 737: {INTLIB}, A Portable {FORTRAN 77} Interval Standard Function Library," *ACM Trans. Math. Software*, **20**, 447 (1994).

Kearfott, R. B., *Rigorous Global Search: Continuous Problem*, Kluwer Academic Publishers, Dordrecht, The Netherlands (1996).

Kearfott, R. B., J. Dian, and A. Neumaier, “Existence Verification for Singular Zeros of Nonlinear Systems,” *SIAM J. Numer. Anal.*, in press (2000).

Levelt Sengers, J. M. H., “Thermodynamics of Solutions Near the Solvent’s Critical Point,” in *Supercritical Fluid Technology: Reviews in Modern Theory and Applications* (T. J Bruno and J .F. Ely, eds.), CRC Press, Boca Raton, FL (1991).

Luks, K. D., E. A. Turek and L. E. Baker, “Calculation of Minimum Miscibility Pressure,” *SPE Res. Eng. J.*, November, 501 (1987).

Maier, R. W., J. F. Brennecke and M. A. Stadtherr, “Reliable Computation of Homogeneous Azeotropes,” *AIChE J.*, **44**, 1745 (1998).

Merrill, R. C., *Liquid-liquid-vapor Phenomena in Cryogenic Liquefied Natural Gas Systems,* Ph. D. Thesis, University of Notre Dame, Notre Dame, Indiana (1983).

Michelsen, M. L. and R. A. Heidemann, “Calculation of Critical Points from Cubic Two-Constant Equations of State,” *AIChE J.*, **27**, 521 (1981).

Michelsen, M. L., “Calculation of Critical Points and Phase Boundaries in the Critical Region,” *Fluid Phase Equilib.*, **16**, 57 (1984).

Munoz, F. and E. H. Chimowitz, “Critical Phenomena in Mixtures. I. Thermodynamic Theory for the Binary Critical Azeotrope,” *J. Chem. Phys*., **99**, 5438 (1993).

Nagarajan, N. R., A. S. Cullick and A. Griewank, “New Strategy for Phase Equilibrium and Critical Point Calculations by Thermodynamic Energy Analysis. Part I. Stability Analysis and Flash,” *Fluid Phase Equilib.*, **62**, 191 (1991a).

Nagarajan, N. R., A. S. Cullick and A. Griewank, “New Strategy for Phase Equilibrium and Critical Point Calculations by Thermodynamic Energy Analysis. Part II. Critical Point Calculations,” *Fluid Phase Equilib.*, **62**, 211 (1991b).

Neumaier, A., *Interval Methods for Systems of Equations*, Cambridge University Press, Cambridge, UK (1990).

Peng, D.-Y. and D. B. Robinson, “A Rigorous Method for Predicting the Critical Properties of Multicomponent Systems from an Equation of State,” *AIChE J.*, **23**, 137 (1977).

Reid, R. C., J. M. Prausnitz and B. E. Poling, *The Properties of Gases and Liquids*, 4th Ed., McGraw-Hill, New York (1987).

Reid, R. C. and B. L. Beegle, “Critical Point Criteria in Legendre Transform Notation,” *AIChE J.*, **23**, 726 (1977).

Rochocz, G. L., M. Castier and S. I. Sandler, “Critical Point Calculations for Semi-Continuous Mixtures,” *Fluid Phase Equilib.*, **139**, 137 (1997).

Sadus, R. J., “Calculating Critical Transitions of Fluid Mixtures: Theory vs. Experiment,” *AIChE J.*, **40**, 1376 (1994).

Schnepper, C. A. and M. A. Stadtherr, “Robust Process Simulation using Interval Methods,” *Comput. Chem. Eng.*, **20**, 187 (1996).

Spear, R. R., R. L. Robinson and K.-C. Chao, “Critical States of Ternary Mixtures and Equations of State,” *Ind. Eng. Chem. Fundam.*, **10**, 588 (1971).

Stadtherr, M. A., C. A. Schnepper and J. F. Brennecke, “Robust Phase Stability Analysis Using Interval Methods,” *AIChE Symp. Ser.*, **91**(304), 356 (1995).

Stockfleth, R. and R. Dohrn, “An Algorithm for Calculating Critical Point in Multicomponent Mixtures which Can Be Easily Implemented in Existing Programs to Calculate Phase Equilibria,” *Fluid Phase Equilib*., **145**, 43 (1998).

Teja, A. S. and H. W. Kropholler, “Critical states of Mixtures in which Azeotropic Behavior Persists in the Critical Region,” *Chem. Eng. Sci*., **30**, 435 (1975).

Teja, A. S. and J. S. Rowlinson, “The Prediction of the Thermodynamic Properties of Fluids and Fluid mixtures-IV. Critical and Azeotropic States,” *Chem. Eng. Sci*., **28**, 529 (1973).

Tessier, S. R., J. F. Brennecke and M. A. Stadtherr, “Reliable Phase Stability Analysis for Excess Gibbs Energy Models,” *Chem. Eng. Sci*., **55**, 1785 (2000)..

van Hentenryck, P., L. Michel and Y. Deville, Y., *Numerica: A Modeling Language for Global Optimization*, MIT Press, Cambridge, Mass. (1997).

van Konynenburg, P. H. and R. L. Scott, “Critical Lines and Phase Equilibria in Binary van der Waals Mixtures,” *Philos. Trans. Roy. Soc. London A*, **298**, 495 (1980).

Xu, G., A. M. Scurto, M. Castier, J. F. Brennecke, M. A. Stadtherr, “Reliable Computation of High Pressure Solid-Fluid Equilibrium,” *Ind. Eng. Chem. Res.*, **39**, 1624 (2000).

APPENDIX

This Appendix explains in detail the notation used in Eqs. (4) and (5) in the text, which are derived from a generalized cubic EOS model. Eqs. (4) and (5) are repeated here for convenience.

$$\sum_{j=1}^{C} A_{ij}\Delta n_j =$$

$$\frac{RT}{n}\left(\frac{\Delta n_i}{y_i} + F_1\left(\beta_i \overline{N} + \overline{\beta}\right) + \beta_i {F_1}^2 \overline{\beta}\right) + \frac{a}{bn}\left(\beta_i \overline{\beta} F_3 - \frac{F_5}{a}\sum_{j=1}^{C} a_{ij}\Delta n_j + F_6\left(\beta_i \overline{\beta} - \alpha_i \overline{\beta} - \overline{\alpha}\beta_i\right)\right)$$

$$i = 1 \ldots C \qquad (4)$$

$$\sum_{i=1}^{C}\sum_{j=1}^{C}\sum_{k=1}^{C} A_{ijk}\Delta n_i \Delta n_j \Delta n_k =$$

$$\frac{RT}{n^2}\left(-\frac{\sum_{i=1}^{C}\Delta n_i^3}{y_i^2} + 3\overline{N}(\overline{\beta}F_1)^2 + 2(\overline{\beta}F_1)^3\right) + \frac{a}{n^2 b}(3\overline{\beta}^2(2\overline{\alpha} - \overline{\beta})(F_3 + F_6) - 2\overline{\beta}^3 F_4 - 3\overline{\beta}\,\overline{a}F_6) \qquad (5)$$

Here

C : total number of components.

A_{ij} : second order derivative of the Helmholtz free energy with respect to the number of moles of species i and j.

Δn_j : change in total number of moles of species j. This is used in the context of a Taylor series expansion of the Helmholtz free energy in terms of composition.

R : ideal gas constant.

T : absolute temperature.

n : total number of moles.

n_i : number of moles of species i. Analogous meaning for other subindices.

$\overline{N}$: parameter used in the equations for the computation of critical points, it is defined as,

$$\overline{N} = \sum_{i=1}^{C} \Delta n_i$$

y_i : mole fraction of component i. Analogous meaning for other subindices.

a : average energy parameter of the equation of state for the mixture of components. This is computed using standard van der Waals mixing rules:

$$a = \sum_{i=1}^{C}\sum_{j=1}^{C}\left(\frac{n_i n_j}{n^2}\right)a_{ij}$$

$$a_{ij} = \left(a_i a_j\right)^{0.5}(1 - k_{ij})$$

a_{ij} : energy of interaction parameter between species i and j.

a_i : energy parameter of species i. The meaning is the same for other subindices. It is computed using the following correlation:

$$a_i = \frac{(RT_{c_i})^2 \eta}{P_{c_i}}\left[1 + c_i\left(1 - \left(\frac{T}{T_{c_i}}\right)^{0.5}\right)\right]$$

$\eta = 0.42748$ for the Soave-Redlich-Kwong (SRK) Equation of State.
$\eta = 0.45724$ for the Peng-Robinson (PR) Equation of State.

$c_i = 0.48 + 1.574 w_i - 0.176 w_i^2$ for SRK EOS
$c_i = 0.37464 + 1.54226 w_i - 0.26992 w_i^2$ for PR EOS

w_i : acentric factor of species i.

T_{c_i} : critical temperature of species i.

P_{c_i} : critical pressure of species i.

k_{ij} : binary interaction parameter between species i and j.

α_k : parameter used in the equations for the computation of critical points, it is defined as,

$$\alpha_k = \frac{\sum_{i=1}^{C} y_i a_{ik}}{a}$$

$\bar{\alpha}$: parameter used in the equations for the computation of critical points, it is defined as,

$$\bar{\alpha} = \sum_{i=1}^{C} \Delta n_i \alpha_i$$

$\bar{a}$: parameter used in the equations for the computation of critical points, it is defined as,

$$\bar{a} = \frac{1}{a} \sum_{i=1}^{C} \sum_{j=1}^{C} \Delta n_i \Delta n_j a_{ij}$$

b : average van der Waals molar volume in the Equation of State. This is computed using standard van der Waals mixing rules,

$$b = \sum_{i=1}^{C} \left(\frac{n_i}{n} \right) b_i$$

b_i : van der Waals molar volume of species i. This is computed as follows,

$$b_i = 0.08664 RT_{c_i} / P_{c_i} \qquad \text{for SRK EOS}$$

$$b_i = 0.07780 RT_{c_i} / P_{c_i} \qquad \text{for PR EOS}$$

β_i : parameter used in the equations for the computation of critical points, it is defined as,

$$\beta_i = \frac{b_i}{b}$$

$\bar{\beta}$: parameter used in the equations for the computation of critical points, it is defined as,

$$\bar{\beta} = \sum_{i=1}^{C} \Delta n_i \beta_i$$

F_{1-6} : auxiliary functions used in the computation of critical points, they are defined as,

$$F_1 = \frac{1}{K-1}$$

$$F_2 = \frac{2}{D_1 - D_2}\left[\frac{D_1}{K+D_1} - \frac{D_2}{K+D_2}\right]$$

$$F_3 = \frac{1}{D_1 - D_2}\left[\left(\frac{D_1}{K+D_1}\right)^2 - \left(\frac{D_2}{K+D_2}\right)^2\right]$$

$$F_4 = \frac{1}{D_1 - D_2}\left[\left(\frac{D_1}{K+D_1}\right)^3 - \left(\frac{D_2}{K+D_2}\right)^3\right]$$

$$F_5 = \frac{2}{D_1 - D_2}\ln\left(\frac{K+D_1}{K+D_2}\right)$$

$$F_6 = \frac{2}{D_1 - D_2}\left[\left(\frac{D_1}{K+D_1} - \frac{D_2}{K+D_2}\right) - \ln\left(\frac{K+D_1}{K+D_2}\right)\right]$$

K : dimensionless volume, it is defined as,

$$K = \frac{V}{nb} = \frac{v}{b}$$

D_{1-2} : parameters of the equation of state. Their values are calculated with the following formulas,

$$D_1 = \frac{u_o + \sqrt{u_o^2 - 4w_o}}{2}$$

$$D_2 = \frac{u_o - \sqrt{u_o^2 - 4w_o}}{2}$$

where,

$u_o = 1,\quad w_o = 0$ for the SRK EOS

$u_o = 2,\quad w_o = -1$ for the PR EOS

δ_{ij} : Kronecker delta operator, which is defined as,

$$\delta_{ij} = \begin{cases} i = j & \delta_{ij} = 1 \\ i \neq j & \delta_{ij} = 0 \end{cases}$$

Table 1. Computed critical points for mixtures of methane (1) and hydrogen sulfide (2).

Feed Composition		Δn_1	Δn_2	Critical Volume (cm^3/gmol)	Critical Temperature (K)	Critical Pressure (bar)	Total time (s)
n_{CH_4}	n_{H_2S}						
0.998	0.002	0.9999	0.0042	114.26	190.82	46.3	0.52
0.97	0.03	0.9977	0.0682	107.70	196.74	50.4	1.42
0.9475	0.0525	0.9916	0.1292	102.18	201.37	53.9	3.15
0.94	0.06	0.9884	0.1517	100.30	202.86	55.1*	4.06
0.93	0.07	0.9830	0.1837	97.75	204.78	56.7*	5.64
		0.6185	0.7858	44.72	114.77	-283.6	
0.86	0.14	0.8651	0.5016	77.95	213.71	65.5*	20.9
		0.6003	0.7998	56.59	181.31	-1.7	
0.85	0.15	0.8189	0.5739	74.03	212.99	64.5*	25.4
		0.6239	0.7815	59.41	190.98	22.5*	
0.84	0.16			NCP			39.0
0.75	0.25			NCP			14.5
0.53	0.47			NCP			19.6
0.52	0.48	0.2017	-0.9795	59.26	270.02	146.1	35.0
		0.2874	-0.9578	54.94	260.27	149.0	
0.51	0.49	0.1352	-0.9908	63.37	279.25	145.0	27.8
		0.3896	-0.9210	50.31	249.01	160.1	
0.49	0.51	0.6814	-0.7319	34.89	208.15	1800.2	26.4
		0.5229	-0.8524	44.26	231.67	230.4	
		0.0846	-0.9964	67.59	288.86	144.0	
0.36	0.64	0.0628	-0.9999	83.21	323.07	132.6	8.87
0.229	0.771	0.0435	0.9999	95.58	345.50	117.1	4.87
0.24	0.76	0.0412	0.9999	94.58	343.86	118.4	5.14
0.09	0.91	0.0297	0.9999	107.91	363.58	100.0	1.95

NCP: no critical point was found.
* Critical point is not stable.

Table 2. Computed critical points for mixtures of carbon dioxide (1) and *n*-octane (2).

Feed Composition		Δn_1	Δn_2	Critical Volume (cm^3/gmol)	Critical Temperature (K)	Critical Pressure (bar)	Total time (s)
n_{CO_2}	$n_{C_8H_{18}}$						
0.90	0.10	0.7377	0.6751	128.03	384.70	137.0	38.9
		0.9895	-0.1447	55.50	128.43	-1006.3	
0.88	0.12	0.6093	0.7929	136.55	398.50	140.5	35.5
		0.9901	-0.1403	58.75	126.17	-1020.3	
0.878	0.122	0.5964	0.8027	137.43	399.83	140.8	36.1
		0.9902	-0.1399	59.07	125.90	-1022.1	
0.875	0.125	0.5771	0.8167	138.76	401.82	141.1	34.9
		0.9902	-0.1394	59.53	125.48	-1024.9	
0.871	0.129	0.5517	0.8341	140.55	404.43	141.4	34.6
		0.9903	-0.1388	60.14	124.90	-1028.9	
0.80	0.20	0.2197	0.9756	174.81	444.61	136.8	27.6
		0.9913	-0.1315	70.27	112.90	-1118.2	
0.60	0.40	0.0422	0.9999	283.70	510.01	94.7	14.5
0.40	0.60	0.0116	-0.9999	398.67	540.74	61.7	7.46
0.20	0.80	0.0689	-0.9999	515.50	557.93	39.9	2.91
0.10	0.90	0.0344	-0.9999	574.23	563.92	31.7	1.53

Table 3. Computed critical points for mixtures of carbon dioxide (1) and *n*-hexadecane (2).

Feed Composition		Δn_1	Δn_2	Critical Volume (cm^3/gmol)	Critical Temperature (K)	Critical Pressure (bar)	Total time (s)
n_{CO_2}	$n_{C_{16}H_{34}}$						
0.97	0.03	0.6058	0.7956	100.95	368.00	170.7	84.8
		0.9982	-0.0606	58.10	173.23	-593.6	
		0.9958	-0.0912	50.97	188.30	-220.5	
0.94	0.06	0.6773	-0.7357	127.27	440.54	230.3	70.4
		0.9985	-0.0552	69.93	159.95	-677.8	
0.93	0.07	0.7219	-0.6920	137.61	463.11	237.7	66.6
		0.9985	-0.0544	73.50	155.07	-710.1	
0.58	0.42	0.2358	-0.9673	606.39	686.92	74.0	11.4
0.50	0.50	0.1890	-0.9820	718.15	696.59	58.3	7.52

Table 4. Binary interaction parameters (k_{ij}) used in Example 4.

Binary interaction parameters(1) (k_{ij})

	CO_2	N_2	H_2S	CH_4	C_6H_{14}
CO_2	0.0		0.0989 **0.0974**	0.0933 **0.0919**	0.1178 **0.1100**
N_2		0.0		0.0278	0.1496
H_2S	0.0989 **0.0974**		0.0	0.08 (2) **0.0**	
CH_4	0.0933 **0.0919**	0.0278	0.08 (2) **0.0**	0.0	0.0374 **0.0422**
C_6H_{14}	0.1178 **0.1100**	0.1496		0.0374 **0.0422**	0.0

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(1) Parameters for the SRK EOS are in plain face type, and for the PR EOS in bold face type. Except as noted, these values are from the Aspen Plus (version 9.3) database.

(2) Value used by Hua *et al.* (1998).

Table 5. Computed critical points for ternary mixtures in Example 4.

Feed Composition			Δn_1	Δn_2	Δn_3	Critical Volume (cm^3/gmol)	Critical Temperature (K)	Critical Pressure (bar)	Total time (s)
n_{CH_4}	n_{N_2}	$n_{C_6H_{14}}$							
0.46	0.07	0.47	0.1137	0.0485	-0.9923	228.83	462.64	117.0	110
0.52	0.08	0.40	0.1525	0.0655	-0.9862	196.63	448.58	141.5	116
0.68	0.02	0.30	0.2621	0.0217	-0.9648	153.82	415.32	176.2	114
n_{CH_4}	n_{CO_2}	$n_{C_6H_{14}}$							
0.70	0.10	0.20	0.3720	-0.0245	-0.9279	113.53	362.39	206.2	936
0.74	0.01	0.25	0.3360	-0.0137	-0.9419	132.40	391.35	196.1	139
0.78	0.15	0.07	0.9112	-0.1707	-0.3748	49.42	142.70	-142.0	3146
			0.7168	-0.2533	-0.6494	60.68	208.29	77.7	
0.78(1)	0.15	0.07	0.9106	-0.1756	-0.3740	43.88	143.58	-155.9	2104
			0.6594	-0.2920	-0.6927	54.71	210.11	80.0	
0.79	0.05	0.16	0.5246	-0.0168	-0.0852	93.20	323.67	226.0	781
n_{CH_4}	n_{CO_2}	n_{H_2S}							
0.50	0.10	0.40	0.3892	-0.0901	-0.9167	50.21	235.18	108.3	609
			0.2752	-0.1312	-0.9910	68.00	274.01	123.4	
0.50(1)	0.10	0.40	0.2247	0.1384	0.9645	72.35	285.58	113.8	442
			0.6541	-0.0606	-0.7540	32.38	144.36	8.9	

(1) Computed using the PR EOS.

Table 6. Binary interaction parameters (k_{ij}) used in Example 5.

Binary interaction parameters$^{(1)}$ (k_{ij})

	CO_2	N_2	H_2S	CH_4	C_2H_4	C_3H_8	C_4H_{10}	C_5H_{12}	C_7H_{16}
CO_2	0.0		0.0974	0.0919					
N_2		0.0		0.0311		0.0852			
H_2S	0.0974		0.0	0.0					
CH_4	0.0919	0.0311	0.0	0.0		0.0140			
C_2H_4					0.0		0.0096	0.0078	0.0067
C_3H_8		0.0852		0.0140		0.0			
C_4H_{10}					0.0096		0.0		0.0033
C_5H_{12}					0.0078			0.0	0.0074
C_7H_{16}					0.0067		0.0033	0.0074	0.0

(1) Values from Aspen Plus (version 9.3) database.

Table 7. Computed critical points for ternary mixtures in Example 5.

Feed Composition			Δn_1	Δn_2	Δn_3	Critical Volume (cm^3/gmol)	Critical Temperature (K)	Critical Pressure (bar)	Total time (s)
n_{CH_4}	n_{CO_2}	n_{H_2S}							
0.07	0.616	0.314	0.0318	0.8200	0.5715	98.61	312.15	83.3	155
			0.0730	0.4224	-0.9035	35.35	132.12	-1144.7	
$n_{C_2H_6}$	$n_{C_4H_{10}}$	$n_{C_7H_{16}}$							
0.429	0.373	0.198	0.2961	0.6821	0.6686	237.95	439.54	63.2	682
0.726	0.171	0.103	0.7651	0.4361	0.4738	174.03	388.64	74.9	724
0.514	0.412	0.074	0.4451	0.8525	0.27407	205.92	403.54	62.5	542
$n_{C_2H_6}$	$n_{C_5H_{12}}$	$n_{C_7H_{16}}$							
0.801	0.064	0.135	0.7737	0.1991	0.6015	170.02	394.71	82.9	665
0.612	0.271	0.117	0.5041	0.7359	0.4529	214.25	424.77	70.4	782
0.615	0.296	0.089	0.5098	0.7916	0.3368	211.27	419.54	69.39	709
n_{CH_4}	$n_{C_3H_8}$	n_{N_2}							
0.415	0.542	0.043	0.1264	0.9919	-0.0121	139.36	327.47	87.0	29.9
0.360	0.545	0.095	0.1069	0.9939	-0.0276	137.11	328.15	92.5	45.9
0.453	0.5005	0.0465	0.1492	0.9887	-0.0141	132.06	321.27	91.8	37.1
0.4115	0.5030	0.0855	0.1328	0.9908	-0.0266	130.04	321.76	96.2	52.2