Available online at www.sciencedirect.com

ScienceDirect

J. of Supercritical Fluids 39 (2007) 287–295

THE JOURNAL OF Supercritical Fluids

www.elsevier.com/locate/supflu

Global phase equilibrium calculations: Critical lines, critical end points and liquid–liquid–vapour equilibrium in binary mixtures

Martín Cismondi*, Michael L. Michelsen

IVC-SEP, Department of Chemical Engineering, Bygning 229, DTU, DK 2800 Lyngby, Denmark

Received 9 August 2005; received in revised form 21 February 2006; accepted 16 March 2006

Abstract

A general strategy for global phase equilibrium calculations (GPEC) in binary mixtures is presented in this work along with specific methods for calculation of the different parts involved. A Newton procedure using composition, temperature and volume as independent variables is used for calculation of critical lines. Each calculated point is analysed for stability by means of the tangent plane distance, and the occurrence of an unstable point is used to determine a critical endpoint (CEP). The critical endpoint, in turn, is used as the starting point for constructing the three-phase line. The equations for the critical endpoint, as well as for points on the three-phase line, are also solved using Newton's method with temperature, molar volume and composition as the independent variables.

The different calculations are integrated into a general procedure that allows us to automatically trace critical lines, critical endpoints and three-phase lines for binary mixtures with phase diagrams of types from I to V without advance knowledge of the type of phase diagram. The procedure requires a thermodynamic model in the form of a pressure-explicit EOS but is not specific to a particular equation of state.

Keywords: Calculation; Critical lines; Critical end points; LLV; Binary mixtures; EOS

1. Introduction

Phase equilibrium calculations are most often focused on calculation of phase equilibrium at given temperature, pressure and composition (the isothermal flash) or on correlation or prediction of specific isothermal or isobaric data. Calculation of critical lines, three-phase lines and critical end points (CEP) are less common although for any binary system these lines and points enable us to distinguish between single phase regions and regions of two or three coexisting phases. Global phase equilibrium diagrams, i.e. phase diagrams containing those lines in different projections of the P–T–v–x space, are therefore useful in the analysis of potential conditions for separation processes, as well as in analysing the ability of thermodynamic models to qualitatively and quantitatively reproduce experimental behaviour.

In the present work we propose a procedure for the automated construction of global phase equilibrium diagrams, together with the methods used to calculate the individual elements. The procedure automatically handles all types of fluid phase behaviour from I to V according to the classification of Scott and van Konynemburg [1]. In order to clearly define the scope of the present work and avoid confusion, two important remarks need to be made.

First, two particular kinds of problems towards which research efforts are devoted in the field of thermodynamic modeling and phase equilibrium calculations should be clearly differentiated. One problem is to establish whether a particular qualitative behaviour can be predicted with a certain model or equation of state and given values or relations between the parameters of the two pure compounds which constitute a binary system. Additionally, this requires delimiting the regions, over the interaction parameters space, where each type of phase behaviour will be predicted. Another completely different problem, more basic perhaps, is the following: given an equation of state and parameter values for two pure compounds and their interactions, obtain the complete picture of the phase

---

Abbreviations: CEP, critical endpoint; LCEP, lower critical endpoint; LLV, liquid–liquid–vapour; tpd, tangent plane distance; SRKSoave–Redlich–Kwong equation of state; UCEP, upper critical endpoint

* Corresponding author at: Planta Piloto de Ingenieria Química, PLAPIQUI-UNS-CONICET, Cmno. La Carrindanga Km. 7, 8000 Bahia Blanca, Argentina. Tel.: +54 291 4861700x233; fax: +54 291 4861600.

E-mail addresses: mcismondi@plapiqui.edu.ar (M. Cismondi), mlm@kt.dtu.dk (M.L. Michelsen).

0896-8446/$ – see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.supflu.2006.03.011

Nomenclature

b	first condition to be satisfied in a critical point (defined in Eq. (3))
$\boldsymbol{B}$	matrix defined in Eq. (2) or (11) for calculation of critical points
c	second condition to be satisfied in a critical point (defined in Eq. (4))
$\hat{f}_i$	fugacity of component i in a mixture ($\hat{f}_i = x_i\hat{\varphi}_i P$)
$\boldsymbol{F}$	vector of equations, e.g. in the calculation of critical points
g	specification equation for a marching procedure (defined in Eq. (6))
$\boldsymbol{I}$	identity matrix
$\boldsymbol{J}$	Jacobian matrix for $\boldsymbol{F}$ with respect to $\boldsymbol{X}$
n	number of moles
P	pressure
s	distance parameter (calculation of critical points)
S	specified variable or its value, in a marching procedure
T	temperature
$\boldsymbol{u}$	normalized eigenvector of the $\boldsymbol{B}$ matrix
v	molar volume
V	total volume
$\boldsymbol{X}$	vector of independent variables, e.g. in the calculation of critical points
x, y, w	molar fractions for the more volatile component (1) if no index is specified
z_i	molar fraction of component i

Greek letters

δ_{ij}	Kronecker delta function: 0 for $i \neq j$ and 1 for $i = j$
Δ	half of specified difference in composition between two quasi-critical phases for the first point after a CEP on a three-phase line
η	perturbation for numerical calculation of derivatives by central differences
λ	eigenvalue (or smallest eigenvalue) of the matrix $\boldsymbol{B}$ defined in Eq. (2) or (11)
$\hat{\varphi}_i$	fugacity coefficient of component i in a mixture

Subscripts

1, 2, i	component index
c	critical property
S	specified
U	denoting upper critical end point
V	vapour
x, y, w	denoting a phase in LLV or three-phase line calculation

equilibrium predicted, which is essentially delimited by critical lines, liquid–liquid–vapour equilibrium lines and, in some cases, azeotropic lines. Since the pioneer works of Scott and van Konynemburg [1,2] many other important contributions have been made concerning the first kind of problems (see for example [3–5] and the references cited therein). Nevertheless, only the calculation of single critical points, most often for mixtures of specified composition, has received attention in relation to the second kind of problems. On the other hand, and at least to our knowledge, procedures for the automated calculation of critical lines exhibiting maxima and minima in composition have not been published, nor for their integration with LLV lines and critical end points, particularly without knowing in advance the type of phase behaviour predicted. Therefore, the request for a strategy and for procedures for the automated calculation of global phase equilibrium in binary systems has not been satisfied yet. The development of such tools for the engineering and the research community is the goal of this paper. The reader interested in *global phase diagrams*, meaning the boundaries of different types of phase behaviour on the space of model parameters or related variables, is referred to the works cited above.

We address here the general problem of obtaining, from an equation of state and given parameters, the global phase equilibrium diagram of a binary system, namely critical lines, LLV lines and critical end points in the P–T–V–x space. How well they compare to experimental data will depend on the model and parameters used, and that is completely beyond the scope of this paper. The examples given are illustrative.

2. Overall strategy for global phase equilibrium calculations

As indicated by Scott and van Konynemburg [1] and Deiters and Pegg [3], there are essentially five qualitatively different critical lines that are of interest in binary mixtures both in terms of experiments and calculations. Their combinations cover all possibilities in systems of Type I–V in the classification of Scott and van Konynemburg [1]. These lines are defined in terms of their ending points:

A. A continuous liquid–vapour critical locus connecting the critical points of the two pure components (C_1 and C_2, with lower and higher T_c, respectively). This is characteristic of systems showing phase behaviour of Type I or II.
B. A liquid–liquid critical line descending from C_m (a liquid–liquid critical point at infinite pressure) to an upper critical end point (UCEP) is found in systems of Type II or IV.
C. A characteristic line in systems of Type III, descending from C_m to C_2. It may exhibit relative minima and maxima in pressure.
D. A line going from C_1 to an UCEP in systems of Type III, IV or V.
E. The line going from the LCEP to C_2 in systems of Type IV or V.

These lines and their relation with Types I–IV in the classification of Scott and van Konynemburg are exemplified in Fig. 1. Type V is exactly as Type IV but without a liquid–liquid critical line (B) and the associated three-phase line.

The approach chosen here is shown schematically in Fig. 2. It starts with calculating the critical line starting at C_2, i.e. the

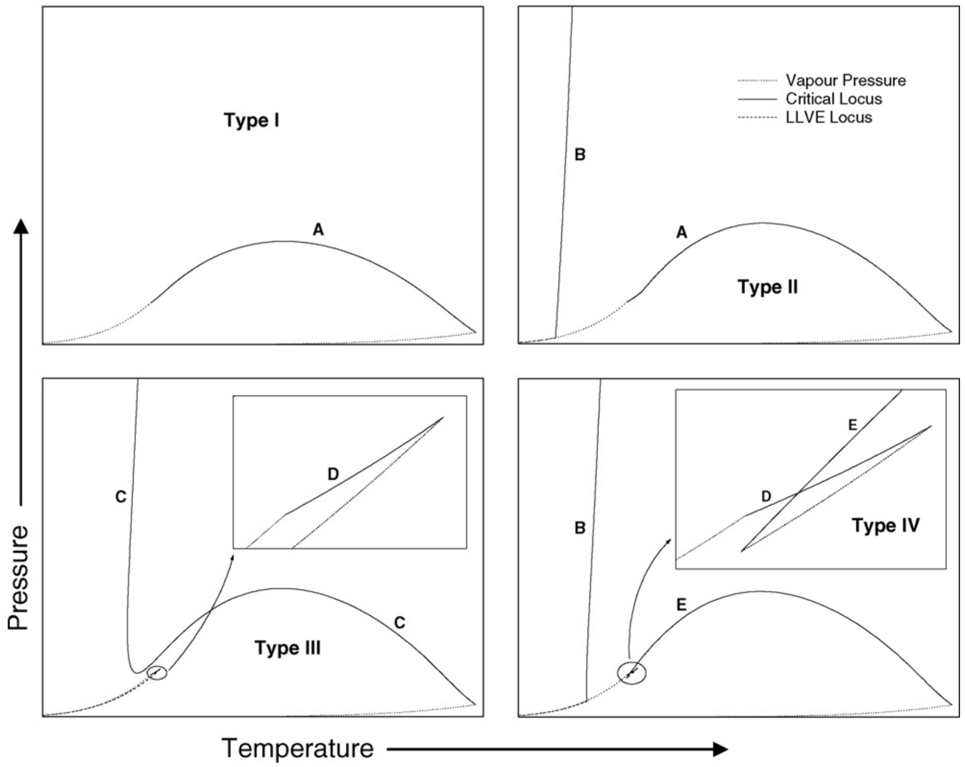

Fig. 1. Different critical lines of interest in binary systems showing phase behaviour of Types I–IV in the classification of Scott and van Konynemburg.

critical point for the pure component with the higher critical temperature. This line may end in three different ways:

1. A stable critical line that ends in C_1. This indicates a phase diagram of Type I or II.
2. A stable critical line that tends toward infinite pressure. This behaviour is characteristic of Type III.
3. A point on the line becomes unstable. The occurrence of a critical endpoint is an indication of Type IV or V phase behaviour.

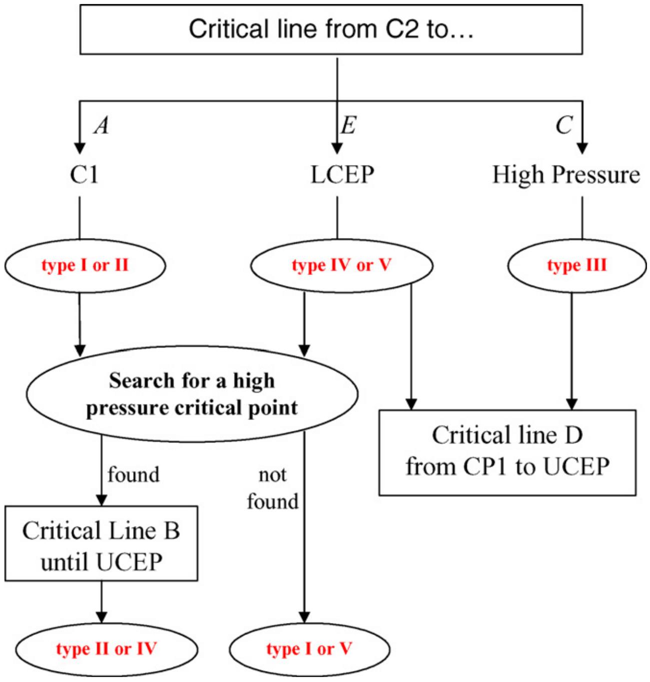

Fig. 2. Algorithm flow sheet for calculation of all critical lines determining the type of phase behaviour.

In addition to this, it is necessary to search for the existence of an isolated critical line (i.e. a critical line that is not connected to any of pure component endpoint). The existence of such a line distinguishes between Types I and II in case (1) above, and between Types IV and V in case (3). Finally we need procedures for locating and calculating the individual elements, i.e.

- critical lines originating at pure component endpoints;
- isolated critical lines;
- stability analysis and critical endpoints;
- three-phase lines.

Procedures for each of these are given in the following sections.

3. Calculation of critical lines

A comprehensive review on calculation of critical points was published by Sadus [6]. All the methods discussed prescribe how to find the critical temperature and volume (and therefore also the pressure) for a mixture of known composition. Methods for calculation of critical points requiring the specification of composition, and which are based on the use of temperature and volume, such as the classical method of Heidemann and Khalil

[7], as iteration variables, are accurate and robust. In addition to being more well behaved, they are able to handle cases where the use of temperature and pressure fails, like pure components and critical azeotropes. In this work, we formulate the criticality conditions from a variant of the Heidemann–Khalil approach that avoids the nested loops of that method.

3.1.1. Criticality conditions

Following Michelsen and Heidemann [8] in their analysis of higher order critical points, Appendix (A9)–(A18), we proceed as follows:

We consider a binary mixture at temperature T, molar volume v and composition $(z_1, z_2 = 1 - z_1)$. Let the number of total moles $n_t = n_1 + n_2$ be 1 and therefore total volume $V = n_t v = v$. Define composition variables by

$$n_1 = z_1 + s\sqrt{z_1}u_1; \qquad n_2 = z_2 + s\sqrt{z_2}u_2 \tag{1}$$

where s is a distance parameter and (u_1, u_2) a normalized vector, $u_1^2 + u_2^2 = 1$. This vector is chosen as the eigenvector corresponding to the smallest eigenvalue λ_1 of the matrix $\boldsymbol{B}$ given by

$$B_{ij} = \sqrt{z_i z_j}\left(\frac{\partial \ln \hat{f}_i}{\partial n_j}\right)_{T,V} \tag{2}$$

evaluated at $s = 0$, i.e. $n_1 = z_1$, $n_2 = z_2$. The conditions that must be satisfied at a critical point are then

$$b = \lambda_1 = 0 \tag{3}$$

$$c = \left(\frac{\partial \lambda_1}{\partial s}\right)_{s=0} = 0 \tag{4}$$

Note that for an ideal gas, $\boldsymbol{B} = \boldsymbol{I}$ and all eigenvalues are equal to 1.

We evaluate the elements of $\boldsymbol{B}$ analytically from the given EOS and solve analytically for λ_1. c is subsequently calculated numerically using central differences:

$$c \approx \frac{\lambda_1(s = \eta) - \lambda_1(s = -\eta)}{2\eta} \tag{5}$$

Regarding the value for the perturbation, there is a balance between accuracy (favoured by small values) and roundoff (favoured by large values). The value $\eta = 0.0001$ was found to be a reasonable compromise.

3.1.2. Newton procedure for tracing out critical lines

In cases where composition varies monotonically along the critical line it is possible to trace the line by specifying z_1 and solving Eqs. (3) and (4) for T, v using the results from the previous point on the line as initial estimate. Monotonic variation is not always the case, and e.g. Type III systems often exhibit maxima and minima in composition along a critical line. We therefore extend the system of equations to be solved with a *specification equation*:

$$g(z, T, v) = X_S - S = 0 \tag{6}$$

where X_S represents one of the variables z_1, $\ln T$ and $\ln v$, and S the value specified for that variable in the point to be calculated. The set of equations to be solved is thus

$$F = \begin{pmatrix} X_S - S \\ b \\ c \end{pmatrix} = 0 \tag{7}$$

and Newton's method is used for solving the equations:

$$J\begin{pmatrix} \Delta z_1 \\ \Delta \ln T \\ \Delta \ln v \end{pmatrix} + \begin{pmatrix} 0 \\ b \\ c \end{pmatrix} = 0 \tag{8}$$

The evaluation of the Jacobian requires the derivatives of b and c with respect to z_1, $\ln T$ and $\ln v$. These are all evaluated numerically by central differences with an increment of 0.0001.

When a converged solution has been determined we can evaluate the vector of sensitivities $\mathrm{d}\boldsymbol{X}/\mathrm{d}S$ which is calculated from

$$J\begin{pmatrix} \mathrm{d}z_1/\mathrm{d}S \\ \mathrm{d}\ln T/\mathrm{d}S \\ \mathrm{d}\ln v/\mathrm{d}S \end{pmatrix} + \begin{pmatrix} -1 \\ 0 \\ 0 \end{pmatrix} = 0 \tag{9}$$

The vector of sensitivities is used for two purposes:

- its numerically largest element determines the variable that is specified in the following step;
- it is used to obtain an initial estimate for the solution vector in the following step from

$$X_{\text{new}} = X_{\text{old}} + \left(\frac{\mathrm{d}X}{\mathrm{d}S}\right)\Delta S \tag{10}$$

The increment in the specification, ΔS is controlled by the number of iterations required to solve for the current point. If the solution is found in three iterations or less, the numerical value of ΔS is increased, and if five or more are required, ΔS is decreased. This is complemented with a maximum step allowed.

Finally, if we are unable to converge the equations at a specific point, we revert to the previous point $\boldsymbol{X}_{\text{old}}$, reduce the step by a factor of 2 and calculate a new estimate using Eq. (9). The construction is started at (a known) pure component critical point, and as the initial specification for the first point on the line we chose composition. Subsequent points are calculated automatically.

The procedure used for tracing out a critical line is essentially identical to that used by Michelsen [9] to trace phase boundaries in multicomponent mixtures.

4. High-pressure critical line

Types II and IV phase diagrams are characterized by the presence of a critical line that is not connected to any of the pure component endpoints. The line extends from infinite pressure down to zero (and negative) pressure with very modest variations in temperature, molar volume and composition. We search for the existence of such a line as follows:

1. The pressure is fixed to a specified, high value, typically 200 MPa. Initially, the temperature is set to 300 K.
2. At the current temperature we calculate the minimum eigenvalue of the matrix given by

$$B_{ij} = \delta_{ij} + \sqrt{z_i z_j}\left(\frac{\partial \ln \hat{\varphi}_i}{\partial n_j}\right)_{T,P} \tag{11}$$

   as a function of composition (50 equidistant points). The Gibbs–Duhem equation shows that one of the eigenvalues is always 1. The sum of the eigenvalues equals the trace of the matrix, and for a binary the other eigenvalue, i.e. the one we are interested in, is therefore found from

$$\lambda = 1 + z_1\left(\frac{\partial \ln \hat{\varphi}_1}{\partial n_1}\right)_{T,P} + z_2\left(\frac{\partial \ln \hat{\varphi}_2}{\partial n_2}\right)_{T,P} \tag{12}$$

   From the Gibbs–Duhem equation:

$$z_1\left(\frac{\partial \ln \hat{\varphi}_1}{\partial n_1}\right) + z_2\left(\frac{\partial \ln \hat{\varphi}_1}{\partial n_2}\right) = 0,$$

$$z_1\left(\frac{\partial \ln \hat{\varphi}_2}{\partial n_1}\right) + z_2\left(\frac{\partial \ln \hat{\varphi}_2}{\partial n_2}\right) = 0$$

   and therefore,

$$\lambda = 1 - \left(\frac{\partial \ln \hat{\varphi}_1}{\partial n_2}\right)_{T,P} \tag{13}$$

   At the limit of intrinsic stability (the spinodal) the smaller eigenvalue is exactly zero. The mixture is critical at a composition z_c if
   a. the smallest value of λ_1 is found at z_c, and
   b. this value is exactly zero.
3. At fixed z_S (the composition at which λ_1 is minimum at the specified T and P) we now reduce T (if λ_1 is positive), or increase T (if λ_1 is negative), until we arrive at a temperature where $\lambda_1(T, z_S)$ equals zero. We abandon the search if the temperature falls below a pre-specified limit, typically 30 K.
4. The procedure with first determining z_S as the composition where λ_1 is smallest and subsequently T as the temperature where the eigenvalue is zero, is repeated twice.

Unless the search was abandoned in step 3 an initial estimate of composition, temperature and molar volume of a critical point at 200 MPa is now available. We specify the molar volume and calculate the first point. The next step is taken in the direction that leads to a decreased pressure, and this usually corresponds to an increased molar volume. All subsequent steps are performed with the automatic procedure described earlier.

It may, in particular for the initial point on the high-pressure line, be advantageous to increase the set of equations with (the log of) pressure as a new variable. The corresponding extra equation is the EOS, i.e.

$$F_4 = P - P(z_1, \ln T, \ln v) = 0 \tag{14}$$

If this approach is used we specify for the initial point $P = 200$ MPa and for the next point a reduction in pressure.

5. Critical endpoints

At a critical endpoint the critical phase (z_c, T, v_c) is at equilibrium with another phase, (y, T, v_y). The five unknown are determined from the set of equations:

$$b(z_c, T, v_c) = 0 \tag{15}$$

$$c(z_c, T, v_c) = 0 \tag{16}$$

$$P(z_c, T, v_c) = P(y, T, v_y) \tag{17}$$

$$\ln \hat{f}_1(z_c, T, v_c) = \ln \hat{f}_1(y, T, v_y) \tag{18}$$

$$\ln \hat{f}_2(z_c, T, v_c) = \ln \hat{f}_2(y, T, v_y) \tag{19}$$

The equations are solved using Newton's method with numerical derivatives of b and c as described earlier and analytic derivatives for the remaining. Good initial estimates are required, and these are obtained from stability analysis.

6. Stability analysis of critical lines

The computational cost of an extensive stability analysis for a binary mixture is very modest. We have therefore adopted a procedure where each calculated point on a critical line is tested for stability. If the current point is unstable and the previous stable we know that a critical endpoint is located on the section of the critical line that connects the two points.

The test for stability is performed as follows:

At the current point on the critical line we calculate the pressure P_c and the component fugacities $\hat{f}_{c1}$, $\hat{f}_{c2}$. The critical point is *unstable* provided a composition y exists where

$$\text{tpd}(y) = y(\ln \hat{f}_1(T, P_c, y) - \ln \hat{f}_{c1}) + (1-y)(\ln \hat{f}_2(T, P_c, y) - \ln \hat{f}_{c2}) < 0 \tag{20}$$

We divide the composition interval in 50 equidistant points and evaluate the tangent plane distance at each. This table is used to locate possible minima in the tangent plane distance. If minima with a negative value of the tpd exist, the critical point is unstable. The composition of the minimum y_m together with the critical composition, the temperature and the molar volumes of the two phases are used as the initial estimate for solving the equations for the CEP.

7. Calculation of LLVE lines

The seven unknown are temperature T, molar volume of the three phases, v_x, v_y, v_w, and molar compositions x, y, w. These are found from the six equations:

$$P(x, T, v_x) = P(y, T, v_y) = P(w, T, v_w) \tag{21}$$

$$\ln \hat{f}_1(x, T, v_x) = \ln \hat{f}_1(y, T, v_y) = \ln \hat{f}_1(w, T, v_w) \tag{22}$$

$$\ln \hat{f}_2(x, T, v_x) = \ln \hat{f}_2(y, T, v_y) = \ln \hat{f}_2(w, T, v_w) \tag{23}$$

together with a specification equation. Newton's method with analytic derivatives is used to solve the equations and the entire three-phase line is constructed by a marching procedure similar

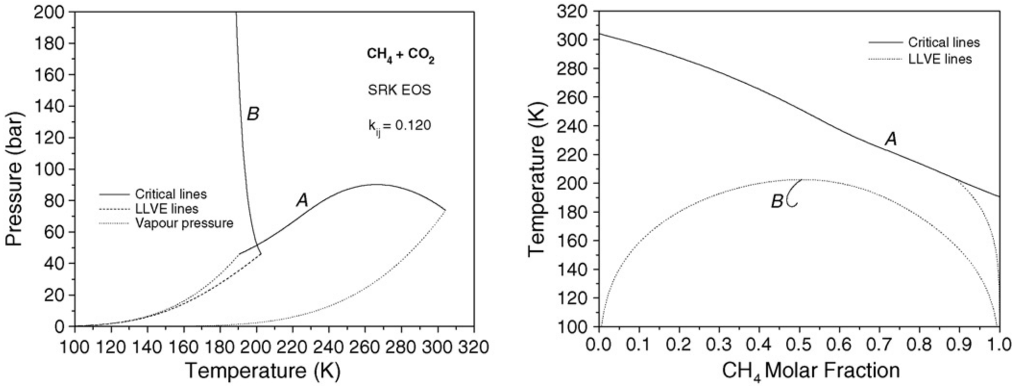

Fig. 3. Phase behaviour of Type II predicted for methane + carbon dioxide with the SRK EOS and $k_{ij} = 0.120$. The critical line *B* shows a minimum in composition and therefore could not be calculated by a method requiring specification of composition.

to that used for the critical line. The natural variable for specification is temperature, except in the regions close to a CEP, where specification of the intermediate composition is more convenient.

The starting point for the construction is a critical endpoint, typically an UCEP, where two of the phases, e.g. the *x*- and *y*-phase are identical in composition and volume. Therefore, special attention must be paid to the calculation of the first point (after the CEP) in order to prevent for the trivial solution. We calculate this point as follows:

- Let x^* be the smaller of x_{cU} and $1 - x_{\mathrm{cU}}$. Set $\Delta = 0.025\,x^*$.
- Use as initial estimate $x = x_{\mathrm{cU}} - \Delta$. and $y = x_{\mathrm{cU}} + \Delta$.
- Solve the pressure equations:

$$P_{\mathrm{UCEP}} = P(x, T_{\mathrm{UCEP}}, v_x); \qquad P_{\mathrm{UCEP}} = P(y, T_{\mathrm{UCEP}}, v_y)$$

to generate initial estimates for v_x and v_y.

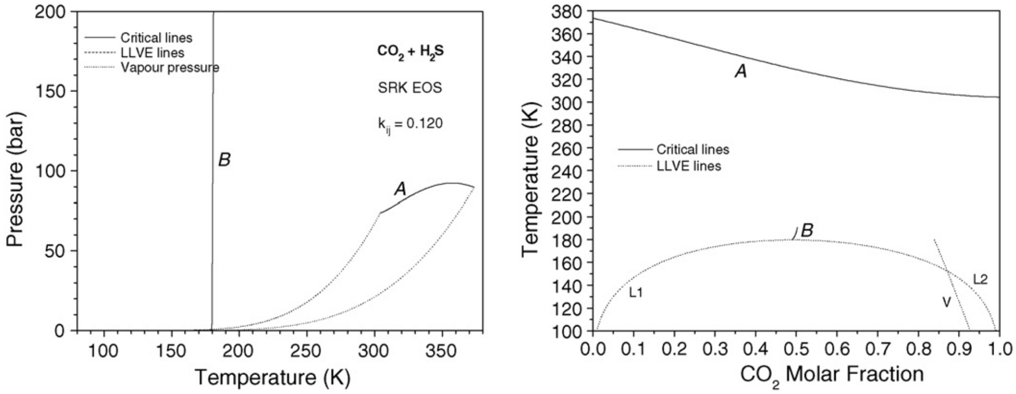

Fig. 4. Phase behaviour of Type II predicted for carbon dioxide + hydrogen sulphide with the SRK EOS and $k_{ij} = 0.120$. Standard LLVE is observed at temperatures higher than 152 K up to the UCEP while heterogeneous azeotropy appears at lower temperatures.

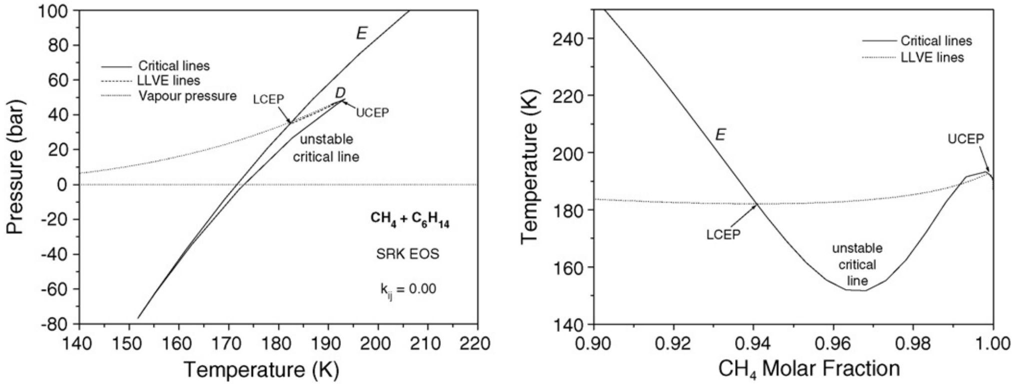

Fig. 5. Phase behaviour of Type V predicted for methane + *n*-hexane with the SRK EOS and $k_{ij} = 0.00$. The unstable part of the critical line is shown, connecting the stable lines *D* and *E*.

- Use $y - x - 2\Delta = 0$ as the specification equation.
- Use T_{UCEP} as the initial estimate for T, and the composition and volume of the non-critical phase at the CEP as the initial estimates for w and v_w.

For the following points on the line either y or $\ln T$ are to be specified. The three-phase line will terminate at another critical endpoint or when the temperature falls below a prescribed value.

For binary mixtures where the components vary widely in volatility round-off error may be a problem unless precautions are taken. Supposing for example that w is very close to 1 the mole fraction of second component, required for the calculation of its fugacity, is determined from $w_2 = 1 - w$ and will therefore loose most of its significant digits, which may prevent convergence. In this case we replace w by $\ln(w_2)$ as independent variable. The same applies to y in the calculation of CEP's.

Alternatively, such problems can be eliminated with more generality and robustness if we choose two composition variables for each phase. Replacing the variable x by x_1 and x_2 (or, even better, $\ln x_1$ and $\ln x_2$) that are formally treated as mole

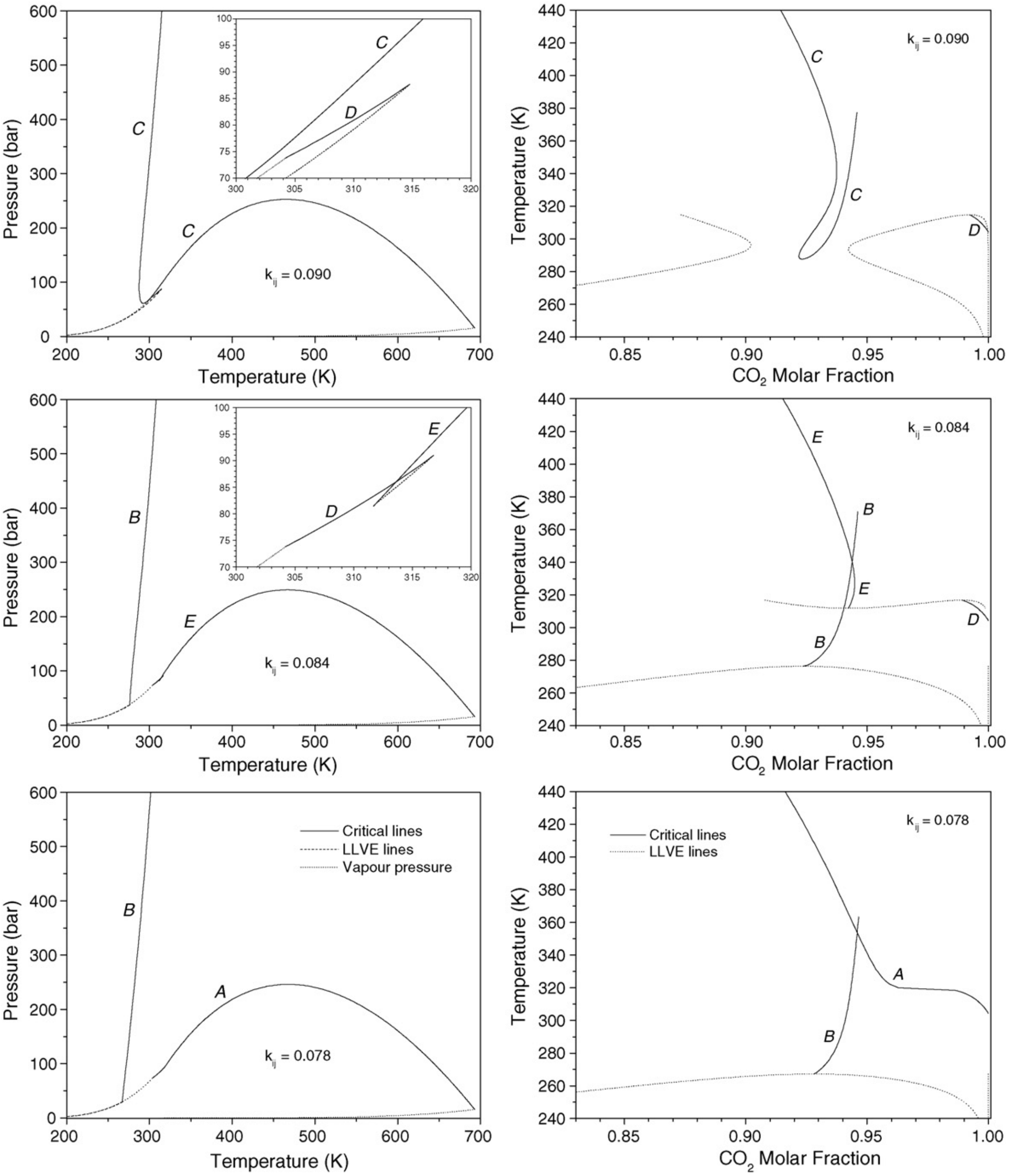

Fig. 6. GPEC plots in the PT and T–x projections for the system carbon dioxide + n-tetradecane. Three different values for the k_{ij} interaction parameter (0.078, 0.084 and 0.090) were used with the SRK EOS, leading to predicted phase behaviour of Types II, IV and III, respectively. Critical lines are indicated with letters according to Fig. 1.

numbers requires that we introduce the additional equation:

$$x_1 + x_2 - 1 = 0$$

and similarly for the other phases. The extension from 7 to 10 equations does not require the evaluation of new properties or derivatives and has only marginal influence on the computational cost.

8. Illustration of the algorithm for different types of systems

The model used in Figs. 3–6 for illustration purposes is the very well known Soave–Redlich–Kwong equation of state (SRK EoS, [10]) with quadratic mixing rules and one interaction parameter for the energetic parameter. Nevertheless, it must be pointed out that the proposed strategy and methods are applicable to any equation of state or any model for the Helmholtz energy of mixtures (see Fig. 7 for an example with a non-cubic group contribution equation of state).

The examples given for systems of Types II, III, IV and V were chosen to show minima or maxima in composition as well as other particularities discussed in the following paragraphs. These examples are only for illustration of the methods and, according to the scope defined in the introduction, no attention has been paid in this work to the correspondence with experimental data or the appearance of solid phases.

8.1. Liquid–liquid critical lines in systems of Type II

The *P*–*T* projection of the global phase equilibrium of the system methane + carbon dioxide is shown in Fig. 3. A temperature-composition (*T*–*x*) projection is also shown. Unlike the line *A*, which shows a monotonic variation of composition between both pure components, the line *B* exhibits a maximum molar fraction of carbon dioxide. Although the critical line *B* looks small compared to line *A* in the *T*–*x* projection, it actually covers a pressure range up to 5000 bar, going through a minimum temperature which cannot be seen in the limited pressure range of the *P*–*T* projection included in the figure.

Fig. 4 corresponds to the system carbon dioxide + hydrogen sulphide and Type II is observed again. Nevertheless, some important differences are observed, namely the relative position of line *B* and the UCEP respect to line *A*, the *P*–*T* slope of line *B* at the UCEP (negative in Fig. 3 and positive in Fig. 4) and more important the appearance of heterogeneous azeotropy in the second case. The latter is indicated by a crossing between the light liquid (L2 in the figure) and vapour branches in the *T*–*x* projection, resulting in a vapour with intermediated composition at lower temperatures.

8.2. Unstable critical points in Types IV and V

We have observed that for some systems of Type IV and V lines *D* and *E* are actually part of a continuous critical line that connects the pure component endpoints. This is illustrated in Fig. 5 for the mixture methane–*n*-hexane. The part of the critical line between the two critical endpoints, which includes the two cusps and extends to negative pressures, is unstable but is constructed without problems with the procedure described above provided the stability check is not used to terminate the calculation.

8.3. Type III and the transformation to Types IV and II

Fig. 6 shows diagrams equivalent to those in Figs. 3 and 4 but for an asymmetric system for which phase behaviour of Type III has been experimentally measured: carbon dioxide + *n*-tetradecane. Predictions obtained with $k_{ij} = 0.090$ (or higher) agree at least qualitatively with experiments. The complex behaviour of line *C*, exhibiting minima and/or maxima in all variables: *P*, *T*, *x* and *v*, indicates that for tracking a critical line like this it is crucial to specify the proper variable and to control the step length to each new point. Note that modest decrements in the k_{ij} parameter results in transformations to Types IV and II. It is interesting to observe the continuity of these transformations for the critical lines and LLVE compositions in the *T*–*x* projections, including the breaking of line *C* into lines *B* and *E*, and the later fusion of lines *D* and *E* into a continuous line *A*. Note the particularity of this line *A* or a Type II as shown in Fig. 6 (exhibiting a pronounced tendency to Type IV) when compared to the more typical lines *A* in Figs. 3 and 4.

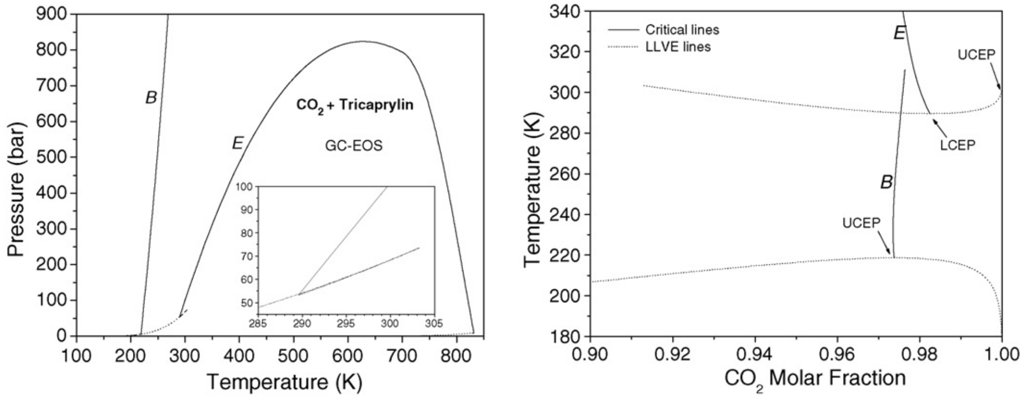

Fig. 7. Phase behaviour of carbon dioxide + tricaprylin (Type IV) as predicted by the GC-EOS [11,12] and parameters from Espinosa et al. [13].

In order to illustrate the general applicability of the methods proposed to any equation of state, we show in Fig. 7 the global phase equilibrium diagram for a highly asymmetric system like carbon dioxide + tricaprylin, calculated with the group contribution equation of state GC-EOS [11,12] and parameters from Espinosa et al. [13]. This system is experimentally known to be of Type IV [14,15].

9. Conclusions

We have developed a rapid and robust procedure for automatic calculation of global phase equilibrium diagrams for binary mixtures. No advance knowledge of the type of phase diagram is needed, and diagrams of Types I–V are all handled.

The robustness of the method is due to many factors, the most important being:

- Points on the critical lines and the three-phase lines are solved by Newton-based methods, where temperature, molar volume and composition are used as the independent variables.
- Extensive use of analytic derivatives is made. In cases where numerical derivatives are needed, these are calculated by central differences.
- Criticality conditions are likewise formulated in terms of temperature, volume and composition.
- Sensitivity equations permit effective tracing of the equilibrium lines.
- Stability analysis based on the tangent plane distance is used to locate critical endpoints.

The approach presently cannot be used for Type VI phase diagrams that exhibit closed critical lines. To handle such systems an approach for verifying the existence of such lines would be needed.

Acknowledgements

Martin Cismondi gratefully acknowledges the National Research Council of Argentina (CONICET) for the fellowship, which made possible his stay in Denmark and also the support received from IVC-SEP.

References

[1] R.L. Scott, P.H. van Konynemburg, Part 2. Static properties of solutions. van der Waals and related models for hydrocarbon mixtures, Discuss. Faraday Soc. 49 (1970) 87–97.

[2] P.H. van Konynemburg, R.L. Scott, Critical lines and phase equilibria in binary van der Waals mixtures, Philos. Trans. R. Soc. London Ser. A 298 (1980) 495–540.

[3] U.K. Deiters, I.L. Pegg, Systematic investigation of the phase behaviour in binary fluid mixtures. Part I. Calculations based on the Redlich–Kwong equation of state, J. Chem. Phys. 90 (11) (1989) 6632–6641.

[4] A. van Pelt. Critical phenomena in binary fluid mixtures: classification of phase equilibria with the simplified perturbed hard chain theory, Ph.D. Thesis, Technische Universiteit Delft, The Netherlands, 1992.

[5] I. Polishuk, J. Wisniak, H. Segura, L.V. Yelash, T. Kraska, Prediction of the critical locus in binary mixtures using equation of state II. Investigation of van der Waals type and Carnahan–Starling–type equations of state, Fluid Phase Equilib. 172 (2000) 1–26.

[6] R.J. Sadus, Calculating critical transitions of fluid mixtures: theory vs. experiment, AICHE J. 40 (8) (1994) 1376–1403.

[7] R.A. Heidemann, A.M. Khalil, The calculation of critical points, AICHE J. 26 (5) (1980) 769–779.

[8] M.L. Michelsen, R.A. Heidemann, Calculation of tri-critical points, Fluid Phase Equilib. 39 (1988) 53–74.

[9] M.L. Michelsen, Calculation of phase envelopes and critical points for multicomponent mixtures, Fluid Phase Equilib. 4 (1980) 1–10.

[10] G. Soave, Chem. Eng. Sci. 27 (1972) 1197.

[11] S. Skjold-Jørgensen, Gas solubility calculations. Part II. Application of a new group-contribution equation of state, Fluid Phase Equilib. 16 (1984) 317–351.

[12] S. Skjold-Jørgensen, Group contribution equation of state (GC-EOS): a predictive method for phase equilibrium computations over wide ranges of temperature and pressures up to 30 MPa, Ind. Eng. Chem. Res. 27 (1988) 110–118.

[13] S. Espinosa, T. Fornari, S.B. Bottini, E.A. Brignole, Phase equilibria in mixtures of fatty oils and derivatives with near critical fluids using the GC-EOS model, J. Supercrit. Fluids 23 (2002) 91–102.

[14] C. Borch-Jensen, J. Mollerup, Phase equilibria of carbon dioxide and tricaprilyn, J. Supercrit. Fluids 10 (1997) 87–93.

[15] L.J. Florusse, T. Fornari, S.B. Bottini, C.J. Peters, Phase behavior of carbon dioxide–low-molecular weight triglycerides binary systems: measurements and thermodynamic modelling, J. Supercrit. Fluids 31 (2004) 123–132.