Bubble and Dew Point Calculations in Multicomponent and Multireactive Mixtures

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Bubble and dew point calculations are useful in chemical engineering and play an important role in the study of separation equipments for non-reactive and reactive mixtures. To the best of the authors's knowledge, few methods have been proposed for these calculations in systems with several chemical reactions. The objective of this paper is to introduce new conditions for performing bubble and dew point calculations in reactive mixtures. We have developed these conditions based on the application of transformed variables of *Ung* and *Doherty* (1995). Using these transformed variables, the solution space is restricted to compositions that are already at chemical equilibrium and by consequence the problem dimension is also reduced. The reliability and efficiency of three equation-solving methods are tested and compared using our equilibrium conditions: a) a simultaneous equation-solving approach using Newton method (SESN), b) an equation-decoupling approach using successive substitution method (EDSS) and c) an optimization approach using the stochastic optimization method Simulated Annealing (OSA). Our results indicated that even for simple reactive systems, bubble and dew point calculations are challenging for classical equation-solving methods and require robust strategies. We conclude that OSA and EDSS methods are reliable to locate bubble and dew points in reactive systems. EDSS is more efficient than OSA; however, OSA does not need initial guesses and is more suitable for difficult problems.

Key words:
Chemical equilibrium, phase equilibrium, bubble point, dew point, global optimization, equation-solving method comparison

Introduction

The description of phase equilibrium in multireaction mixtures is an important topic involved in several industrial applications and it is the basis for design, analysis, and synthesis of separation processes.[1] The phase equilibrium problem with several chemical reactions is highly non linear and multivariable.[2] During the last years, there has been a growing interest for developing new methods to treatment the thermodynamic behavior of mixtures under physical and chemical equilibrium.[2–13] Almost all developed methods use the mole fractions and reaction extents as independent variables and unknowns of the reactive phase equilibrium problem. Until now, only a few methods have used theories of variable transformation with the aim of reducing problem dimensionality and improving the numerical behavior (efficiency and reliability) of solution methods.[1,9] These kinds of algorithms are very attractive for the simulation of separation process and favor the study of complex multireactive multicomponent systems.

A special case of phase equilibrium problems are the bubble and dew point calculations. These calculations are useful in chemical engineering and play an important role in the study of separation equipments.[14] Under this context, robust, and efficient methods for these calculations are desirable. To the best of the authors's knowledge, few methods have been developed to calculate bubble and dew points in multireactive mixtures.[9,12]

This paper introduces a new method for performing dew and bubble point calculations in multireactive and multicomponent systems. We have proposed new conditions for these equilibrium problems based on the theory of reactive variables of *Ung* and *Doherty.*[13] Also, we have tested and compared three equation-solving methods for performing those calculations, using our equilibrium conditions.

Formulation of new conditions for bubble and dew point calculations in multireactive mixtures

Ung and *Doherty*[13] showed that the Gibbs energy in a reactive system behaves as in a non-reac-

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tive system if transformed composition variables are used instead of the conventional composition variables. Using transformed compositions, we restrict the solution space to the compositions that are already in chemical equilibrium. This reduces the problem dimension by the number of independent reactions and makes it possible to represent phase equilibrium in reactive systems in a similar way as in non-reactive mixtures. So, the reactive phase diagrams look similar to the non-reactive ones and the non-reactive flash algorithms can be easily modified to account for the equilibrium reactions.[12] Also, *Ung* and *Doherty*[13] showed that the chemical potential follows all the thermodynamic relationships of a non-reactive system as long as all the thermodynamic properties are functions of the transformed composition variables. Considering this, equilibrium conditions among two phases of a reactive mixture, with n components and n_{R} independent chemical reactions, are met when

$$\frac{\Delta\hat{\mu}_i^{\alpha}}{RT} = \frac{\Delta\hat{\mu}_i^{\beta}}{RT} \quad i = 1,\ldots,n - n_{\mathrm{R}} \tag{1}$$

where

$$\frac{\Delta\hat{\mu}_i^{j}}{RT} = \frac{\Delta\hat{\mu}_i^{j}\{\hat{x}\} - \mu_i^0}{RT} \tag{2}$$

with R the universal gas constant, μ_i^0 the chemical potential of the pure component and $\hat{\mu}_i^j$ the transformed chemical potential of component i at phase j which is a function of the transformed mole fraction $\hat{x}$. Eq (2) can be expressed in terms of fugacity or activity coefficients as follows

$$\frac{\Delta\hat{\mu}_i}{RT} = \ln\left(\frac{x_i\hat{\varphi}_i\{\hat{x}\}}{\varphi_i}\right) = \ln(x_i\,\gamma_i\{\hat{x}\}) \quad i = 1,\ldots,n - n_{\mathrm{R}} \tag{3}$$

where x_i is the mole fraction of component i, $\hat{\varphi}_i$ is the fugacity coefficient of component i in the mixture, φ_i is the fugacity coefficient of the pure component, and γ_i is the activity coefficient of component i, respectively. Using Eq (1) and (3), we can deduce the following relation for mole fractions at phase equilibrium

$$x_i^{\beta} = x_i^{\alpha}\left(\frac{\hat{\varphi}_i^{\alpha}}{\hat{\varphi}_i^{\beta}}\right) = x_i^{\alpha}\left(\frac{\gamma_i^{\alpha}}{\gamma_i^{\beta}}\right) \quad i = 1,\ldots,n - n_{\mathrm{R}} \tag{4}$$

Then, we define the transformed phase equilibrium constant $\hat{K}_i$ as

$$\hat{K}_i\{\hat{x}_{\alpha},\hat{x}_{\beta}\} = \frac{\hat{\varphi}_i^{\alpha}}{\hat{\varphi}_i^{\beta}} = \frac{\gamma_i^{\alpha}}{\gamma_i^{\beta}} \quad i = 1,\ldots,n - n_{\mathrm{R}} \tag{5}$$

and the transformed mole fractions $\hat{x}_i$ are given by[8,9,13]

$$\hat{x}_i = \frac{\boldsymbol{x}_i - \boldsymbol{v}_i N^{-1}\boldsymbol{x}_{\mathrm{ref}}}{1 - \boldsymbol{v}_{\mathrm{TOT}} N^{-1}\boldsymbol{x}_{\mathrm{ref}}} 0 \quad i = 1,\ldots,n - n_{\mathrm{R}} \tag{6}$$

where $\boldsymbol{x}_{\mathrm{ref}}$ is the column vector of n_{R} reference component mole fractions, $\boldsymbol{v}_i$ is the row vector of stoichiometric number of component i for each reaction $\boldsymbol{v}_{\mathrm{TOT}}$, is a row vector where each element corresponds to reaction r and it is the sum of the stoichiometric number for all components that participate in reaction r, and N is a square matrix formed from the stoichiometric number of the reference components in the n_{R} reactions.[8,9,13] The reference mole fractions are calculated using Eq (6) and from the equilibrium constants for each reaction K'_{eq} by solving a system of n_{R} nonlinear equations given by

$$K'_{\mathrm{eq}} = \prod_{i=1}^{n} a_i^{v_i^r} \quad r = 1,\ldots,n_{\mathrm{R}} \tag{7}$$

where a_i is the activity of component i and v_i^r is the stoichiometric number of component i in reaction r, respectively. When we know the reference mole fractions, the remaining mole fractions are calculated using Eq (6).

We write the phase equilibrium condition in terms of transformed variables, using Eq (4) – (6), as follows

$$\hat{x}_i^{\beta} = \hat{x}_i^{\alpha}\hat{K}_i\theta + \delta_i \quad i = 1,\ldots,n - n_{\mathrm{R}} \tag{8}$$

and

$$\theta = \frac{1 - \boldsymbol{v}_{\mathrm{TOT}} N^{-1}\boldsymbol{x}_{\mathrm{ref}}^{\alpha}}{1 - \boldsymbol{v}_{\mathrm{TOT}} N^{-1}\boldsymbol{x}_{\mathrm{ref}}^{\beta}} \tag{9}$$

$$\delta_i = \frac{\boldsymbol{v}_i N^{-1}(\hat{K}_i\boldsymbol{x}_{\mathrm{ref}}^{\alpha} - \boldsymbol{x}_{\mathrm{ref}}^{\beta})}{1 - \boldsymbol{v}_{\mathrm{TOT}} N^{-1}\boldsymbol{x}_{\mathrm{ref}}^{\beta}} \quad i = 1,\ldots,n - n_{\mathrm{R}} \tag{10}$$

The material balance on component i is

$$\hat{x}_{\mathrm{F}.i} - (1 - \hat{x}_{\Phi}^{\beta})\hat{x}_i^{\alpha} - \hat{x}_{\Phi}^{\beta}\hat{x}_i^{\beta} = 0 \quad i = 1,\ldots,n - n_{\mathrm{R}} \tag{11}$$

and the transformed mole phase fraction $\hat{x}_{\Phi}^{\beta}$ is defined as

$$\hat{x}_{\Phi}^{j} = \frac{x_{\Phi}^{j}(1 - \boldsymbol{v}_{\mathrm{TOT}} N^{-1}\boldsymbol{x}_{\mathrm{ref}}^{j})}{(1 - \boldsymbol{v}_{\mathrm{TOT}} N^{-1}x_{\mathrm{Fref}})} \quad j = \alpha,\beta \tag{12}$$

where x_{Φ}^{j} is the conventional mole fraction of phase j whose feasible domain is (0, 1) and $\boldsymbol{x}_{\mathrm{Fref}}$ is the column vector of n_{R} reference component mole fractions in the initial overall composition. Using Eq (8) – (11), $\hat{x}_i^{\alpha}$ is given by

$$\hat{x}_i^{\alpha} = \frac{\hat{x}_{\mathrm{F},i} - \hat{x}_{\Phi}^{\beta}}{1 + \hat{x}_{\Phi}^{\beta}(\hat{K}_i\theta - 1)} \quad i = 1,\dots,n - n_{\mathrm{R}} \quad (13)$$

From the transformed mole fraction restriction $\sum_{i=1}^{n-n_{\mathrm{R}}} \hat{x}_{i,j} = 1$, we have

$$\sum_{i=1}^{n-n_{\mathrm{R}}} \left[\frac{\hat{K}_i\theta(\hat{x}_{\mathrm{F},i} - \delta_i \hat{x}_{\Phi}^{\beta})}{1 - \hat{x}_{\Phi}^{\beta} + \hat{K}_i\theta\hat{x}_{\Phi}^{\beta}} + \delta_i \right] - 1 = 0 \quad (14)$$

$$\sum_{i=1}^{n-n_{\mathrm{R}}} \left[\frac{\hat{x}_{\mathrm{F},i} - \hat{x}_{\Phi}^{\beta}\delta_i}{1 + \hat{x}_{\Phi}^{\beta}(\hat{K}_i\theta - 1)} \right] - 1 = 0 \quad (15)$$

By applying the conditions $\hat{x}_{\Phi}^{\beta} = 0$ and $\hat{x}_{\Phi}^{\beta} = 1$, we obtain the following new functions for bubble and dew point calculations in multireactive mixtures

$$f_{\text{bubble}} = 1 - \sum_{i=1}^{n-n_{\mathrm{R}}} (\hat{K}_i\theta\hat{x}_{\mathrm{F},i} + \delta_i) = 0 \quad (16)$$

$$f_{\text{dew}} = 1 - \sum_{i=1}^{n-n_{\mathrm{R}}} \left[\frac{\hat{x}_{\mathrm{F}} - \delta_i}{\hat{K}_i\theta} \right] = 0 \quad (17)$$

In contrast with other formulations,[11,15] our functions are independent of reaction extents and have fewer unknowns. Eq (16) and (17) are a function of temperature or pressure and $n - n_{\mathrm{R}}$ transformed mole fraction $\hat{x}_i$ of the liquid or vapor phase, respectively. On the other hand, these equilibrium problems are nonlinear and multivariable so that conventional numerical methods may present difficulties, such as poor initialization or divergence behavior. We have performed a comparison of three approaches to solve our bubble and dew point functions. In the next section we describe the strategies applied in this work.

Solution approaches

Simultaneous equation-solving with Newton method (SESN)

This is the classical approach used for performing flash calculations in non-reactive and reactive systems since it is conceptually simple and straightforward. The popular Newton method is used because it provides quadratic convergence when the initial estimates are close to the solution and it is readily available in computer programs.[16] Bubble and dew points are calculated by solving simultaneously the following $n - n_{\mathrm{R}}$ equations

$$F_i = \hat{x}_i^{\beta} - \hat{x}_i^{\alpha}\hat{K}_i\theta - \delta_i \quad i = 1,\dots,n - n_{\mathrm{R}} - 1 \quad (18)$$

$$F_{n-n_{\mathrm{R}}} = f_{\Phi^{\beta}} \quad (19)$$

where $f_{\Phi^{\beta}}$ is the bubble or dew point function, Eq (16) or (17), respectively. The unknowns are $n - n_{\mathrm{R}} - 1$ transformed mole fractions of vapor or liquid phase and the temperature or pressure. In this work, the above equations are solved using the Numerical Recipes Fortran subroutine NEWT.

Equation-decoupling with Successive Substitution method (EDSS)

This approach is often described in textbooks on thermodynamics for flash calculations in non-reactive mixtures and is based on the Rachford-Rice formulation. This method is reliable for flash calculations in non-reactive systems and has a linear rate of convergence.[16] The procedure used for bubble and dew point calculations in reactive systems is as follows: in the inner loop, we have applied a Newton method, using the Numerical Recipes Fortran subroutine NEWT, to update the temperature or pressure by solving Eq (16) or (17), while in the outer loop the transformed mole fractions are updated with a successive substitution method using Eq (8) or (13). In this work, we have not applied an acceleration technique for this approach.

Optimization approach using Simulated Annealing method (OSA)

We have tested an optimization technique for solving our equilibrium conditions. As indicated by *Henderson* et al.,[17] the formulation of thermodynamic calculations for optimization problems offers some advantages: a) the use of a robust optimization method, b) the possibility of using a direct optimization method which requires only calculations of the objective function and c) the use of an iterative procedure whose convergence is independent on the initial guess. Thus, the calculation of bubble and dew point conditions can be performed by minimizing the next objective function

$$f_{\text{obj}} = \sqrt{f_{\Phi^{\beta}}^2 + \sum_{i=1}^{n-n_{\mathrm{R}}} F_i^2} \quad (20)$$

where F_i is described by Eq (18) for $i = 1,\dots, n - n_{\mathrm{R}}$ and $f_{\Phi^{\beta}}$ is the bubble or dew point function, respectively. At the bubble and dew point conditions, the global minimum of the objective function must be zero, but we assume that a solution is found when we find the transformed mole fractions and temperature or pressure that make the value of the objective function less than $1 \cdot 10^{-6}$. The stochastic global optimization method Simulated Annealing (SA) is used to minimize our objective function. SA is inspired in the thermodynamic process of cooling of molten metals to achieve the lowest free energy state.[18] The SA algorithm presents ease of computational implementation and, if the values for its algorithm parameters are properly selected, it can converge to the global optimum independently of initial guesses. This optimization method has been successfully used in the resolution of several thermodynamic problems.[17,19–24] It is important to note that other phase equilibrium problems (e.g. calculations of critical points and homogeneous azeotropes) have been solved using an optimization approach coupled with the SA method.[17,24]

In our calculations, we have used the algorithm proposed by *Corana* et al.[25] because of its high reliability in thermodynamic calculations. In this algorithm, a trial point is randomly chosen within the step length *VM* (a vector of length *n* variables) of a starting point defined in the feasible domain of optimization variables. The function is evaluated at this trial point and its value is compared to its value at the initial point. The Metropolis criterion,[26] with a parameter called annealing temperature *T*, is used to accept or reject the trial point. If the trial point is accepted, the algorithm moves on from that point. If it is rejected, another point is chosen instead for a trial evaluation. Each element of *VM* is periodically adjusted so that half of all function evaluations in that direction are accepted. A fall in *T* is imposed upon the system with the *R T* variable by $T_{j+1} = R\,T \times T_j$, where *j* is the iteration counter and *R T* is the temperature reduction factor. Thus, as *T* declines, downhill moves are less likely to be accepted and the percentage of rejections rises. Given the scheme for the selection for *VM*, *VM* falls. Thus, as *T* declines, *VM* falls and SA focuses upon the most promising area for optimization. A full description of this algorithm is found in *Corana* et al.,[25] and the FORTRAN subroutine implemented by *Goffe* et al.[27] is used in this work.

The choice of the cooling schedule is a crucial aspect in the implementation of SA because it affects the numerical performance of the optimization procedure. Based on preliminary calculations, we propose the following values for the quantities of SA: $T_0 = 10.0$, $R\,T = 0.85$ and $N_T = 5$, where N_T is the iteration number before temperature reduction.

Results and discussion

For the present study, four examples are used to compare the numerical performance of the three equation-solving methods. In all examples, we have considered a tolerance of $1 \cdot 10^{-6}$ for the convergence of all methods. All examples are solved 25 times to evaluate the reliability and efficiency of solving methods, using in each time different random initial values for unknowns $\hat{x}_i, T$ or p. All calculations were performed on a Processor Intel Centrino 1600 MHz with 1.00 GB of RAM. The performance of the three equation-solving methods is tested using the following criterions: a) success rate of finding the bubble or dew point in the performed calculations, b) average number of $\hat{K}$-value evaluations and c) computation time.

Phase stability of all calculated bubble and dew points is evaluated by minimizing the tangent plane distance function for reactive mixtures[12]

$$\mathrm{RTPDF} = \sum_{i=1}^{n-n_R} \hat{x}_i (\hat{\mu}_i\{\hat{x}\} - \hat{\mu}_i\{\hat{x}_F\}) \qquad (21)$$

The RTPDF function is globally minimized using the Simulated Annealing method. *Bonilla-Petriciolet*[24] has tested the SA method with several reactive systems and found that this method is robust for reactive phase stability analysis. All calculated bubble and dew points are stable.

Example 1.
isobutene + methanol ⇔ methyl *ter*-butyl ether

Our first example is the equilibrium reaction of isobutene (1) and methanol (2) to produce methyl *ter*-butyl ether (3), $A_1 + A_2 \leftrightarrow A_3$. This system has been analyzed by *Okasinski* and *Doherty*,[28] *Maier* et al.[29] and *Harding* and *Floudas*[30] in the context of calculation of reactive homogeneous azeotropes. We have considered non-ideality in the liquid phase and ideal gas in the vapor phase. We use the Wilson equation for the activity coefficient in the liquid phase and the Antoine equation to calculate the properties of vapor phase. *Maier* et al.[29] report the parameters for both equations. The reaction equilibrium constant is assumed to be independent of temperature $K_{eq} = 0.04$, and methyl *ter*-butyl ether (MTBE) is the reference component so that the transformed mole fractions are $\hat{x}_1 = \dfrac{x_1 + x_3}{1 + x_3}$ and $\hat{x}_2 = \dfrac{x_2 + x_3}{1 + x_3} = 1 - \hat{x}_1$.. We use $\hat{x}_1$ and temperature as unknowns for all equation-solving methods. The initial values are randomly generated in the feasible domains of (0, 1) for $\hat{x}_1$ and (0.01, 300) °C for temperature. These domains are also used in the implementation of the OSA method. Bubble and dew point calculations are performed at different pressures for a feed of $\hat{x}_F(0.5, 0.5)$ and the results are reported in Tab 1. The numerical performance of tested methods appears in Tab 2. In all calculations,

Table 1 – *Bubble and dew point calculations for isobutene + methanol ↔ methyl ter-butyl ether. Wilson equation and ideal gas, K_{eq} = 0.04 and $\hat{x}_F$ (0.5, 0.5).*

p / atm	Dew point		Bubble point	
	T / °C	$\hat{x}_\alpha$	T / °C	$\hat{x}_\beta$
2	64.943	(0.0196, 0.9804)	13.944	(0.96245, 0.03755)
4	83.894	(0.02741, 0.97259)	36.425	(0.94082, 0.05918)
6	96.156	(0.03353, 0.96647)	51.356	(0.92324, 0.07676)
8	105.462	(0.03882, 0.96118)	62.859	(0.90804, 0.09196)

Table 2 – *Performance of equation-solving methods tested in bubble and dew point calculations in reactive systems Success rate in percent (No. of $\hat{K}$-values evaluations)*[1]

Example No.	T or p	Bubble point			Dew point		
		SESN	DESS	OSA	SESN	DESS	OSA
1	2atm	**16** (73)	100 (56)	100 (21089)	**16** (30)	100 (142)	100 (21345)
	4atm	**44** (72)	100 (52)	100 (21409)	**36** (54)	100 (59)	100 (21329)
	6atm	**44** (84)	100 (48)	100 (21265)	**20** (33)	100 (102)	100 (21145)
	8atm	**60** (84)	100 (43)	100 (21289)	**24** (44)	100 (106)	100 (21273)
2	50°C	**68** (55)	100 (371)	**96** (42977)	**4** (22)	100 (379)	100 (43297)
	70°C	**76** (53)	100 (247)	100 (43345)	**20** (32)	100 (275)	100 (43377)
	90°C	**68** (59)	100 (208)	100 (43297)	**40** (56)	100 (220)	100 (43505)
3	1atm	**76** (86)	100 (270)	100 (32341)	**4** (22)	100 (591)	100 (32677)
	5atm	**28** (50)	100 (329)	100 (31861)	**12** (29)	100 (420)	100 (32233)
	10atm	**64** (64)	100 (370)	100 (32005)	**8** (22)	100 (300)	100 (32449)
4	1atm	**28** (20)	**88** (92)	100 (21337)	**28** (23)	100 (49)	100 (21217)
	4atm	**36** (16)	**80** (46)	100 (21257)	**28** (24)	100 (33)	100 (21241)
	6atm	**28** (15)	**56** (40)	100 (21305)	**56** (23)	100 (27)	100 (21417)
	8atm	**28** (13)	**48** (35)	100 (21169)	**72** (24)	100 (35)	100 (21433)

[1] Both parameters are calculated based on 25 calculations with random initial values.

DESS and OSA methods find the bubble and dew points without problems while SESN diverged several times. We observe that SESN shows more failures in dew point calculations. These results indicated, that even for simple reactive systems, bubble and dew point calculations are challenging for classical equation-solving methods and require robust strategies. The number of $\hat{K}$-value evaluations of solving-methods is given by: OSA >>> DESS > SESN. Computation time maintains around of 6 s for OSA, 0.03 s for DESS and 0.02 s for SESN, respectively.

Example 2.

isobutene + methanol ⇔ methyl *ter*-butyl ether with *n*-butane as inert

In the second example, we use the same reaction as before but include n-butane (4) as an inert. *Ung* and *Doherty*,[9] *Harding* and *Floudas*[30] and *Maier* et al.[29] have also studied this reactive equilibrium problem. The transformed mole fractions for this mixture are $\hat{x}_1 = \dfrac{x_1 + x_3}{1 + x_3} . \hat{x}_2 = \dfrac{x_2 + x_3}{1 + x_3}$ and

Table 3 – *Bubble and dew point calculations for isobutene + methanol ⇔ methyl ter-butyl ether with n-butane as inert. Wilson equation and ideal gas.* x_z *(0.3, 0.3, 0.4)*

T / °C	Dew point		Bubble point	
	p / atm	$\hat{x}_\alpha$	p / atm	$\hat{x}_\beta$
50	1.950	(0.43001, 0.45659, 0.11341)	3.339	(0.12692, 0.12009, 0.75299)
70	3.834	(0.41602, 0.44792, 0.13606)	5.713	(0.14796, 0.14425, 0.70779)
90	7.006	(0.40177, 0.43648, 0.16176)	9.302	(0.16826, 0.17076, 0.66099)

$\hat{x}_4 = \dfrac{x_4}{1+x_3} = 1-\hat{x}_1-\hat{x}_2$, where the MTBE is the reference component. Again, the Wilson and Antoine equations are used for the calculation of thermodynamic properties. *Maier* et al.[29] report the parameters for both equations. The reaction equilibrium constant is determined from $\Delta G^0_{\text{rxs}} / R = -4205.05 + 10.0982\,T - 0.2667\,T \ln T$, where T is in K. For SESN and DESS methods, we use $\hat{x}_1, \hat{x}_2$ and T as unknowns while in the optimization approach, the objective function is minimized with respect to $\hat{x}_1, \hat{x}_2, \hat{x}_4$ and T. We set a feasible domain of (0, 1) for all the transformed mole fractions and (0.0001, 20) bar for pressure. The initials values are randomly generated in these domains. For OSA method, at each evaluation of the objective function, the transformed mole fractions are normalized to unity. We have analyzed an initial global composition of $\hat{x}_{\text{F}}(0.3, 0.3, 0.4)$. Tab 3 shows the results of bubble and dew point calculations at different temperatures and Tab 2 shows the performance of the three equation-solving methods. For this case, DESS shows 100 % reliability for the location of bubble and dew points at all tested temperatures, while OSA method fails only one time in all calculations performed. Again, SESN shows several failures in the location of reactive saturation conditions. For dew point calculations, the performance of SESN method is very poor. OSA method shows the highest computation time (22 s) while SESN and DESS showed a computation time of 0.08 and 0.11 s, respectively.

Example 3.

acetic acid + isopropanol ↔ isopropyl acetate + water

Third example is the formation of isopropyl acetate through esterification reaction of isopropanol and acetic acid: acetic acid (1) + isopropanol (2) ⇔ isopropyl acetate (3) + water (4). *Harding* and *Floudas*[30] and *Maier* et al.[29] have studied this system. For the liquid phase, we use activity coefficients from the NRTL equation and consider the association of acetic acid in the vapor phase, using a correction factor as suggested by *Maier* et al.[29] The correction factor ζ_i for the association is given by

$$\zeta_1 = \frac{1+(1+4k_1 p_1^{\text{sat}})^{1/2}}{1+[1+4kpx_1(2-x_1)]^{1/2}} \tag{22}$$

and

$$\zeta_i = \frac{2\{1-x_1+[1+4kPx_1(2-x_1)]^{1/2}\}}{(2-x_1)\{1+[1+4kPx_1(2-x_1)]^{1/2}\}} \quad \text{for } i = 2, 3, 4 \tag{23}$$

where p_i^{sat} is the saturation pressure of pure component i and the dimerization constant is calculated from $\log_{10} k = \log_{10} k_1 = -12.5454 + 3166/T$ with T in Kelvin and k and k_1 in Pa^{-1}. *Maier* et al.[29] gives the Antoine and NRTL equation parameters. The reaction equilibrium constant is independent of temperature, $K_{\text{eq}} = 8.7$, and water is the reference component. The transformed mole fractions are given by $\hat{x}_1 = \dfrac{x_1+x_4}{1+x_4}$, $\hat{x}_2 = \dfrac{x_2+x_4}{1+x_4}$ and $\hat{x}_3 = \dfrac{x_3-x_4}{1+x_4} = 1-\hat{x}_1-\hat{x}_2$. We use $\hat{x}_1, \hat{x}_2$ and T as unknowns for all methods. The initial values are randomly generated using the feasible domain (0, 1) for transformed mole fractions and (50, 200) °C for temperature. Bubble and dew point calculations are performed for a feed of $\hat{x}_{\text{F}}(0.5, 0.3, 0.2)$ at different pressures (see Tab 4 and Tab 2) shows the numerical performance of all tested methods. DESS and OSA methods are very reliable to find the bubble and dew point conditions and they did not show any failures in all the calculations performed. Again, SESN showed the worst performance and its numerical behavior is highly dependent on initial guesses. The mean number of $\hat{K}$-value evaluations is given by: SESN < DESS << OSA, while the computation time maintains around of 17 s for OSA, 0.2 s for DESS and 0.03 s for SESN.

Table 4 – *Bubble and dew point calculations for acetic acid + isopropanol ↔ isopropyl acetate + water. NRTL equation and ideal gas, K_{eq} = 8.7 and $\hat{x}_F$(0.5, 0.3, 0.2).*

p / atm	Dew point		Bubble point	
	T / °C	$\hat{x}_\alpha$	T / °C	$\hat{x}_\beta$
1	94.35	(0.70299, 0.1786, 0.11842)	85.55	(0.3791, 0.41569, 0.20522)
5	149.683	(0.63046, 0.14396, 0.22558)	138.272	(0.42525, 0.4785, 0.09625)
10	179.781	(0.59782, 0.13138, 0.27081)	166.451	(0.44323, 0.50417, 0.05260)

Example 4.

$A_1 + A_2 \leftrightarrow A_3$ and $2A_3 \leftrightarrow A_4 + A_2$

Our last example is a hypothetical quaternary system that follows the reactions: $A_1 + A_2 \leftrightarrow A_3$ and $2A_3 \leftrightarrow A_4 + A_2$. *Ung* and *Doherty*[9] have studied the phase equilibrium behavior of this mixture. We have considered ideal behavior for both liquid and vapor phases. The Antoine equation is used to calculate the vapor pressures of pure components with the parameters reported by *Ung* and *Doherty*.[9] The transformed mole fractions are defined using A_3 and A_4 as reference components, so they are given by $\hat{x}_1 = \dfrac{x_1 + x_3 + 2x_4}{1 + x_3 + 2x_4}$ and $\hat{x}_2 = \dfrac{x_2 + x_3 + x_4}{1 + x_3 + 2x_4} = 1 - \hat{x}_1$. The chemical equilibrium constants are calculated using $K^1_{\text{eq}} = \exp\left(-22.57 + \dfrac{7368}{T}\right)$ and $K^2_{\text{eq}} = \exp\left(-7.0265 + \dfrac{6844.1}{T} - \dfrac{1391790}{T^2}\right)$, where T is given in Kelvin. We use $\hat{x}_1$ and temperature as unknowns and their feasible domains are (0, 1) and (273.15, 400) K, respectively. Random initial values are generated inside these domains. Bubble and dew point calculations are performed for a feed $\hat{x}_\text{F}$(0.5, 0.5) at several pressures. The results of phase equilibrium calculations appear in Tab 5 and performance of all tested methods are reported in Tab 2. Only, the OSA method showed 100 % reliability to locate the bubble and dew points in this reactive system, however, it showed the highest computation time (3.3 seconds) and the highest mean number of $\hat{K}$-values evaluations. On the other hand, several failures are reported for the DESS and SESN methods. For non-reactive systems, *Michelsen*[31] has indicated that bubble and dew point calculations using hybrid models rarely present convergence problems. However, our results show that this doesn't apply for phase equilibrium calculations in reactive systems. Even for simple reacting systems, SESN and DESS methods present convergence problems and depend on the initial guesses. The OSA method is very reliable to find the bubble and dew points and its performance is almost independent of initial values. However, we can not offer a theoretical guaranty for the location of bubble and dew points using this optimization approach.

Finally, we have tested the performance of these equation-solving methods with other reactive systems reported by *Okasinski* and *Doherty*,[28] *Harding* and *Floudas*[30] and *Maier* et al.;[29] and the results, not reported in this paper, indicated that OSA and DESS methods are reliable strategies for the calculation of dew and bubble points in multireactive mixtures.

Conclusions

New conditions for bubble and dew point calculations in multireactive mixtures have been derived in terms of the variable transformation theory of *Ung* and *Doherty*.[13] We have tested and compared the numerical performance of three equation-solving meth-

Table 5 – *Bubble and dew point calculations for a hypothetical quaternary mixture A_1+A_2 ↔ A_3 and $2A_3$ ↔ A_4+A_2. Ideal solution and ideal gas. $\hat{x}_F$(0.5, 0.5)*

p / atm	Dew point		Bubble point	
	T / K	$\hat{x}_\alpha$	T / K	$\hat{x}_\beta$
1	355.488	(0.02678, 0.97322)	306.95	(0.96045, 0.03955)
4	395.265	(0.0452, 0.9548)	328.17	(0.97759, 0.02241)
6	409.034	(0.05399, 0.94601)	337.393	(0.97911, 0.02089)
8	419.525	(0.06133, 0.93867)	345.829	(0.97829, 0.02171)

ods in the calculation of bubble and dew points using the new equilibrium conditions. Our results indicate that an optimization approach using Simulated Annealing is very reliable for this kind of phase equilibrium calculations in multireactive systems. However, it shows the highest computation time. In the other hand, the equation-decoupling method with successive substitution also presents a good numerical performance and is efficient. It is clear that the simultaneous equation solving approach, using Newton method, is not suitable for bubble and dew point calculations in reactive systems because it can diverge very frequently and depends significantly on initial values.

Based on reliability, we consider that the optimization approach using Simulated Annealing is the most suitable method and preferable choice for these equilibrium calculations in reactive systems, due to its acceptable convergence speed, and that initial guesses are not required. We will extend this procedure for performing these equilibrium calculations using equations of state.

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Notation

a – activity, mol dm^{-3}
n – number of components
K_{eq} – chemical equilibrium constant
K – transformed phase equilibrium constant
N – iteration number
p – pressure given in atm, 1 atm = 101 325 Pa
n_R – reaction number
R – universal gas constant, J mol^{-1} K^{-1}
T – temperature given in °C or K
ν_i^r – stoichiometric number of component i
$\hat{x}$ – transformed mole fraction, 1
x – mole fraction, 1
$\hat{x}_F$ – transformed feed composition, 1
x_F – feed composition, 1
$\hat{x}_\Phi$ – transformed phase mole fraction, 1
VM – vector length

Greek letters

α, β – phase at equilibrium
μ – chemical potential, J mol^{-1}
γ – activity coefficient, 1
φ – fugacity coefficient, 1

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F – feed composition
ref – reference component
Φ – phase

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