# Automated Generation of Phase Diagrams for Binary Systems with Azeotropic Behavior

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In this work, we propose a computational strategy and methods for the automated calculation of complete loci of homogeneous azeotropy of binary mixtures and the related *Pxy* and *Txy* diagrams for models of the equation-of-state (EOS) type. The strategy consists of first finding the system's azeotropic end points (AEPs). These can exist on vapor-liquid (VL) critical lines (CAEPs), on liquid-liquid-vapor (LLV) lines (HAEPs), and on pure-compound vapor pressure lines (PAEPs). Next, for the chosen binary system, we generate one or two azeotropic lines. Each of these lines has, as its starting point, one of the previously identified AEPs. We calculate the azeotropic lines using a numerical continuation method that solves the nonlinear azeotropic system of equations under a range of conditions and efficiently tracks entire azeotropic curves. We have integrated our strategy for calculating azeotropic lines into a general algorithm for the single-run computation of binary global phase equilibrium diagrams (GPEDs). GPEDs are defined by pure-compound, critical, LLV, and azeotropic lines. We implemented this general algorithm in the computer program GPEC (Global Phase Equilibrium Calculations), which makes it possible to evaluate, at a glance, the behavior of a given model-parameter values combination, for a chosen model and binary system.

# 1. Introduction

In this work, we focus on the calculation of azeotropic lines and isothermal or isobaric diagrams showing azeotropic points, within the general context of the automated generation of phase equilibrium diagrams for binary fluid systems, using models of the equation-of-state (EOS) type.

Azeotropes are of practical importance in many applications, especially in distillation. The knowledge of azeotropic behavior is also important when considering mixtures for their use as refrigerants.<sup>1</sup>

Equations of state (EOSs) constitute a very important type of thermodynamic models. They can be used to model properties of liquid, vapor, and supercritical phases. Unlike other modeling approaches, EOSs offer a continuous description of these three different states, as they occur in nature. This was already clear to van der Waals, at least with respect to pure fluids, when he published his pioneering thesis in 1873.<sup>2</sup> One century later, with much more experimental and theoretical knowledge available,<sup>3,4</sup> van Konynemburg and Scott<sup>5</sup> showed, systematically, that the simple van der Waals equation of state, combined with simple quadratic mixing rules, is able to qualitatively reproduce the richly varied experimentally observed phase behavior of fluid binary mixtures.

One of the most important applications of EOSs are phase equilibrium calculations for fluid mixtures, which are not trivial. They require iterative procedures that have no guarantee for convergence; rely on often crucial initial estimates; and provide solutions that, typically, need to be tested for stability. Moreover, despite the increasing speed of modern computers, efficiency is still an issue when these calculations are to be run a very large number of times, for example, in process or reservoir simulators. Special attention has been paid in the scientific literature during the past several decades to the development of calculation procedures for two-phase and multiphase flashes, saturation points, phase envelopes, critical points, and so on.<sup>6</sup> However, this field of study has not reached its maturity as of yet.

Binary systems are the most studied fluid mixtures, in terms of both experiments and calculations. Knowledge on the behavior of binary mixtures is important to understand the behavior of multicomponent systems. Also, thermodynamic models are typically pairwise-additive; i.e., when modeling multicomponent phase equilibria, binary interaction parameters are required, and these are obtained from fittings to experimental binary data. Therefore, it is important to have available robust algorithms for the rapid generation of global and/or isothermal and/or isobaric and/or isoplethic phase equilibrium diagrams for binary fluid systems.

The number of degrees of freedom available to binary mixtures makes possible to use two-dimensional diagrams to represent the (experimental or calculated) global phase equilibrium behavior of a given binary system over wide ranges of temperature and pressure and for all possible system compositions. Such global binary maps are set in terms of critical, azeotropic, and liquid-liquid-vapor (LLV) lines, as well as the two pure-compound saturation lines. These lines develop in the four-dimensional pressure-temperature-composition-density space ( $PTx\rho$ ). [More variables such as enthalpy, entropy, or Helmholtz energy could be added, but the four indicated variables ( $PTx\rho$ ) suffice to identify the different lines involved and their phases and to clearly distinguish critical or azeotropic end points from coincidental crossings, which are intersection

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points appearing in some projections of the phase equilibrium hypersurfaces but not in all projections.] These are the primary variables for models of the EOS type. Although the *PT* projection can be regarded as the most important and frequent among the different possible two-dimensional projections of this space, it should be noted that calculated lines provide information on the relationship among the four variables. We bear in mind such  $PTx\rho$  relationships when we use the terms azeotropic, critical, saturation, and LLV lines and/or the expression global phase equilibrium diagram (GPED).

Tools for the automated calculation of global phase equilibrium diagrams are important, first, because they provide a global view of the phase behavior that a given model and specified parameters predict for a system over a wide range of conditions and, second, because the intersections of these lines with lines of constant temperature or constant pressure provide the limiting points of isothermal (*Pxy*) or isobaric (*Txy*) phase equilibrium diagrams. Such key points make the calculation of complete *Pxy* or *Txy* diagrams possible, without the need for stability analysis.<sup>7</sup>

In a previous work, Cismondi and Michelsen<sup>8</sup> presented a general algorithm, applicable to binary systems, for the calculation of nonazeotropic global phase equilibrium diagrams. They also presented specific methods for calculating entire critical and LLV lines and for detecting critical end points. Based on such work and also on strategies for the construction of complete Pxy and Txy diagrams,<sup>7</sup> a software program for global phase equilibrium calculations (GPEC) was developed.<sup>9</sup> In this work, we present a strategy to account for the different types of azeotropic behavior in binary systems, and we also propose a robust and efficient numerical continuation method for tracking the corresponding azeotropic lines. In the present article, we do not account for the possible presence of solids.

For some historical perspective and comments on the work of Lecat on azeotropy in the 1920s and 1930s, which was published in French,<sup>10</sup> see Jaubert and Privat.<sup>11</sup> In the cited article, they study the relation between the existence of azeotropy and the excess Gibbs energy function.

Already in the 1970s, Teja and Rowlinson<sup>12</sup> tackled the calculation of simple azeotropic lines using an equation of state. Contemporaneously, as already mentioned, van Konynemburg and Scott<sup>5</sup> undertook an exhaustive study of the types of phase behavior that could be calculated from the van der Waals EOS, identifying several possible types of azeotropic lines.

Since then, several authors have worked on the computation of azeotropy in different ways, focusing on calculation methods,<sup>13–19</sup> on the discovery and analysis of new types of possible phase behavior using different models,<sup>20–23</sup> or on an exhaustive study of the conditions for the occurrence of polyazeotropy.<sup>24,25</sup> Nevertheless, we have not found in the literature any attempt to develop a general algorithm for the automated calculation of azeotropic lines as part of global phase equilibrium diagrams and/or for the further generation of *Pxy* and *Txy* diagrams showing azeotropic behavior.

#### 2. Azeotropic Lines and Azeotropic End Points (AEPs)

A homogeneous azeotrope is a mixture that boils without any change in composition. An azeotropic line in a binary system is a curve that continuously connects the homogeneous azeotropic points at different conditions, i.e., those points where the equilibrium liquid and vapor phases have equal compositions but different densities.

Binary critical lines end/originate at critical end points where they meet either LLV lines or pure-compound critical points. Analogously, azeotropic lines can end or originate at three different types of azeotropic end points (AEPs): (1) A pure azeotropic end point (PAEP) is a point where an azeotropic line meets one of the two pure-compound vapor pressure curves. At this point, one component is under conditions of infinite dilution in the other component, as the pressure of the system is equal to the pure-compound vapor-liquid saturation pressure of the concentrated component at the system temperature. At a PAEP, the distribution coefficient of the infinitely dilute component equals unity. (2) A critical azeotropic end point (CAEP) corresponds to an azeotropic line meeting a liquid-vapor critical line. Here, the densities of the vapor and liquid azeotropic phases converge to the same critical value. Notice that a CAEP is not a critical end point; i.e., a CAEP is an end point for the involved azeotropic line but not for the critical line. (3) A heterogeneous azeotropic end point (HAEP) is a point on an LLV line where the vapor-phase composition equals the composition of one of the liquid phases. Therefore, this point distinguishes a homogeneous from a heterogeneous azeotropic region, and it is the origin of an azeotropic line. This point also separates the LLV line into two parts: the heteroazeotropic portion and the regular LLV portion.

Alternatively, azeotropic lines can proceed to lower temperatures down to 0 K, within the universe of EOS models, where we do not account for the possible presence of solid phases. The case of predicting a closed loop of polyazeotropy, i.e., an azeotropic line that might appear as a circle in the T-x plane, has also been detected (as stated by an unidentified reviewer of the present work). In our view, such infrequent lines having no end points would not be of significant practical interest, especially when modeling real systems. Nevertheless, they could be considered in future works.

The implied effects of each type of AEP on the phase behavior will be clearly illustrated through the examples given in section 8, which include projections of azeotropic lines, as well as *Pxy* or *Txy* diagrams in the neighborhood of AEPs.

Notice that, when we defined the PAEPs, we excluded the case of binary systems of optical isomers. Such systems are always azeotropic in the fluid state, regardless of the relative concentrations of the isomers in the system.<sup>26</sup>

Before considering the detection of AEPs and the calculation of azeotropic lines, we discuss the different types of azeotropic behaviors that can be found experimentally or calculated for binary systems, in order to propose a general algorithm covering all possible situations identified.

# 3. Classification of Azeotropic Behaviors in Binary Mixtures

In their original studies with the van der Waals equation of state, van Konynemburg and Scott<sup>5</sup> identified four major types of azeotropic phase behavior, namely, I-A, II-A, III-A, and V-A, corresponding to variations of the previously identified non-azeotropic behaviors.<sup>5,27</sup> Type III-A implies only heterogeneous azeotropy; i.e., the vapor-phase composition is intermediate between those of the two liquids in the whole LLV equilibrium region, and therefore no line of homogeneous azeotropy needs to be considered. (Note that many water—hydrocarbon mixtures, for example, are known to show phase behavior of type III-A experimentally.<sup>28</sup>)

Both types I-A and V-A present an azeotropic line that, at its upper temperature limit, meets either the critical line (CAEP) or one of the pure-compound saturation lines (PAEP). The lower limit can be a PAEP, or the curve can continue down to zero

Table 1. Homogeneous Azeotropic Behaviors Considered in the Algorithm Proposed in This Work

by an azeotropic line <sup>a</sup>	number of AEPs	azeotropy <sup>b</sup>	possible types <sup>c</sup>	examples in this work	case
0 to PAEP	1	P or N	I, V		1
0 to CAEP	1	Ν	I, V		2
PAEP to PAEP	2	P, N, or D	I, II, V	Figures 9 and 10/Figure 11 ( $k_{ij} = -0.04$ )	3
PAEP to CAEP	2	P, N, or D	I, II	Figure 11 ( $k_{ij} = -0.02$ )	4
HAEP to PAEP	2	Р	II, IV	Figures 1, 7, and 8	5
HAEP to CAEP	2	Р	II, IV	Figures 2–6	6
CAEP to CAEP	2	P or D	I, II	-	7
$PAEP(2)^d$ to $HAEP(LT)^e$	4	Р	II		8
$HAEP(HT)^e$ to $PAEP(1)^d$					
$PAEP(2)^d$ to $HAEP(LT)^e$	4	Р	II	Figure 11 ( $k_{ij} = 0.00$ )	9
$HAEP(HT)^{e}$ to CAEP					

<sup>*a*</sup> For example, 0 to PAEP indicates a line of homogeneous azetropy that goes from zero temperature to a PAEP. <sup>*b*</sup> P, positive; N, negative; D, double. <sup>*c*</sup> Possible types of phase behavior are indicated based on our experience and reasoning and only to provide an orientation to the reader. <sup>*d*</sup> PAEP(*i*) = PAEP on the pure-compound vapor pressure curve of component *i*. Component 2 is the less volatile component in the (1,2) binary system. <sup>*e*</sup> When two HAEPs are found, HAEP(LT) and HAEP(HT) are used to identify the HAEPs with lowest and highest temperatures, respectively.



**Figure 1.** Detection of a PAEP: Difference in the logarithm of the fugacity coefficients of the infinitely dilute component, between the liquid and vapor phases, along vapor pressure lines. This example: Carbon dioxide (1) + hydrogen sulfide (2), SRK EOS with  $k_{ij} = 0.12$ , as in Figure 7 below.



**Figure 2.** First derivative of pressure with respect to volume, at constant temperature and composition, along the liquid–vapor critical line, for the system carbon dioxide (1) + ethane (2) as represented by the SPHCT EOS with  $k_{ij} = 0.10$  (as in Figure 3 below). The CAEP is detected as the nontrivial point at which this derivative is zero.

temperature. The azeotropic line can even show a temperature minimum, giving rise to double azeotropy (see Figure 43 of van Konynemburg and Scott<sup>5</sup> for schematic temperature– composition projections of the different possibilities corresponding to type I-A systems). Type I-A systems have a continuous

critical locus, whereas, for type V-A, there are two critical loci linked by an LLV line.

Type II-A is characterized by an azeotropic line starting from an HAEP in the lower temperature limit and proceeding usually to a CAEP or alternatively a PAEP.

When changing the interaction parameters in the EOS modeling of binary systems, in order to obtain a transition between types II-A and III-A, we detected behaviors that are similar to those named III-Am\* and III-Am\*\* by van Konynemburg and Scott (ref 5, Figure 39). [Note, however, that, in some cases, for example, carbon dioxide + ethane with the Peng-Robinson EOS, quadratic mixing rules, and  $k_{ij}$  around 0.40 (and  $l_{ii} = 0$ ), the critical line going to infinite pressure starts not from compound 2 but from the critical point for compound 1, in this case  $CO_2$ . This is analogous to what was found in ref28.] Types III-Am\* and III-Am\*\* contain additional lines-both critical and LLV-and additional critical end points not considered in our algorithm for automated calculation of global phase equilibrium diagrams.<sup>8</sup> Nevertheless, it is very unlikely that the correlation of data for a system of interest will require interaction parameters leading to these transition behaviors. Therefore, because our goal is to develop procedures for the automated calculation of phase behavior occurring in real systems that might be of interest for applications, we consider the general algorithm proposed by Cismondi and Michelsen,<sup>8</sup> covering types I-V, as a base algorithm to which we can add the construction of azeotropic lines.

Even though there are several possible different combinations of AEPs for the azeotropic lines present in types I-A, II-A, and V-A, as shown by van Konynemburg and Scott,<sup>5</sup> one general and very important characteristic that a general algorithm could exploit is that, in all of those cases, there is only one line of homogeneous azeotropy. Kolafa et al.,<sup>20</sup> in their study of an attractive-hard-sphere model, also detected some complex behaviors for which the azeotropic line splits into two or three different branches. Some of these behaviors, in particular those presenting three branches, seem to be available only to certain models within narrow ranges for the values of the interaction parameters, and, to our knowledge, they have not been observed in nature. (The exploration of the tradeoffs between enhanced flexibility and artificiality of the different models available in the literature is beyond the scope of the present work. The reader should be aware of the fact that increased model flexibility does not necessarily lead to a better model and could even make it worse.) In our investigation of different models and systems that tend to form azeotropes, we have found only two AEPs per binary system in the vast majority of cases. Nevertheless,



**Figure 3.** Pressure–temperature and temperature–composition projections of the calculated global fluid phase equilibrium diagram for the system carbon dioxide (1) + ethane (2). Model: SPHCT EOS with  $k_{ij} = 0.10$ . Phase behavior type: II-A.

we observed the occurrence of four AEPs in cases where the liquid-liquid immiscibility reaches (and therefore interrupts) a homogeneous azeotropic line of wide composition range, either between two PAEPs or between a PAEP and a CAEP. Therefore, the presence of four AEPs is likely to occur in binary systems exhibiting a Bancroft point (i.e., an intersection point of the two pure-compound vapor pressure curves), which tend to develop azeotropy in the whole range of composition. We show examples of systems with four AEPs in section 8. In summary, we consider in this work systems with a single line of homogeneous azeotropy and also special systems having two azeotropic lines. In other words, the algorithm we present in this work is able to build two azeotropic lines only for the case of an LLV locus interrupting a line of homogeneous azeotropy. In every other case, it will build, at most, a single azeotropic line.

# 4. Overall Strategy for the Automated Calculation of Azeotropic Lines

From the discussion in the previous section, there are different combinations of azeotropic end points (AEPs) that can be found in the calculation of the global phase equilibrium diagram for a specified binary system, thermodynamic model, and parameter values. In Table 1, we list these possibilities, indicating also the type of phase behavior to which they correspond and the type of azeotropy involved, i.e., positive, negative, or double.



**Figure 4.** (Top) Enlargement of the P-T projection in the range containing the CAEP. (Bottom) *Pxy* diagrams at different temperatures corresponding to the vertical dashed lines of the top plot. System and model as in Figure 3. *Pxy* cases (Table 3): case IV at 288 K, case VIII at 289.5 K. Other cases: ref 7. Phase behavior type: II-A.

 Table 2. Specification Functions Used in This Work for the

 Calculation of Azeotropic Lines

NS	g(X)
0	$g(X) = \ln(v^{V}/v^{L}) = \ln v^{V} - \ln v^{L} = X_{4} - X_{3}$
1	$g(X) = \ln T = X_1$
2	$g(X) = z = X_2$
3	$g(X) = \ln v^{\mathrm{L}} = X_3$
4	$g(X) = \ln v^{\mathrm{V}} = X_4$

For instance, case 5 in Table 1 corresponds to an azeotropic line, of a system of type II or type IV, that goes from an HAEP to a PAEP, giving positive azeotropy (P).

Similarly to the strategy adopted for calculation of LLV lines,<sup>8</sup> azeotropic lines should be calculated starting from previously detected end points, i.e., from the identified AEPs. Critical end points (CEPs) present only three possible cases (UCEP, LCEP, K point<sup>27</sup>), all of which have to be sought along critical lines.<sup>8</sup> In contrast, in this work, we search for azeotropic end points on pure-compound vapor pressure lines (PAEPs), on critical lines (CAEPs), and/or on LLV lines (HAEPs). Furthermore, all types of combinations of pairs of azeotropic end points are possible (Table 1). Therefore, we cannot save much testing effort from our knowledge of the characteristics of the phase behavior, as the construction of the global phase equilibrium diagram progresses. This is not an important problem because, as we discuss in the next section, the three types of tests for the

Table 3. Fluid–Fluid Equilibrium Regions To Be Calculated When Generating Isothermal *Pxy* Diagrams with Homogeneous Azeotropic Behavior

-	_	_				
NLLV	NSAT	NCRI	NAZ	Two-phase Regions	Pxy Case	
	0	2	1	$(\mathbf{C}_{A1} \mathbf{A})  (\mathbf{C}_{A2} \mathbf{A})$	I	
	1	1	1	(C   A) (S2   A)  or  (C   A) (S1   A)	П	
	1	1	2	[(S1   A1) (A1   A2) (C   A2)] or [(C   A1) (A1   A2) (S2   A2)]	III	
0			1	(S1 A) (S2 A)	١V	
		0	2	$(S1 \ A1)(A1 \ A2)(S2 \ A2)$	V	
	2	1	1	(S1   A) (S2   A) (C   O)	VI	
	2	I	2	(S1 A1) (A1 A2) (S2 A2) (C O)	VII	
		2	1	$(S1 \ A) \ (S2 \ C_{A1}) \ (C_{A2} \ A)$	VIII	
		3	1	$(S1 A) (S2   C_{A1}) (C_{A2}   A) (C_B   O)$	IX	
		0	1	$(L_1 V   S2) (L_{1I} V   A) (S1   A) (LL   O) z_A > z_F$	Х	
				$(VL_{11}   S1) (VL_{1}   A) (S2   A) (LL   O) z_A \le z_F$	XI	
				$(L_{I}V \mid S2) (L_{II}V \mid A2) (S1 \mid A1) (A1 \mid A2)$ $(L_{I} \mid O) \qquad \qquad z_{1} \geq z_{1}$	XII	
	2			2	$(VL_1   S_1) (VL_1   A_1) (S_2   A_2) (A_1   A_2)$	
1				$(LL \mid O) \qquad \qquad z_4 < z_{l'}$	XIII	
		4	1 2	As cases X, XI, XII and XIII but with (LL   C)	XIV to	
		1	1	instead of (LL   O)	instead of (LL   O)	XVII
		2	2 1	1	As cases X, XI, XII and XIII but with (LL   C)	XVIII to
			1012	instead of (LL   O) plus a (C   O) region.	XXI	
NLLV     Number of LLV points detected at the set temperature       NSAT     Number of pure compound LV saturation points detected at the set temperature       NCRI     Number of critical points detected at the set temperature       NA7     Number of azeotropes detected at the set temperature       S1.52     Liquid-vapor saturation point of component 1 or 2       L1     Liquid phases in the L1.V point       LV     Heave liquid phases and vapor phase at the L1.V point						

 $L_0V$  Light liquid phase and vapor phase at the LLV point

C<sub>X</sub> Critical point corresponding to a critical line of type X [8]

Table 4. Fluid–Fluid Equilibrium Regions To Be Calculated When Generating Isobaric *Txy* Diagrams with Homogeneous Azeotropic Behavior

NLLV	NSAT	NCRI	NAZ	Two-phase Regions	Txy Case	
	0	2	1	$(C_{A1} \Lambda)$ $(C_{A2} \Lambda)$ or $(C_{E1} \Lambda)$ $(C_{E2} \Lambda)$	I	
		1	1	(S1 A) (C A)	II	
	1	2	1	$(S1 A)$ $(C_A A)$ $(C_B O)$	Ш	
		0	1	(S1 A) $(S2 A)$	IV	
0			2	(S1   A1)(A1   A2)(S2   A2)	V	
	2			1	(S1 A) $(S2 A)$ $(C O)$	VI
			1	2	(S1 A1)(A1 A2)(S2 A2)(C O)	VII
	-		_	$(S1   A) (S2   C_{A1}) (C_{A2}   A) = 7 + 27$	VIII	
		2	2   1	$\frac{(01 11)}{(02 0A1)} \frac{(02 0A1)}{(0A2 11)} = \frac{1}{24} \frac{2}{26}$	IX	
		3	1	As cases VIII and IX plus a $(C_{\mathbf{P}} \mid \mathbf{O})$ region	X and XI	
	1	1	1	$(LV   C) (L_{II}V   A) (S1   A) (LL   O)$	XII	
	-	-		$(L_V   S_2) (L_V   A) (S_1   A) (L_U   O) z_4 \ge z_1$	XIII	
	2		1	$(VL_{II}   S1) (VL_{I}   A) (S2   A) (LL   O) z_{A} \le z_{V}$	XIV	
1		0	2	$\begin{array}{c} (L_{4}V \mid S2) (L_{4}V \mid A2) (S1 \mid A1) (A1 \mid A2) \\ (LL \mid O) & z_{A} > z_{V} \end{array}$	XV	
					2	$\begin{array}{c} (\mathrm{VL}_{\mathrm{II}} \mid \mathrm{S1}) (\mathrm{VL}_{\mathrm{I}} \mid \mathrm{A1}) (\mathrm{S2} \mid \mathrm{A2}) (\mathrm{A1} \mid \mathrm{A2}) \\ (\mathrm{LL} \mid \mathrm{O}) & z_{\mathcal{A}} \leq z_{\mathcal{V}} \end{array}$
$\label{eq:linear_state} \begin{array}{ c c c c c c c c c c c c c c c c c c c$						

location of AEPs are simple, robust, and computationally inexpensive compared to the location of CEPs, which involves, first, stability analysis of critical points and then convergence of the set of equations for a CEP.<sup>8</sup> Therefore, we propose here to test the complete vapor pressure and LLV lines as they are calculated and also to test the critical line starting at the critical point of pure compound 2, i.e., the first critical line calculated.<sup>8</sup> (Note that component 1 is the more volatile compound of the binary system, i.e., the one with higher vapor pressure, whereas

component 2 is the less volatile compound. In the case of a Bancroft point, the highest-temperature region is taken into account to label the components as 1 or 2.)

Once the complete global phase equilibrium diagram (GPED) has been calculated, excluding the azeotropic lines, following the algorithm of Cismondi and Michelsen,<sup>8</sup> all azeotropic end points will be known. The situations that can occur and the approach applied in each case are as follows: (1) When one AEP is detected (cases 1 and 2 of Table 1), we generate one azeotropic line starting from a PAEP or CAEP and stop when the temperature falls below a predefined minimum value, e.g., 20 or 50 K. (2) When two AEPs are detected (cases 3-7 of Table 1), we generate one azeotropic line starting from, in order of preference, a PAEP(2), a PAEP(1), or a CAEP and ending at the other AEP, which can be of any type. (3) When four AEPs are detected (cases 8 and 9 of Table 1), two of them are HAEPs: a lower temperature HAEP and a higher temperature HAEP. In these cases we generate two azeotropic lines: The first line starts from a PAEP(1) or CAEP and ends at the HAEP of higher temperature [HAEP(HT)]. The second line starts from the PAEP(2) and ends at the lower-temperature HAEP [HAE-P(LT)].

The binary homogeneous azeotropic condition has one degree of freedom; i.e., one specification must be made for the system of nonlinear azeotropic conditions to have the same number of equations and variables. For instance, we could specify a temperature value at which we want to calculate the composition, pressure and phase densities of the homogeneous azeotrope. The reason for preferring a PAEP or a CAEP over an HAEP as the starting point for the calculation of an azeotropic line, is that, in such cases, it is always clear which specification should be made in the first step to the second point on the azeotropic line and in which direction. When we start a line from a PAEP, we specify, for the second point, the azeotropic composition, and when the first point of the line is a CAEP, we specify the relation between the volumes of the liquid and vapor azeotropic phases.

# 5. Detection of Azeotropic End Points

**5.1. Pure Azeotropic End Points (PAEPs).** Every azeotrope, including the limiting case of a PAEP, satisfies the condition of equal fugacity coefficients for each component in the liquid and vapor phases of identical composition. At every pure-compound vapor pressure point, this equality is, by definition, always satisfied for the pure compound, and therefore, the corresponding equality for the other component, at infinite dilution, is the condition that has to be tested along each vapor pressure curve in order to detect the existence of a PAEP. In our implementation, after convergence of each pure-compound vapor pressure point, we compute the difference

$$\mathrm{DIF}_{\mathrm{PAEP}} = \ln \phi_i^{\mathrm{L}}(z_i = 0) - \ln \phi_i^{\mathrm{V}}(z_i = 0) \tag{1}$$

where z stands for mole fraction and *i* corresponds to the infinitely dilute component.<sup>14</sup> Note that  $\hat{\varphi}_i^L$  is the fugacity coefficient of component *i* in the liquid phase, and  $\hat{\varphi}_i^V$  is the fugacity coefficient of component *i* in the vapor phase. A change of sign in DIF<sub>PAEP</sub> with respect to the previous point on the pure-compound saturation line indicates the presence of a PAEP. We obtain its coordinates in temperature, pressure, and volumes of the phases through linear interpolation. Note that the calculation of DIF<sub>PAEP</sub> is explicit once the calculation of the pure-compound saturation point of the concentrated component has converged.<sup>14</sup> In other words, the phase densities that enter into eq 1 are those of the concentrated component in the pure



**Figure 5.** Pressure–temperature and temperature–composition projections of the calculated global fluid phase equilibrium diagram for the system hydrogen sulfide (1) + propane (2). Model: Peng–Robinson EOS with  $k_{ij}$  = 0.05. Pressures indicated by dashed horizontal lines correspond to the isobaric *Txy* diagrams in Figure 6. Phase behavior type: II-A.

state at saturation. The typical behavior of DIF<sub>PAEP</sub> for a binary system as a function of temperature is shown in Figure 1. In this illustrative example (carbon dioxide + hydrogen sulfide as described by the SRK EOS with  $k_{ij} = 0.12$ ), we observe that DIF<sub>PAEP</sub> is never zero on the pure hydrogen sulfide saturation line (excluding the trivial solution at the hydrogen sulfide critical point). On the other hand, a nontrivial PAEP happens on the pure carbon dioxide saturation line, at about 226 K. We stress that, in this work, we do not account for the interference of solid-fluid transitions. Note, for example, that the experimental melting point of CO<sub>2</sub> is about 217 K.

**5.2.** Critical Azeotropic End Points (CAEPs). Consider a pressure vs density curve at constant temperature and at a constant composition equal to the azeotropic composition, generated using an EOS. The azeotropic point is located on such a curve at the azeotropic pressure. This pressure value is such that the fugacities of the mixture as a whole are equal for both the vapor and liquid phases.<sup>14</sup> Therefore, every azeotropic point is also a pseudo-pure-compound vapor pressure point,<sup>14</sup> with vapor and liquid densities at saturation on both sides of the van der Waals loop. In other words, a noncritical azeotrope needs to have three density roots (in order to obtain vapor and liquid properties that are different). As the azeotrope becomes critical, these roots merge to a single root, which immediately gives the following conditions for a critical point to become a CAEP, which are the same as the conditions for a pseudocritical point<sup>29</sup>

$$\left(\frac{\partial P}{\partial v}\right)_{z,T} = 0 \tag{2a}$$

$$\left(\frac{\partial^2 P}{\partial v^2}\right)_{z,T} = 0 \tag{2b}$$

where v is the molar volume. We stress that eqs 2a and 2b are necessary but not sufficient conditions. The CAEP conditions consist of the general pseudocritical point conditions (eqs 2a and  $2b^{29}$ ) plus the criticality conditions.<sup>6,8</sup>

Because all critical points satisfy the condition of mechanical stability, i.e.,  $(dP/dv)_{z,T} \leq 0$ , a CAEP is characterized not by a change of sign in this first derivative along the critical line but by a maximum that is exactly zero, as stated by eq 2a. We illustrate this in Figure 2 for the system carbon dioxide + ethane as represented by the SPHCT EOS with  $k_{ij} = 0.10$ . Figure 2 shows the existence of a CAEP at about 0.74 CO<sub>2</sub> mole fraction. We show in Appendix A that if condition 2a is fulfilled for a point belonging to a vapor-liquid critical line, then condition 2b is also automatically satisfied. Therefore, in our computational implementation, we compute the value of only the first derivative after convergence of each critical point. If we denote the values for (dP/ $dv_{z,T}$  corresponding to the last three calculated vapor-liquid critical points as A, B, and C, respectively, the existence of a CAEP is indicated by B having the smallest absolute value and this value being zero within a given numerical tolerance. In our experience, we found 0.01 bar mol/L to be an acceptable tolerance. The temperature, pressure, composition, and density at the CAEP are estimated by quadratic interpolation. Note that the zero slope of the function  $[(dP/dv)_{z,T}]_{critical}$  at the CAEP in Figure 2 does not directly correspond to condition 2b. The curve in Figure 2 is neither isothermal nor isoplethic. Otherwise, vapor-liquid criticality is the condition held constant for every point in such curve.

**5.3. Heterogeneous Azeotropic End Points.** The test for the detection of an HAEP is the simplest of the three. A change of sign in the composition difference between the vapor and the closest liquid phase along the LLV line is sufficient to determine the presence of an HAEP. Temperature, pressure, composition and densities are estimated through linear interpolation.

#### 6. Calculation Procedure for Azeotropic Lines

Our goal in this work is to develop a general procedure for efficient calculation of homogeneous azeotropy lines. The procedure should be applicable to the full spectrum of equations of state and mixing rules, which spans from the simplest EOSs coupled to one-fluid mixing rules to the more complex EOSs with mixing rules that are not of the one-fluid type, as is the case for PC-SAFT<sup>30</sup> or the GC-EOS.<sup>31</sup> Because the method is to be used not for single azeotropic points but for the calculation of entire azeotropic lines, it should be able, after convergence of a given point of the line, to properly choose the variable to be specified for calculating the next point; to set a suitable value for such variable; and to generate good initial estimates for all remaining variables of the azeotropic system of equations, based on the knowledge of the previous converged point. In other words, our method for generating entire azeotropic lines should have the features of a good numerical path-following method.<sup>32</sup> For these reasons, our approach here is similar to that followed for calculations of critical lines and three-phase lines.<sup>8</sup>

Defining z, for simplicity, as the component 1 molar fraction of both the liquid and vapor azeotropic phases, we set the system of azeotropic equations, for the calculation of each point along the binary azeotropic line, as follows

$$F = \begin{bmatrix} \ln P^{L}(z,T,v^{L}) - \ln P^{V}(z,T,v^{V}) \\ \ln \hat{f}_{1}^{L}(z,T,v^{L}) - \ln \hat{f}_{1}^{V}(z,T,v^{V}) \\ \ln \hat{f}_{2}^{L}(z,T,v^{L}) - \ln \hat{f}_{2}^{V}(z,T,v^{V}) \\ g(X) - S \end{bmatrix} = 0$$
(3a)

where the vector of system variables is

$$X = \begin{bmatrix} \ln T \\ z \\ \ln v^{L} \\ \ln v^{V} \end{bmatrix}$$
(3b)

(Note that, for numerical reasons, we scale the variables T,  $v^{L}$ , and  $v^{V}$  using logarithms. Using ln *z* as the independent variable instead of *z* is convenient, for example, in the calculation of LLV lines,<sup>8</sup> where one molar fraction usually decreases exponentially along the line. This is not the case for azeotropic lines, which, in turn, can end abruptly at pure-compound end points. Therefore, the linear scale is preferred for composition; i.e., a given step in *z* means the same in regions rich in either compound 1 or compound 2.)

We define the variables in eqs 3a and 3b as follows: *T* is the absolute temperature.  $v^{L}$  and  $v^{V}$  are the molar volumes of the liquid and vapor phases, respectively.  $\hat{f}_{i}^{L}$  and  $\hat{f}_{i}^{V}$  are the fugacities of component *i* in the liquid and vapor phases, respectively. g(X) is the specification function, and *S* is its specified value.

Note that P(z,T,v) and  $\hat{f}_i(z,T,v)$  are, respectively, the pressurevolume-temperature-composition and fugacity-volumetemperature-composition relationships corresponding to the chosen EOS model. It should be noted that using volumes instead of pressure as independent variables not only saves solving the pressure equation a large number of times along the calculation of an azeotropic line. It also facilitates the numerical convergence for points close to a CAEP, where the solution for volume roots degenerates.

The system in eq 3a is solved for each point using a full multidimensional Newton method. The sensitivity values contained in vector dX/dS are used to generate initial estimates for each new point, as is described by Michelsen for the calculation of phase envelopes<sup>33</sup> or by Cismondi and Michelsen for the calculation of critical lines.<sup>8</sup> We also use vector dX/dS to choose the most convenient expression for the specification function g(X) from the list given in Table 2, where we use the index NS to label the different options for g(X).

Appendix B provides additional details on system of eqs 3a and 3b and on the corresponding continuation method. The Jacobian matrix of the vector function F (eq 3a) is given in Appendix C.

#### 7. Pxy and Txy Diagrams with Azeotropic Points

In a previous work,<sup>7</sup> we presented strategies and methods for the construction of complete isothermal (Pxy) and isobaric



Figure 6. *Txy* diagrams for different pressures indicated as dashed lines in Figure 5. System and model as in Figure 5. Phase behavior type: II-A. *Txy* cases (Table 4): case VI at 0.166 bar (but very close to case XIII), case VI at 0.3 bar, and case III at 55 bar. See ref 7 for the case at 0.1 bar.



**Figure 7.** Pressure-temperature and temperature-composition projections of the calculated global fluid phase equilibrium diagram for the system carbon dioxide (1) + hydrogen sulfide (2). Model: SRK EOS with  $k_{ij} = 0.12$ . Temperatures indicated by dashed lines correspond to *Pxy* diagrams in Figure 8. Phase behavior type: II-A.

(Txy) binary fluid phase equilibrium diagrams and provided tables indicating the different two-phase regions to be calculated, depending on the number of previouly detected critical, LLV, and pure saturation points at the specified temperature or pressure. Those tables did not consider homogeneous azeotropic behavior. These cases are now presented in Tables 3 and 4. Table 3 corresponds to isothermal Pxy fluid phase equilibrium diagrams. It establishes the number and nature of two-phase regions to be calculated, as a function of the number of LLV (NLLV), azeotropic (NAZ), critical (NCRI), and pure-compound saturation (NSAT) points detected. The nature of a given region is defined by the nature of its limiting points, which can be critical points (e.g., C, CA1, CA2, CB), azeotropic points (e.g., A, A1, A2), pure-compound vapor-liquid saturation points (i.e., S1 or S2), liquid-liquid points at LLV conditions (i.e., LL), and liquid-vapor points at LLV conditions (i.e, L<sub>I</sub>V, L<sub>II</sub>V). Also, a region can extend to indefinitely high pressures. We identify such regions as open (O) regions. To fix ideas, consider the Pxy case IV in Table 3, whose regions are (S1|A) and (S2|A). This corresponds to a vapor-liquid region (S1IA) extending from the vapor-liquid saturation point of component 1 (S1) to the only dectected azetrope (A) and to a second vapor-liquid region (S2|A) whose limiting points are the azeotrope (A) and the vapor-liquid saturation point for component 2 (S2). Pxy case XIII corresponds to a more complex situation with regions

 $(VL_{II}|S1)$ ,  $(VL_{I}|A1)$ , (S2|A2), (A1|A2), and (LL|O). Thus, there are three regions stemming from the LLV point [ $(VL_{II}|S1)$ ,  $(VL_{I}|A1)$ , and (LL|O)]: the  $(VL_{II}|S1)$  region ends at S1, the  $(VL_{I}|A1)$  region ends at one of the two detected azeotropes, and the (LL|O) is an open liquid–liquid region. The region (S2|A2) goes from the pure-compound point S2 to the second detected azeotrope A2, whereas the region (A1|A2) connects the two azeotropes (A1 and A2). The variety of cases that Tables 3 and 4 cover are based on our knowledge and experience. There might be other cases not included in Tables 3 and 4. However, Tables 3 and 4 definitely account for most of the cases of practical interest and even some rare ones. Cases not considered so far could be incorporated in the future into our algorithm without much effort, and thus Tables 3 and 4 could be extended.

Tables 3 and 4 follow the notation used in ref 7. When two or more critical points need to be distinguished in the specification of limiting points, the type of critical line (according to the classification in ref 8) is indicated as a subscript for each point (e.g., for Txy case III in Table 4, CA and CB). The types of critical lines considered in ref8 are A-E. If more than one critical point from a given line are present, they are numbered according to their position in the line, starting at the critical point of component 2 for lines of type A or E (e.g., Pxy case I in Table 3: CA1 and CA2; and Txy case I in Table 4: CE1 and  $C_{\text{E2}}\text{)}.$  In the case of double azeotropy, A1 and A2 refer to the azeotropic points closer in composition to compounds 1 and 2 respectively (e.g., for Pxy case V in Table 3, A1 and A2). Some cases corresponding to the same specification (NLLV, NSAT, NCRI, NAZ) are distinguished depending on the relation between the compositions of some points present:  $z_A$ ,  $z_C$ , and  $z_{\rm V}$  denote the azeotropic composition (A), critical composition (C), and vapor composition at an LLV point (V), respectively, in terms of the mole fraction of component 1. Cases with same specification are, for instance, cases X and XI in Table 3 and cases XV and XVI in Table 4.

The numerical procedures described in ref 7 apply here for the construction of each Pxy or Txy region, including prescriptions about which specification should be made when starting from a saturation, critical, or LLV point. Nevertheless, azeotropy was not considered in that work. The case of regions of type (A1IA2), i.e., of regions extending between two different azeotropes, is special because we cannot avoid using an azeotropic point as the starting point when building such regions. We describe how we deal with this problem in Appendix D.

# 8. Illustration of the Proposed Methods

Figures 3–11 illustrate what can be obtained when using the methods proposed in this work, through different types of diagrams and with different systems and models. Although we chose real systems to illustrate the implementation of our proposed algorithm and, in some cases, used interaction parameter values that predict the proper qualitative behavior, we emphasize that quantitative comparisons to experimental data are not within the scope of the present work.

Figure 3 shows the global fluid-phase equilbrium diagram (GPED) for the system carbon dioxide + ethane as described by the SPHCT EOS<sup>34</sup> with  $k_{ij} = 0.10$ . The top part is the pressure-temperature projection of the GPED, and the bottom part is the temperature-composition projection. We observe that the two pure-compound vapor-liquid saturation curves (SAT-Eth and SAT-CO<sub>2</sub>) have an intersection point (Bancroft point). Also present are a liquid-vapor critical line (CRI-LV); a liquid-liquid critical line (CRI-LL) that meets a liquid-liquid-vapor line (LLV) at an upper critical end point (UCEP); and,



Figure 8. *Pxy* diagrams at different temperatures near the HAEP, indicated as dashed lines in Figure 7. System and model as in Figure 7. Phase behavior type: II-A. *Pxy* cases (Table 3): case X at 160.0 and 175.0 K. Other cases: ref 7.

finally, a line of homogeneous azeotropy (AZE). The AZE line goes from a CAEP to an HAEP. The temperature of the HAEP is lower than the UCEP temperature.

Aslam and Sunol<sup>17</sup> applied a homotopy continuation approach for calculating azeotropes for binary and multicomponent mixtures. Their method is based on distorting the nonlinear azeotropic equilibrium equations through a homotopy parameter. As this parameter is changed from zero to unity, the solution of the nonlinear system progresses from the solution of a simple equilibrium model to that of the more complex model of interest. Every single solution obtained for this last model requires the tracking of a complete curve. Therefore, using homotopy continuation to obtain an azeotropic line with the same level of detail as, e.g., that in Figure 3 of the present work requires the tracking of a large number of curves, i.e., one for each set temperature (or pressure) value. On the other hand, the method we propose here obtains a complete azeotropic line by tracking only one curve. For the time being, a version of the present method applicable to ternary or multicomponent azeotropes is not available. The homotopy continuation approach can be used in such cases, in specific regions of phase space, and in problems such as the modeling of multicomponent distillation processes.

Figure 4 shows an enlargement of the P-T diagram from Figure 3 in the region where the azeotropic line meets the critical line on a critical azeotropic end point (CAEP), as well as Pxydiagrams corresponding to four different temperatures in this range. This progression aids in understanding the significance of a CAEP, which is an azeotrope and a critical point at the same time, and how it affects the phase behavior at its surroundings. Note that only the two higher temperatures provide qualitatively equivalent diagrams, which would correspond to the Pxy case VIII in Table 3 except for the absence of azeotropic points. (Actually, because there is no azeotropic point, this case can be found in Table 1 in ref 7.) Diagrams for 289.5 and 288.0 K are identified with lines (0, 2, 2, 1) (*Pxy* case VIII) and (0, 2, 2, 1)0, 1) (Pxy case IV), respectively, in Table 3. The progression is such that, at 288.0 K, there is an azeotrope and no critical points; at 289.5, there are two critical points and still an azeotrope; and at 291.4, there are also two critical points but no azeotropes, as is the case at 293.0 K. Figure 3 corresponds to a type II-A system in the classification of Scott and van Konynemburg.<sup>5</sup> The SPHCT pure-compound parameters were set to reproduce the experimental critical temperature and pressure of the pure constituents.<sup>35</sup> The important remark to make here is that relatively complex figures such as Figure 3 are automatically generated after the user defines the system components, identifies the model, and sets the values for the interaction parameters. Similarly, the only additional information that the user must provide to generate figures such as Figure 4 is the set of temperature values of the isotherms. Each different line in Figure 3 is the result of a specific continuation method. Such continuation methods were defined in a previous work<sup>8</sup> for SAT, CRI, and LLV lines and in the present work for AZE lines.

Figures 5, 7, and 9 show additional calculated global phase equilibrium diagrams for three other systems using three



**Figure 9.** Pressure–temperature and temperature–composition projections of the calculated global fluid phase equilibrium diagram for the system ethanol (1) + *n*-hexane (2). Model: PC-SAFT EOS with  $k_{ij} = 0.047$ . Temperatures indicated by dashed lines correspond to *Pxy* diagrams in Figure 10. Phase behavior type: I-A.

different equations of state: PR,36 SRK,37 and PC-SAFT.30 As was the case for the SPHCT EOS in Figure 3, parameters reproducing the experimental critical temperature and pressure of the constituent pure compounds were used for the PC-SAFT EOS.<sup>35</sup> Figures 5 and 7 are calculated diagrams that correspond to type II-A in the classification of Scott and van Konynemburg,<sup>3</sup> whereas the system of Figure 9 is type I-A. However, from the cases of Figures 3, 5, 7, and 9, an interesting diversity of situations and azeotropic behavior can be observed, for example in terms of the following aspects: (1) distance between UCEP and HAEP (note, for example, the proximity between the HAEP and the UCEP in Figures 3 and 5, whereas an important separation is present in Figure 7); (2) separation between the azeotropic line (AZE) and the nearest saturation line in the P-Tplane (this separation is clear in Figure 3 but essentially negligible in Figure 7 and parts of Figures 5 and 9); and (3) crossing between pure saturation lines, known as Bancroft point. Such a crossing is observed in Figures 3 and 9 but not in Figures 5 and 7, which still show azeotropy. It is interesting to observe that the existence of Bancroft points in two different systems, such as those of Figures 3 and 9, does not imply a similar shape for the azeotropic lines: whereas the azeotropic line is monotonic in both projections of Figure 3, the azeotropic line of Figure 9 is not. The pressure-temperature projection of the azeotropic line in Figure 9, which is better seen in the top left diagram of Figure 10, is highly curved. Therefore, such an azeotropic line

would have been hard to track without using a path-following method, as the one we propose here, that is able to adapt the specification function to the shape of the tracked curve as the calculation progresses.

Figure 7 in this work corresponds exactly to Figure 3 in ref 8, now including the azeotropic line, which was not considered in that work. Regarding Figures 9 and 10, we stress again that comparisons to experimental phase behavior are not within the scope of the present work. Readers interested in studying the ability of the PC-SAFT or any other particular EOS to describe cases of experimentally observed polyazeotropy are directed to refs24 and 25.

Examples of Txy diagrams are given in Figure 6, for the system hydrogen sulfide + propane as described by the Peng–Robinson EOS with  $k_{ii} = 0.05$ . The pressure values of the isobars are indicated as dashed horizontal lines on the P-Tprojection in Figure 5. Here, the behavior around a heterogeneous azeotropic end point (HAEP) is illustrated through the first three low-pressure diagrams. At pressures below the HAEP, such as 0.10 bar, heterogeneous azeotropy is observed. The second pressure, 0.166 bar, is slightly above the UCEP pressure (0.165 bar) and above, but still close, to the HAEP pressure (0.154 bar). From 0.166 bar to higher pressures, no threephase equilibrium is observed; i.e., the liquid-liquid region does not interfere with the liquid-vapor regions, and only homogeneous azeotropy can appear. This is more evident at the third pressure value in Figure 6 (i.e., 0.30 bar). The last Txy diagram corresponds to a much higher pressure, i.e., 55 bar. It shows only the liquid-vapor region and includes one critical point, one azeotropic point, and one saturation point. At 55 bar, there is also a liquid-liquid region that ends at a liquid-liquid critical point (Figure 5). The temperature range of this region is outside the temperature range of the 55.0 bar isobar of Figure 6.

Another example of the evolution of the phase behavior through an HAEP, this time in terms of *Pxy* diagrams, is shown in Figure 8 for the system carbon dioxide + hydrogen sulfide as described by the SRK EOS with  $k_{ij} = 0.12$ . The temperature values corresponding to these isotherms are indicated as horizontal dashed lines on the *T*-*x* projection in Figure 7. Once again, it is clear how an HAEP shapes the transition from heterogeneous to homogeneous azeotropy. In all four isothermal diagrams in Figure 8, there is interference of the liquid-liquid region with the vapor-liquid regions.

The last type of azeotropic end point left for graphic illustration in the progression of phase diagrams is the PAEP. This is done in Figure 10, for the system ethanol + n-hexane as described by the PC-SAFT EOS ( $k_{ij} = 0.047$ ). Figure 10 includes an enlargement of the P-T projection of the GPED of Figure 9 around the Bancroft point. This enlargement covers the whole azeotropic line that goes through a maximum temperature where the azeotropic pressure is also maximum. Such a highly curved line of homogeneous azeotropy is difficult to visualize in Figure 9. The Pxy diagrams in Figure 10 illustrate not only a transition through a PAEP but also the calculation of double azeotropy. At 377.0 K, there is only one homogeneous azeotrope with relatively low ethanol concentration. At 379.6 K, a second azeotrope appears, at conditions of infinite dilution of *n*-hexane in ethanol. This azeotrope is an end point of the locus of homogeneous azeotropy, i.e., a PAEP. At 381.5 K, the second azeotrope has become more concentrated in *n*-hexane. At 389.0 K, both azetropes are quite far from the infinite dilution condition. The size of the interazeotropic region continues to decrease with further increases in temperature to the point of maximum temperature of the azeotropic line, as inferred from



**Figure 10.** Enlargement of the pressure-temperature diagram of Figure 9 in the range containing the azeotropic line (top left) and *Pxy* diagrams at different temperatures near the higher-temperature PAEP, indicated as dashed lines in Figure 9 and in the top left plot of this figure. System and model as in Figure 9. Phase behavior type: I-A. *Pxy* cases (Table 3): Case IV at 377.0 K, case V at 381.5 and 389.0 K, transition between cases IV and V at 379.6 K.

the enlargement in Figure 10 and as clearly shown in the temperature–concentration projection of Figure 9. Notice that a switchback in the P-T projection for the azeotropic line is a sufficient but not a necessary condition of double or polyazeot-ropy. The fact that it is not a necessary condition is illustrated in Figure 4 of ref 15 where single, double, or triple azeotropy occurs, depending on the pressure range. The aforementioned figure shows three azeotropic lines that never meet: they all end at different points of the binary critical line.

#### 9. Comments on Bancroft Points and Azeotropy

As stated by van Konynemburg and Scott,<sup>5</sup> the existence of a Bancroft point always implies azeotropy. Elliott and Rainwater<sup>38</sup> considered a database of 1350 pure compounds and found 64 103 binary systems presenting a Bancroft point. In such cases, the composition of the azeotrope is expected to change significantly along the azeotropic line, from a region rich in component 1 to one rich in component 2. This is the case shown in the temperature-concentration projection of Figure 9, where we find a line of homogeneous azeotropy connecting both infinite dilution ends. As a natural consequence of the existence of an azeotropic line with a wide composition range, in a system characterized by a Bancroft point, the azeotropic line can be interrupted if liquid-liquid phase separation occurs up to temperatures in the range of homogeneous azeotropy. Such interruption leads to a split of the homogeneous azeotropy locus into two different branches,

separated by a heterogeneous azeotropy region. We can improve our understanding of such complex phenomena by applying the algorithm proposed in this work for the automated generation of phase diagrams accounting for homogeneous azeotropy. This is exemplified by the diagrams calculated using the RK-PR EOS<sup>39</sup> for ethanol + *n*-hexane in Figure 11. In this case ( $k_{ij} =$ 0.00, bottom diagrams in Figure 11), the low-temperature homogeneous azeotropy line starts from the vapor pressure line of pure *n*-hexane and ends at a low-temperature HAEP, whereas the high-temperature line goes from the second (high-temperature) HAEP to a CAEP. Another important observation is that azeotropic lines in systems with Bancroft points are very sensitive to interaction parameters, especially in composition. This can be seen explicitly in Figure 11, and it is also the case for Figure 9, where double azeotropy can be obtained only for a very narrow range of  $k_{ij}$  values, approximately from 0.020 to 0.053. (Note that this is valid of course for the PC-SAFT EOS, which was used to generate Figures 9 and 10. Double azeotropy could not be obtained for this system with the other models used in this work.) Actually, double azeotropy is generally associated with a Bancroft point, both in models and in experiments.

#### 10. Remarks and Conclusions

In this work, we have proposed a numerical continuation method for the efficient generation of lines of homogeneous azeotropy for binary mixtures described by models of the



Figure 11. Pressure – temperature and temperature – composition projections of the calculated global fluid phase equilibrium diagrams for the system ethanol (1) + *n*-hexane (2) using the RK-PR EOS with three different  $k_{ij}$  values: -0.04, -0.02, and 0.00. Phase behavior type: II-A in all cases.

equation-of-state type. The efficiency requirement relates not only to the need for low computation times but also to the ability of the method to track highly curved azeotropic lines, as is the case shown in Figures 9 and 10. The key to properly following the path of highly curved lines is to allow changes in the nature of the specified variable as the building of the line progresses. Our algorithm first identifies the end points of the azeotropic lines, which can occur on critical lines and/or on liquid—liquid vapor lines and/or on pure-compound saturation lines. The present method for generating azeotropic lines avoids performing stability analysis due to such in advance location of AEPs.

We described in the present work how our algorithm for construction of entire azeotropic lines is integrated into a more general algorithm that also generates critical lines, liquid—liquid vapor lines, and pure-compound vapor—liquid saturation lines. The result is a procedure that requires the definition of the binary system and the values of the model interaction parameters as the only input information to generate a global phase equilibrium diagram. We also described how complete binary isothermal or isobaric fluid phase equilibrium diagrams can be generated in a single run, by detecting, as first step, all critical, liquid liquid—vapor, and azeotropic points, as well as all purecompound vapor—liquid saturation points, at the set temperature or pressure. In general, the algorithm does not miss any of the possible liquid—liquid or liquid—vapor regions that exist for the model at the set temperature or pressure, in spite of the fact that the corresponding isothermal or isobaric phase diagram can have a significant degree of complexity, as illustrated in Figure 11.

An important conclusion we reached while developing this work is that conventional mixing rules describe double azeotropy only in narrow ranges of the values of the parameters. With such mixing rules, one obtains at most a qualitative description of double azeotropy. A quantitative description would require more flexible mixing rules. The problem of polyazeotropy and the mathematical or modeling conditions for its occurrence are discussed in more detail in refs 24 and 25.

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# Nomenclature

AEP = azeotropic end pointAZE = azeotropicCAEP = AEP on a vapor-liquid critical line CRI = critical $C_X$  = critical point corresponding to a critical line of type X EOS = equation of stateHAEP = AEP on an LLV line K point = vapor-liquid critical end point LCEP = lower critical end point $L_{II}V =$  light liquid phase and vapor phase at the LLV point  $L_I V$  = heavy liquid phase and vapor phase at the LLV point LL = liquid - liquid or liquid phases at the LLV point LLV = liquid-liquid-vapor LV = liquid-vapor NAZ = number of azeotropes at a set temperature (or pressure) NCRI = number of critical points at a set temperature (or pressure) NLLV = number of LLV points at a set temperature (or pressure) NSAT = number of pure-compound LV saturation points at a set temperature (or pressure)

O = open

P = absolute pressure

PAEP = AEP on a pure-compound vapor-liquid line

Pxy = isothermal phase equilibrium diagram

- S1, S2 = liquid-vapor saturation points of components 1 and 2, respectively, at a set temperature (or pressure) (Component 1 is the most volatile compound of the binary system, i.e., the one with higher vapor pressure, and component 2 is the less volatile compound. For binary systems presenting a Bancroft point, the highest temperature region is taken into account.)
- SAT = LV saturation state for a pure compound

T = absolute temperature

Txy = isobaric phase equilibrium diagram

UCEP = upper critical end point

z =component 1 mole fraction

# Appendix A: Minimization of the Computational Effort When Searching for a CAEP along a Stable Critical Line

If the condition of eq 2a is fulfilled for a liquid-vapor critical point, there are in principle three possibilities for this critical phase, regarding its location on a (constant-temperature and constant-composition) pressure-density curve: (1) It is located

on a relative maximum pressure point. (2) It is located on a relative minimum pressure point. (3) Its temperature is equal to the pseudocritical temperature for the composition of the critical phase, and the critical phase is located exactly on the pseudopure critical point.

Possibilities 1 and 2 must be discarded because they correspond to points inside the pseudo-pure-compound saturation bell and are therefore unstable. In other words, for any point inside the pseudosaturation bell, there will be a different possible phase with equal composition, temperature, and pressure, but different density and lower Gibbs energy.

In conclusion, when a stable vapor—liquid critical point satisfies condition 2a (first derivative), then condition 2b (second derivative) will also automatically be satisfied because the critical point will simultaneously be a pseudopure critical point. Therefore, the fulfillment of condition 2a is enough to conclude that a stable vapor—liquid critical point is a critical azeotropic end point (CAEP).

# Appendix B: Details on the Azeotropic System of Equations and on the Continuation Method for Calculation of Azeotropic Lines

Consider eqs 3a and 3b. As an example, we could set  $g(X) = \ln T$  and  $S = \ln(280)$ . Thus, in such a case, we would calculate the azeotropic composition, pressure, and phase densities at a temperature of 280 K. Another possibility would be setting g(X) = z and S = 0.85, which corresponds to the calculation of the azeotropic temperature, pressure, and phase densities when the composition of the azetrope is z = 0.85. In both examples, specifying g(X) and setting a value for S is equivalent to specifying the value of one of the variables of vector X. It is also possible, and often convenient, to define g(X) as a combination of the variables of vector X, e.g.,  $g(X) = \ln(v^{V}/v^{L})$ .

Once we define g(X) and assign a numerical value to the variable *S*, we make the number of unknowns in system 3a become equal to the number of equations and, thus, solve system 3a. By changing the value of *S* and solving system 3a for each new value of *S*, we track a curve in a four-dimensional space relating variables *T*, *z*,  $v^{L}$ , and  $v^{V}$ ; i.e., we generate a locus of homogeneous azeotropy. The solution vector *X* for system 3a is a function of *S*. We define the sensitivity vector dX/dS as

$$\frac{\mathrm{d}X}{\mathrm{d}S} = \begin{bmatrix} \mathrm{d}(\ln T)/\mathrm{d}S\\ \mathrm{d}z/\mathrm{d}S\\ \mathrm{d}(\ln v^{\mathrm{L}})/\mathrm{d}S\\ \mathrm{d}(\ln v^{\mathrm{V}})/\mathrm{d}S \end{bmatrix}_{\mathrm{homogeneous azeotropy}}$$
(B1)

The sensitivity vector dX/dS provides information on how the solution vector X changes as a function of the value S set equal to g(X). Once we have a solution for system 3a, we compute the sensitivity vector dX/dS by solving the following system of equations

$$J(F) \frac{\mathrm{d}X}{\mathrm{d}S} + \frac{\partial F}{\partial S} = 0 \tag{B2}$$

where J(F) is the Jacobian matrix of the vector function F (given in Appendix C) and

$$\frac{\partial F}{\partial S} = \begin{bmatrix} 0\\0\\0\\-1 \end{bmatrix}$$
(B3)

We obtain eq B2 by differentiating eq 3a with respect to parameter *S*. The left-hand side of eq B2 is the total derivative of the vector function F with respect to parameter S. The first term accounts for indirect dependencies of the vector function F on parameter S, whereas the vector  $\delta F/\delta S$  accounts for the direct dependency of F on parameter S.

Notice also that variable *S* is a parameter of system 3a but not one of its variables, which are those of vector *X* (eq 3b). The Jacobian matrix, J(F), involves partial derivatives of the vector function *F* with respect to the variables of vector *X* but not with respect to parameter *S*. Finally, note that elements of the sensitivity vector dX/dS are total rather than partial derivatives.

As indicated in section 5, we start the calculation of an azeotropic line either from a PAEP or from a CAEP. In the first case, composition is initially specified, for example, z = 0.005 or z = 0.995, i.e., NS = 2 in Table 2, g(X) = z and S = 0.005 or S = 0.995.

When starting from a CAEP, the best choice for the specification function is the relation between  $v^{V}$  and  $v^{L}$ , which avoids the possibility of converging to a trivial solution where  $v^{V} = v^{L}$ . This specification is conveniently identified as NS = 0 in Table 2 to distinguish it from specification functions corresponding to the natural variables in the vector X (eq 3b) (NS = 1-4 in Table 2). If we use  $g(X) = X_4 - X_3 = \ln(v^{V}/v^{L})$ , then the last row of the Jacobian J(F) becomes  $[\partial F_4/\partial X_1 \partial F_4/\partial X_2 - \partial F_4/\partial X_3 \partial F_4/\partial X_4] = [0 \ 0 \ -1 \ 1]$ , and the residual F(4) will remain as exactly zero as the iterations proceed. (This is not the case, for example, if the difference  $v^{V} - v^{L}$  is specified.) For the first point departing from a CAEP, we used  $0.99v_{C}$  and  $1.01v_{C}$  as initial estimates for  $v^{L}$  and  $v^{V}$ , respectively, and consistently made the specification  $S = \ln(1.01/0.99)$ . We also initialized T and z, setting them equal to the corresponding CAEP values for T and z. Note that  $v_{C}$  is the volume of the CAEP.

As Table 2 shows, we set the specification function equal to either a natural variable  $(X_1, X_2, X_3, \text{ or } X_4)$  or the difference  $X_4$  $-X_3$ . Vector dX/dS, which we know from solving system B2 after convergence of an azeotropic point, provides the sensitivity of only the natural variables with respect to parameter S. We obtain the sensitivity of  $g_0 = \ln(v^V/v^L) = X_4 - X_3$  with respect to parameter S simply by differentiation, which results in  $dg_0/dg_0$  $dS = dX_4/dS - dX_3/dS$ . When tracking the locus of homogeneous azeotropy, we eventually need to switch from one specification function to another. This is done based on the values of the elements of the augmented sensitivity vector  $[dg_0/dS dX_1/dS dX_2/dS dX_3/dS dX_4/dS]$ . The specification function we use for calculating the next azeotropic point is the one with highest sensitivity, i.e., the function corresponding to the element of the augmented vector having maximum absolute value. A specification function switch typically happens at some point when a CAEP is approached, where the specification function is changed from NS  $\neq$  0 to NS = 0. In this case, the augmented sensitivity vector has to be recalculated as  $dX/dS_{new} =$  $[(dg_0/dS)/(dg_0/dS) (dX_1/dS)/(dg_0/dS) (dX_2/dS)/(dg_0/dS) (dX_3/dS)/$  $(dg_0/dS)$   $(dX_4/dS)/(dg_0/dS)$ ], similarly to what is done when switching from the specification function of a natural variable to another.

# **Appendix C: Jacobian Matrix of the Homogeneous Azeotropy Vector Function** *F*

It is important to note that our independent variable for composition (eq 3b) is the molar fraction z, whereas the derivatives provided by thermodynamic subroutines are usually, and conveniently, with respect to mole numbers.<sup>6</sup> Following the formalism  $n_1 = z$  and  $n_2 = 1 - z$ , the derivative of any function U (which can be the logarithm of the pressure or the

logarithm of the fugacity of a given component) with respect to z can be calculated from the expression

$$\left(\frac{\partial U}{\partial z}\right)_{T,V} = \left(\frac{\partial U}{\partial n_1}\right)_{T,V,n_2} - \left(\frac{\partial U}{\partial n_2}\right)_{T,V,n_1} \tag{C1}$$

The Jacobian matrix  $J [J_{lm} = (\partial F_l / \partial X_m)_{X_{n \neq m}}]$  corresponding to the vectors of eqs 3a and variables specified in 3b is therefore calculated as follows, where the dependence of the pressure and fugacities on temperature, volume, and composition is not declared for the sake of simplicity [e.g., in the following equations, we denote  $P^{L}(z,T,v^{L})$  simply as  $P^{L}$ ]

$$J_{11} = T \left[ \frac{1}{P^{\rm L}} \left( \frac{\partial P^{\rm L}}{\partial T} \right)_{n,V^{\rm L}} - \frac{1}{P^{\rm V}} \left( \frac{\partial P^{\rm V}}{\partial T} \right)_{n,V^{\rm V}} \right] \tag{C2}$$

$$J_{12} = \frac{1}{P^{L}} \left[ \left( \frac{\partial P^{L}}{\partial n_{1}} \right)_{T, V^{L}, n_{2}} - \left( \frac{\partial P^{L}}{\partial n_{2}} \right)_{T, V^{L}, n_{1}} \right] - \frac{1}{P^{V}} \left[ \left( \frac{\partial P^{V}}{\partial n_{1}} \right)_{T, V^{V}, n_{2}} - \left( \frac{\partial P^{V}}{\partial n_{2}} \right)_{T, V^{V}, n_{1}} \right]$$
(C3)

$$J_{13} = \frac{V^{L}}{P^{L}} \left(\frac{\partial P^{L}}{\partial V^{L}}\right)_{n,T} \qquad J_{14} = -\frac{V^{V}}{P^{V}} \left(\frac{\partial P^{V}}{\partial V^{V}}\right)_{n,T} \tag{C4}$$

$$J_{21} = T \left[ \left( \frac{\partial \ln f_1^{\,l}}{\partial T} \right)_{n,VL} - \left( \frac{\partial \ln f_1^{\,v}}{\partial T} \right)_{n,VV} \right] \tag{C5}$$

$$J_{22} = \left(\frac{\partial \ln \hat{f}_1^L}{\partial n_1}\right)_{T, V^L, n_2} - \left(\frac{\partial \ln \hat{f}_1^L}{\partial n_2}\right)_{T, V^L, n_1} - \left[\left(\frac{\partial \ln \hat{f}_1^V}{\partial n_1}\right)_{T, V^V, n_2} - \left(\frac{\partial \ln \hat{f}_1^V}{\partial n_2}\right)_{T, V^V, n_1}\right] (C6)$$

$$J_{23} = V^{L} \left( \frac{\partial \ln \hat{f}_{1}^{L}}{\partial V^{L}} \right)_{n,T} \qquad J_{24} = -V^{V} \left( \frac{\partial \ln \hat{f}_{1}^{V}}{\partial V^{V}} \right)_{n,T} \tag{C7}$$

$$J_{31} = T \left[ \left( \frac{\partial \ln f_2^2}{\partial T} \right)_{n,V^L} - \left( \frac{\partial \ln f_2^2}{\partial T} \right)_{n,V^V} \right]$$
(C8)

$$J_{32} = \left(\frac{\partial \ln \hat{f}_2^{\rm L}}{\partial n_1}\right)_{T,V^{\rm L},n_2} - \left(\frac{\partial \ln \hat{f}_2^{\rm L}}{\partial n_2}\right)_{T,V^{\rm L},n_1} - \left[\left(\frac{\partial \ln \hat{f}_2^{\rm V}}{\partial n_1}\right)_{T,V^{\rm V},n_2} - \left(\frac{\partial \ln \hat{f}_2^{\rm V}}{\partial n_2}\right)_{T,V^{\rm V},n_1}\right] (C9)$$

$$J_{33} = V^{L} \left( \frac{\partial \ln \hat{f}_{2}^{L}}{\partial V^{L}} \right)_{n,T} \qquad J_{34} = -V^{V} \left( \frac{\partial \ln \hat{f}_{2}^{V}}{\partial V^{V}} \right)_{n,T} \quad (C10)$$

When the specification function g(X) is chosen as equal to one of the independent variables (NS = 1-4 in Table 2), the last line in the Jacobian matrix becomes  $J_{4,NS} = 1$  and  $J_{4,i} = 0$ for  $i \neq NS$ . When g(X) is instead chosen as  $g(X) = \ln(v^V) - \ln(v^L)$  (i.e., NS = 0 in Table 2), then  $J_{41} = J_{42} = 0$ ,  $J_{43} = -1$ , and  $J_{44} = 1$ .

The derivatives of fugacities can be obtained from derivatives of the residual Helmholtz energy as follows

$$\left( \frac{\partial \ln \hat{f}_i}{\partial V} \right)_{n,T} = -\frac{1}{RT} \left( \frac{\partial P}{\partial n_i} \right)_{T,V,n_j} = \frac{1}{RT} \left( \frac{\partial^2 A^r}{\partial V \partial n_i} \right)_{T,n_j} - \frac{1}{V} (C11)$$

$$\left( \frac{\partial \ln \hat{f}_i}{\partial T} \right)_{n,V} = \frac{1}{RT} \left[ \left( \frac{\partial^2 A^r}{\partial T \partial n_i} \right)_{V,n_j} - \frac{1}{T} \left( \frac{\partial A^r}{\partial n_i} \right)_{T,V,n_j} \right] + \frac{1}{T} (C12)$$

$$\left( \frac{\partial \ln \hat{f}_i}{\partial n_j} \right)_{T,V} = \frac{\delta_{ij}}{n_i} + \frac{1}{RT} \left( \frac{\partial^2 A^r}{\partial n_i \partial n_j} \right)_{T,V}$$

$$(C13)$$

where  $\delta_{ij}$  is the Kronecker delta function, i.e, 0 for  $i \neq j$  and 1 for i = j. (Note that, in eqs C11–C13, we obtained the expressions by combining other related derivatives in ref 6.)

#### Appendix D: Calculation of Vapor–Liquid Equilibrium Regions That Develop between Two Azetropes

For (A1IA2) regions extending between two different azeotropes, i.e., from  $x_1^{\text{az,start}}$  to  $x_1^{\text{az,end}}$ , we calculate the first nonazeotropic point of the region specifying a value for the composition difference ( $s = x_1 - y_1$ ) between the equilibrium phases. This is also the case when starting from a critical point or from a saturation point. For the (A1IA2) case, the initial value of the vapor-phase composition for the first nonazeotropic point is estimated from the relation

$$y_1 = x_1^{\text{az,start}} + \frac{\left(\frac{\partial \hat{f}_1}{\partial x_1}\right)_{T,P}}{\left(\frac{\partial \hat{f}_1}{\partial y_1}\right)_{T,P}} (x_1 - x_1^{\text{az,start}})$$
(D1)

where the derivatives of fugacity with respect to composition are calculated at the temperature, pressure, and composition of the azeotrope. Equation D1 assumes a negligible change in pressure (or temperature), and therefore a negligible change in the derivatives values, when moving from the azeotropic to the first nonazeotropic point. A linear dependence of the fugacity of component 1 with respect to composition is the fundamental assumption for using eq D1. This assumption is based on the fact that, as illustrated in Figure D1, the fugacity curves corresponding to the liquid and vapor phases are approximately straight lines with different slopes, crossing at the azeotropic point. Therefore, for conditions close to the azeotropic point, eq D1 relates compositions for the two nonazeotropic phases such that the fugacity of component 1 is the same in both, and this condition, together with the solution of the pressure equations for both phase volumes (at the azeotropic temperature and pressure), provides very good starting values for the calculation of the first nonazeotropic point. Still, eq D1 requires first  $x_1$  be chosen in order to then estimate  $y_1$  and, from that, fix the distance s. We found the following relation, in terms of the distance between the two extreme azeotropic points, as a reasonable and well-working criterion

$$x_1 = x_1^{\text{az,start}} - \frac{x_1^{\text{az,start}} - x_1^{\text{az,end}}}{100}$$
(D2)

It is important to note that, following the convention proposed in ref 7, *y* denotes the composition of the phase that is richer in component 1, not necessarily the vapor phase.

#### **Fugacity Derivatives in Equation D1**

Derivatives with respect to molar fractions can be obtained from those with respect to mole numbers, as indicated in eq C1. If derivatives at constant T and V are available (see eq C13), then those at constant T and P can be obtained as follows

$$\left(\frac{\partial \ln \hat{f}_i}{\partial n_j}\right)_{T,P} = \left(\frac{\partial \ln \hat{f}_i}{\partial n_j}\right)_{T,V} + \frac{1}{RT} \frac{\left(\frac{\partial P}{\partial n_i}\right)_{T,V,n_j} \left(\frac{\partial P}{\partial n_j}\right)_{T,V,n_i}}{\left(\frac{\partial P}{\partial V}\right)_{T,n}} \quad (D3)$$

When, in turn, derivatives of the logarithm of fugacity coefficients at constant T and P are already coded, the corresponding derivatives for fugacities are computed as follows



**Figure D1.** Fugacity curve behavior around the azeotropic composition, at constant temperature and pressure. Example corresponding to the system ethanol (1) + *n*-hexane (2), PC-SAFT with  $k_{ij} = 0.047$ , for T = 389 K and  $P^{az} = 3.6435$  bar (see Figure 10). In this example, the liquid is the stable phase, whereas the vapor is unstable, except in the azeotrope, at  $x^{az} = 0.29835$ , which is a maximum-pressure azeotrope (Figure 10).

$$\left(\frac{\partial \ln \hat{f}_i}{\partial n_j}\right)_{T,P} = \left(\frac{\partial \ln \hat{\varphi}_i}{\partial n_j}\right)_{T,P} + \frac{\delta_{ij}}{n_i} - \frac{1}{n}$$
(D4)

These equations can be derived from expressions in Chapter 1 of the book by Michelsen and Mollerup,<sup>6</sup> and we have followed their notation.

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