The object of this column is to enhance our readers' collections of interesting and novel problems in chemical engineering. Problems of the type that can be used to motivate the student by presenting a particular principle in class, or in a new light, or that can be assigned as a novel home problem, are requested, as well as those that are more traditional in nature and that elucidate difficult concepts. Manuscripts should not exceed 14 double-spaced pages and should be accompanied by the originals of any figures or photographs. Please submit them to Professor James O. Wilkes (e-mail: wilkes@umich.edu), Chemical Engineering Department, University of Michigan, Ann Arbor, MI 48109-2136.

COMPUTING LIQUID-LIQUID PHASE EQUILIBRIA:

An Exercise for Understanding the Nature of False Solutions and How To Avoid Them

María del Mar Olaya, Isabel Ibarra, Juan A. Reyes-Labarta,
María Dolores Serrano, and Antonio Marcilla
University of Alicante • Alicante, Spain 03080

One major objective of a thermodynamics course is to introduce the modeling of vapor-liquid equilibrium (VLE) and liquid-liquid equilibrium (LLE). The analysis of flash methods used to obtain this equilibrium data involves the simultaneous solution of a set of equilibrium and mass balance equations. When these methods are used for LLE, finding the equilibrium solution can be difficult, as different problems can arise. For example, the solutions may be very sensitive to the objective function, the initial-guess values, and the algorithm used in the optimization method.

Many papers in the past have discussed different aspects and strategies proposed to solve the LLE calculations. Information published in scientific papers, however, covers different and very specific aspects, and the topic is complex, making it very difficult to extract general and clear conclusions about the best procedure to evaluate LLE data. Nowadays, on the other hand, the commercial process simulators—such as Aspen Plus, Hysys (Aspen Tech), and ChemCAD (Chemstations)—include phase equilibrium calculation strategies capable of overcoming the above important difficulties, but they do not include details about their internal calculations. Process simulators are introduced to and used by students in different graduate courses, but these computer tools are not useful for comprehension of the phase equilibrium problem.

This paper presents an exercise for chemical engineering students in LLE data calculations, and shows limitations of

Antonio Marcilla *is a professor of chemical engineering at Alicante University. He has presented courses in Unit Operations, Phase Equilibria and Unit Operations, and Chemical Reactor Laboratories. His research interests are pyrolysis, liquid-liquid extraction, polymers, and rheology. He is also currently involved with the study of polymer recycling via catalytic cracking and the problem of simultaneous correlation of fluid and condensed phase equilibria.*

María del Mar Olaya *completed her B.S. in chemistry in 1992 and Ph.D. in chemical engineering in 1996. She teaches a wide range of courses from freshman to senior level at the University of Alicante, Spain. Her research interests include phase equilibria calculations and polymer structure, properties, and processing.*

Juan A. Reyes-Labarta *received both his B.S. and Ph.D. in chemical engineering in 1993 and 1998, respectively, at the University of Alicante (Spain). After post doctoral stays at Carnegie Mellon University (USA) and the Institute of Polymer Science and Tecnology-CSIC (Spain), he is now a full-time lecturer in Separation Processes and Molding Design.*

Isabel Ibarra and María Dolores Serrano *are recent chemical engineering graduates of the University of Alicante. They are currently postgraduate students, working on different aspects of phase equilibria.*

the isoactivity criterion as the unique search condition. This criterion is combined with the common tangent line condition to prevent false equilibrium solutions, in a way that is easy for graduate students to program, for example, in EXCEL. Also, an adaptation of the vector method proposed by Eubank, et al.,[1] has been used for LLE calculations, showing some interesting aspects that can be discussed in postgraduate courses on phase equilibria.

THEORETICAL BACKGROUND

The two usual approaches for solving phase equilibrium problems are the K-value method, where a set of material balances and equilibrium equations are solved simultaneously, and the Gibbs energy minimization (GEM) method.[2]

K-Value Method

At constant temperature (T) and pressure (p), a heterogeneous closed system, consisting of P phases and c components, is in equilibrium when the following condition is satisfied:

$$\mu_i^I = \mu_i^{II} = ... = \mu_i^P \qquad (1)$$

where μ_i^P is the chemical potential of the component i in phase P.

For two liquid phases (I and II), Eq. (1) can be written as:

$$a_i^I = a_i^{II} \quad \text{or} \quad \gamma_i^I x_i^I = \gamma_i^{II} x_i^{II} \qquad (2)$$

where a_i^P, γ_i^P, x_i^P are the activity, activity coefficient, and molar fraction of the component i in phase P, respectively. Alternatively, Eq. (2) can also be written as $K_i = x_i^{II} / x_i^I = \gamma_i^I / \gamma_i^{II}$, where K_i is the phase equilibrium constant for the component i.

Consider the problem when calculating compositions of conjugated liquid phases that are obtained from a heterogeneous ternary mixture, M. To solve the problem, mass balances and equilibrium conditions [Eq. (2)] should be combined.

Models such as NRTL or UNIQUAC, which can be used to calculate the activity coefficient, need the values of binary interaction parameters A_{ij} (six parameters for a ternary system). The DECHEMA Chemistry Data Series[3] collects such parameters for most published phase equilibrium data.

Gibbs Energy Minimization Method

The two-liquid phases and the c-component equilibrium problem can be interpreted geometrically in the dimensionless Gibbs energy of mixing ($G^M/RT=g^M$) vs. composition space. In this context, the solution requires determination of the minor common tangent line/plane/hyperplane to the G^M/RT curve/surface/hypersurface at two points (compositions)—without intersections to such curve/surface/hypersurface. The latter condition ensures a global minimum solution to the LLE problem. Therefore, the phase equilibria solution minimizes the total Gibbs energy of the system. Three principal algorithms have been proposed to solve the total GEM problem:

a. *The tangent line/plane method by Michelsen[4] and Iglesias-Silva, et al.[2]*

b. *The maximum area method developed by Eubank, et al.,[1] and Elhassan, et al.[5]*

c. *The equal area method of Eubank and Hall.[6]*

SOME PROBLEMS IN THE LLE CALCULATIONS USING THE K-VALUE METHOD

The usual engineering approach for solving phase equilibrium problems is to use the K-value procedure. This method, however, often fails because of the computational procedure. For example, if the initial guesses for the iterative procedure are too far from the correct solution, the program converges to a local minimum rather than to a global one. Therefore, the K-value method can predict a wrong phase equilibrium. Only one solution, however, minimizes the total Gibbs energy. For binary systems, K-values succeed even with poor initial guesses, but for more complex systems, Gibbs energy minimization is preferable.

The high nonlinearity of the equations in NRTL or UNIQUAC is one of the reasons for the high sensitivity of solutions to initial-guess values and to the algorithm used in the optimization method. There is another reason not often mentioned, that can also cause problems in finding the LLE solution. It is desirable that the dimensionless mixture Gibbs energy function (G^M/RT) give a very good definition of the two equilibrium points, as is shown in Figure 1(side a) for a binary system, where the points with the lower common tangent line are clearly defined. We have, however, verified that

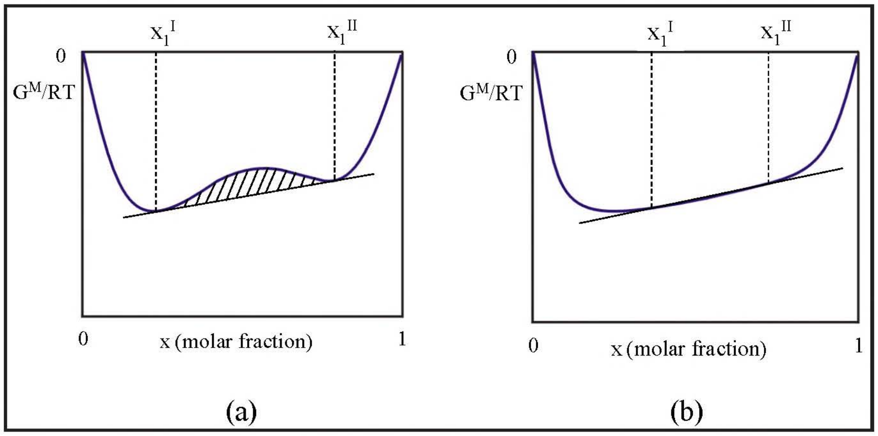

Figure 1*. Different possibilities for dimensionless Gibbs energy of mixing (G^M/RT) for a binary system: a) good definition, and b) poor definition of the equilibrium points.*

for many systems the G^M/RT function obtained with NRTL or UNIQUAC models is very linear between equilibrium points [Figure 1 (side b)]. This poor definition of the equilibrium solution can have dramatic consequences in the tie-line calculations, but the dimension of the problem also depends on the algorithm used to find the equilibrium solution.

The K-value method is affected by this problem. The consequence on LLE calculations in ternary systems, for example, is that many solutions corresponding to very low values of the activity objective function

$$\text{O.F.(a)} = \sum_{i=1}^{3} (a_i^{I} - a_i^{II})^2 \qquad (3)$$

can be obtained and, therefore, wrong tie-lines are calculated. On the other hand, the probability of this problem arising increases when equilibrium compositions are closer to each other.

An Example

The following example illustrates this problem: the methanol (1) + diphenylamine (2) + cyclohexane (3) system at 25 °C. More precisely, the tie-line obtained from the global mixture M (z_1 = 0.5365; z_2 = 0.0230; z_3 = 0.4405) will be calculated. The NRTL model is used to calculate the activity coefficients, with α=0.2 and the values for the binary interaction parameters obtained from DECHEMA Chemistry Data Series[3] (Table 1).

The Solver package of Microsoft Excel 2000, accessible to all the students at Alicante and very easy to use, has been used to solve the problem. In Figure 2, some of the solutions obtained using different initial-guess values are shown together with the experimental data. Obviously, only one of the calculated solutions corresponds with the true tie-line. For this system, there is not a good agreement between experimental and calculated tie-lines. This fact is not relevant for our discussion, but is only an example of the limitations of the NRTL model. What we are concerned with is how wrong tie-lines can be obtained that correspond with very low values of the activity objective function (*i.e.* O.F.(a)<10^{-12}). Even in this example, if the true calculated tie-line is considered with five significant figures for the molar fractions, the value of the objective function is O.F.(a) = $8.75 \cdot 10^{-10}$, higher and worse than those obtained for false calculated tie-lines.

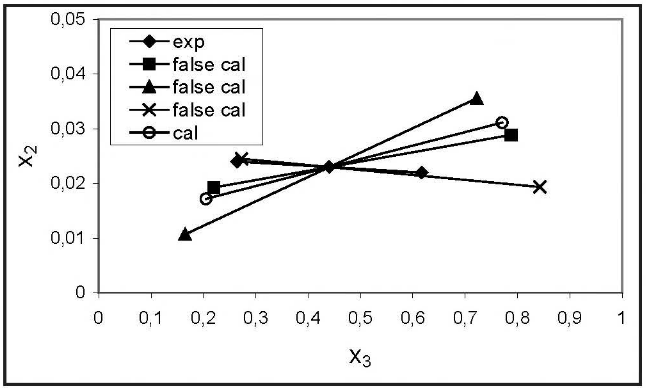

Figure 2. *Comparison between tie-lines: experimental and calculated with NRTL. False calculated tie-lines are included corresponding to O.F.(a)<10^{-12}.*

TABLE 1
NRTL Binary interaction parameters (K) for methanol (1) + diphenylamine (2) + cyclohexane (3) at 25 °C.

A12= 873.57	A21= -1245
A13= 379.39	A31= 578.07
A23= -987.32	A32= -856.11

The previous example shows that sometimes the isoactivity criterion is not sensitive enough to calculate equilibrium data and, as a consequence, problems in finding the true solution can arise depending on the method or algorithm used for the optimization.

MODIFICATION OF K-VALUE METHOD FOR LLE CALCULATIONS

The K-value method can be modified to avoid false solutions and converge more efficiently to the equilibrium solution. A possible modification adds another contribution to the objective function, which considers the deviation of the minor tangent line to the G^M/RT curve common to two compositions, obtained in the sectional plane that contains the two points considered as potential equilibrium points in each iteration.

When the true tie-line is calculated, both of the following conditions are satisfied:

1. *The activities of the three components in the two liquid phases are equal (isoactivity).*
2. *The two liquid phases have a common tangent line to the g^M curve.*

Therefore, the difference between false and true tie-lines, all with very low activity objective function values, is that false tie-lines have no common tangent line. We have checked this second contribution to the objective function, and found it is much more sensitive to very small deviations of the tie-line. The common tangent line contribution to the objective function is:

$$\text{O.F.(t)} = \left[\left(\frac{\partial g^M}{\partial x_3}\right)^{I}_{p,T,D} - \left(\frac{\partial g^M}{\partial x_3}\right)^{II}_{p,T,D}\right]^2 + \left[\left(g^{MI} - g^{MII}\right) + \left(\left(\frac{\partial g^M}{\partial x_3}\right)^{II}_{p,T,D} - \left(\frac{\partial g^M}{\partial x_3}\right)^{I}_{p,T,D}\right) x_3\right]^2 \qquad (4)$$

where D is the slope of the line through the points I and II, calculated as

$$D = \frac{x_2^{II} - x_2^{I}}{x_3^{II} - x_3^{I}} = \frac{x_2^{M} - x_2^{I}}{x_3^{M} - x_3^{I}} \qquad (5)$$

This means the partial derivatives of the dimensionless Gibbs energy of mixing (g^M) are calculated in the direction given by the line from I to II compositions, one that also contains the overall mixture M.

The combined objective function

$$\text{O.F.} = \text{O.F.(a)} + \text{O.F.(t)} \qquad (6)$$

is sharper than the activity objective function, improving the convergence of the optimization and avoiding false solutions. This will be illustrated using the example previously presented. When the same calculation has been carried out, but the activity objective function [O.F.(a)] changed to the combined objective function (O.F.) that also considers the common tangent line condition [O.F.(t)], the true tie-line is always calculated far from the solution—even with bad initial guesses.

For a better understanding of the behavior of both objective functions, we have calculated and represented the minimum values of both functions [O.F.(a) and O.F.] around the solution (Figure 3) using a sheaf of straight lines (defined by the α-angle) passing through the common point corresponding to the composition of the ternary global mixture M, very similar to the vector method explained in the next section.[1]

Figure 3 shows that for all the α-angles around the true tie-line solution it is possible to find two conjugated points that satisfy the mass balance and give a very low activity objective function value: O.F.(a)<10^{-12}. These results show the magnitude of the problem, from which two very important consequences can be derived:

1. *When the isoactivity criterion is used as the equilibrium condition, we should be very strict in the requirements for activity equalities.*
2. *The addition of the common tangent line objective function to the isoactivity condition improves convergence of the optimization because a sharper minimum is obtained (Figure 3).*

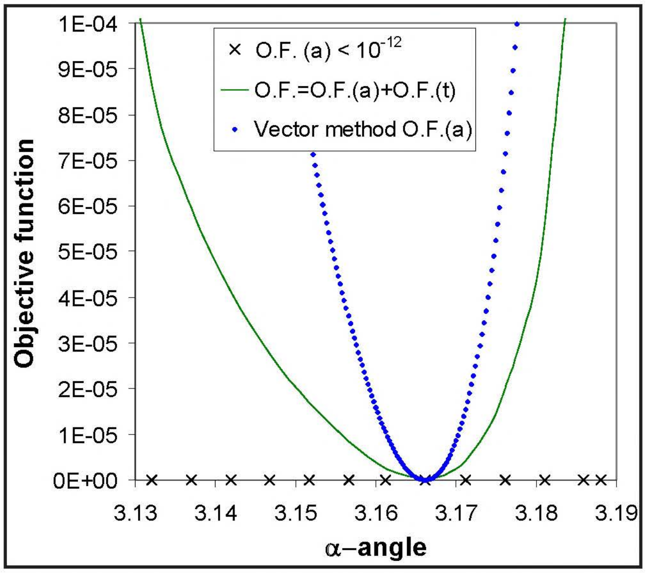

Figure 3. *Objective function values [O.F.(a), O.F., and O.F.(a) using the vector method] vs. α-angle for the ternary tie-line calculation example.*

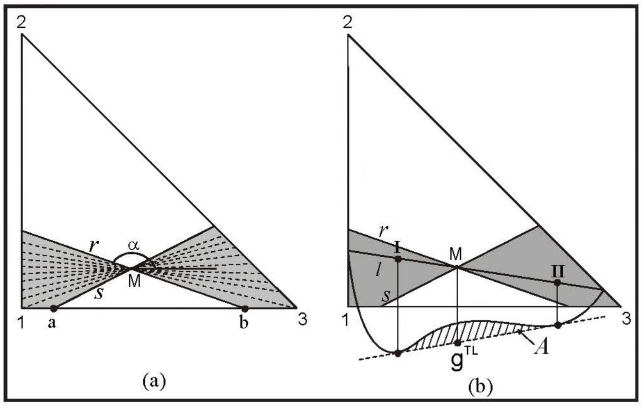

Figure 4. *(a) Graphical explanation of the vector method proposed to calculate the tie-line obtained from the initial mixture M. (b) Scheme showing the G^M/RT curve in a line l between r and s, and the two common tangent points I and II.*

THE VECTOR METHOD FOR LLE CALCULATIONS

The vector method is not an alternative equilibrium condition, but a method for directing or controlling the search for the unknown compositions to find the true tie-line. The vector method needs an equilibrium condition such as the isoactivity criterion, the minimization of the global Gibbs energy of mixing, or the common tangent plane.

In the previous calculations, the iterative procedure to obtain the unknown compositions is directed by the optimization algorithms included in the Solver. Therefore, in those calculations, the vector method has only been used as a tool to study the values of different objective functions in the area around the solution. In this section, a different procedure to calculate the tie-line has been evaluated. In this procedure, an adaptation of the vector method proposed by Eubank, et al.,[1] is used as a guided LLE search. This method is schematically represented in Figure 4.

Consider the ternary system 1-2-3, where the binary 1-3 is partially miscible and the other two binaries, 1-2 and 2-3, are completely miscible. The problem is to find the LLE tie-line that connects the compositions generated from the heterogeneous global mixture M. The tie-line for the 1-3 binary system must be previously known [*i.e.*, a, b in Figure 4(a)]. If not, it will be calculated using, for example, the isoactivity criterion. With the binary tie-line and the initial mixture M, the two lines, r and s, are obtained, which limit the zone where the ternary tie-line (if it exists) will be confined (shaded area in the Figure 4(a)). The α-angle is defined to characterize any lines from r to s with the common point M. This is a modification of the procedure presented in the original paper, where the α-angle (-90°,+90°) was not limited. The benefit is that the tie-line search is restricted to a more limited area, where the solution is probably located, improving the convergence of the calculation. In any of the lines (l) between r to s, the dimensionless mixture Gibbs energy function (g^M) can be calculated using, for example, the NRTL equation for excess contribution.

At this point, Eubank, *et al.*,[1] proposed the area method. For a constant value of the α-angle, this method consists of locating the two points (I and II in Figure 4(b)) where the area (A) confined between the tie-line and the g^M is the largest in absolute value. This condition is equivalent to locating the two points with the lower common tangent to the g^M function on the fixed direction, l. Next, the α-angle for the tie-line must be found using an equilibrium condition. There are several conditions that can be used as the LL equilibrium condition, when common tangent points such as I and II are calculated as a function of the α-angle value.

Representative conditions are:

1. *The isoactivity condition.*
2. *The minimization of the overall Gibbs energy of mixing.*
3. *The minor common tangent plane criterion.*

In this respect, note that the global maximum of the area A, among all maxima obtained at different α-angles, is not an equilibrium condition to find the tie-line α-angle, as discussed by Elhassan, *et. al.*[5]

Next, the results obtained from combining the vector method with two different equilibrium conditions—isoactivity, and minimization of the overall Gibbs energy of mixing—are presented for the example previously discussed.

The Isoactivity Condition

In Figure 3, the values of the activity objective function, O.F.(a) using the vector method calculated by comparing the two points with a minor common tangent line for different values of the α-angle, have been graphically represented as a function of the α-angle for the methanol (1) + diphenylamine (2) + cyclohexane (3) system at 25 °C, and the mixture point of the previous example. The comparison in Figure 3 of the three different approaches used to find the ternary tie-line shows that a sharper minimum, corresponding with the "true" tie-line obtained from the global mixture considered, is obtained when the vector method is used. Using this method, the true solution is obtained without multiple or false solution problems.

On the other hand, it is very important to underline that when the vector method is used both the isoactivity and common tangent line conditions are not simultaneous [as is the case of Eq. (6)] but sequential:

1. *The two compositions I and II in Figure 4, with the minor common tangent line, are obtained for each α-angle.*
2. *The minimum of the activity objective function, calculated comparing these two compositions [Eq. (3)], as a function of the α-angle, is located using,* e.g., *the Newton-Raphson method.*

Therefore, when the isoactivity condition is combined with the common tangent line criterion, either simultaneously [Eq. (6)] or sequentially (vector method), a more efficient equilibrium calculation can be carried out, avoiding false solutions with very low values of the activity objective function.

Minimization of Overall Gibbs Energy of Mixing

The vector method with the equilibrium condition based on the minimization of the overall GEM has also been evaluated. When the lower common tangent points to the (g^M) function are obtained in each line from r to s, the value of the dimensionless GEM for the overall composition M can be calculated (g^{TL} in Figure 4(b) where TL denotes the tangent line). The minimum of the g^{TL} curve vs. α-angle corresponds with the minimization of the global Gibbs energy and, therefore, with the true tie-line obtained from the overall composition M. The results obtained applying this procedure to the previous example are shown in Figure 5. The procedure converges to the solution without false tie-line problems. The false tie-lines obtained for this system using only the isoactivity criterion have also been included in Figure 5.

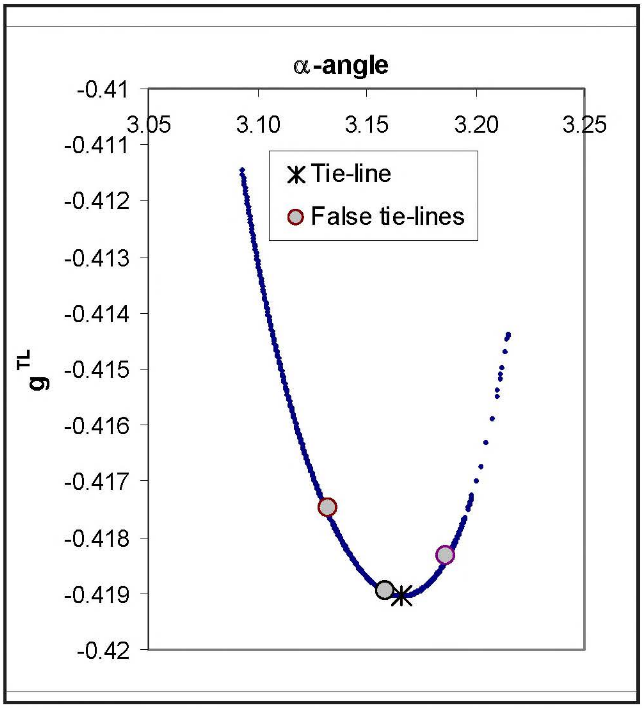

Figure 5. *Dimensionless global Gibbs energy of mixing obtained from the common tangent line (g^{TL}) as a function of the α-angle for the ternary tie-line calculation example.*

TOPOLOGICAL ANALYSIS OF TERNARY G^M CURVES AND SURFACES

The MATLAB (MathWorks, Inc.) tool for the three-dimensional representations is used by the students to represent the dimensionless GEM (g^M) in all the composition space. Figures obtained are discussed in the computer laboratory, while looking for the best views to see the most important topological aspects of this function. In Figure 6, one of these representations is shown as an example that corresponds with the system methanol (1) + diphenylamine (2) + cyclohexane (3) at 25 °C. The g^M surface for this system is very flat, which favors the false solution appearance. The three false tie-lines for this system have been included and a magnification is shown.

Furthermore, the sectional plane of these 3D figures passing through the calculated tie-line can be represented to validate the tangent line condition and show the form of the G^M/RT surface in the direction of the tie-line.

CONSTRUCTION OF LLE DIAGRAMS

After one of the previous strategies for calculating one tie-line is implemented in the computer, the construction of LLE diagrams is carried out by the successive calculation of tie-lines, until the homogeneous region is reached. For example, the procedure sketched in Figure 7 can be used to obtain the next tie-lines. After the first ternary tie-line is calculated from the initial mixture M_1, its middle point is obtained and a new initial mixture point M_2 is considered, maintaining the same ratio of molar fractions in components 1 and 3, and increasing component 2 by a constant amount (Δx_2). The new initial mixture, M_2, will be the heterogeneous composition for the calculation of the second ternary tie-line, and so on for mixture points M_3, M_4, M_5, . . . until the homogeneous region is reached.

If the vector method is used for the LLE calculation, the maximum and minimum values of α-angles that limit the area where the solution is confined must be calculated using the information of the previous tie-line calculated. As an example, in Figure 7 this area is shown where the tie-line passes through the initial mixture M_2, where the limiting lines, r_2 and s_2, are obtained connecting the point M_2 with the conjugated phases of the first tie-line through M_1 (*i.e.*, a_1, b_1), previously obtained.

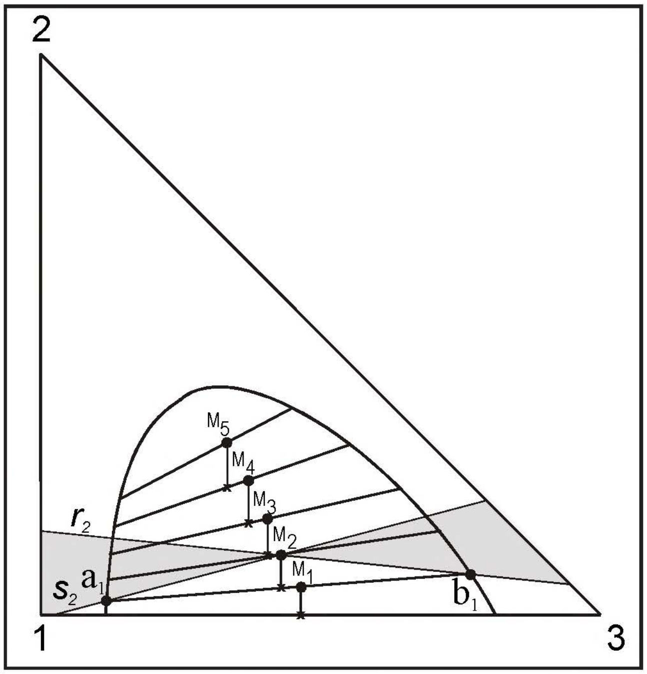

***Figure 7.** Graphical explanation of a possible method to set new initial mixtures to construct the entire LLE diagram.*

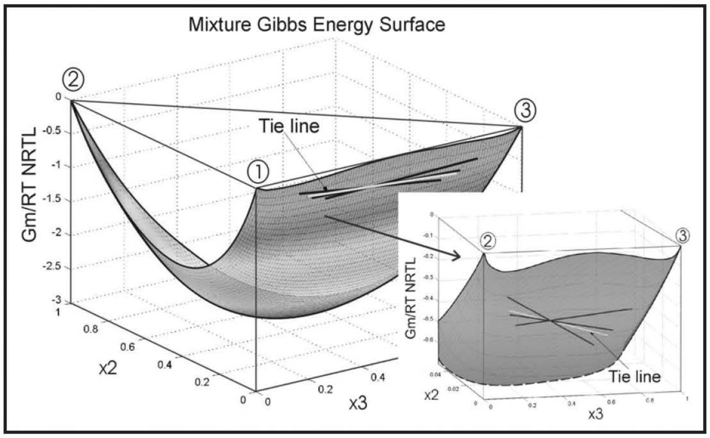

***Figure 6.** Representation of G^M/RT surface for methanol(1) + diphenylamine(2) + cyclohexane(3) at 25 °C, using the NRTL equation, and a magnification of the region where the true and false tie- lines are located.*

This sequential procedure finishes when the overall mixture, M_i, is in the single-phase region. To detect this situation, we propose evaluating the sign of the second derivative of g^M to know whether two common tangent points exist. The method we use is an extension for ternary systems of the condition for the stability of a binary mixture.

For a homogeneous binary mixture at constant T and p, the second derivative is always positive [Figure 8(a), next page]:

$$\left(\frac{\partial^2 g^M}{\partial x^2}\right)_{p,T} > 0 \qquad (7)$$

On the contrary, for a global mixture that splits into two liquid phases, the second derivative has negative values. To be exact, the negative area in the representation of $(\partial^2 g^M / \partial x^2)_{P,T}$ vs. x corresponds to compositions located between the two inflections points, A and B, on the g^M curve shown in Figure 8(b).

This property of the second derivative can be extended to the ternary systems and adapted to the vector method.

For a constant value of the α-angle (or the slope D), the system can be considered as pseudobinary and, therefore, if the second derivative $(\partial^2 g^M / \partial x^2)_{p,T,D}$ is always positive in the sectional plane that corresponds with the α-angle set, no two common tangent points to the g^M will be found. The situation will be similar to that represented in Figure 8(a) for a binary system, and the next α-angle value will be considered for the tie-line search. When the mixture point, M, is within the single-phase region, the sign of the second derivative is always positive for all the values of the α-angle, from the minimum to the maximum one, and the tie-line calculation procedure has finished.

Also, we use the second derivative criterion with another different purpose, to limit the composition values where the two common tangent points must be located. For example, if the situation shown in Figure 8(b) is considered, the search will be confined to the compositions from x = 0 to the point A, for one phase, and from the point B to x=1 for the conjugated phase. Therefore, the compositions located between the two inflection points represented as A and B are removed from the calculations, thus avoiding possible trivial and false solutions and making the convergence of the calculations easier.

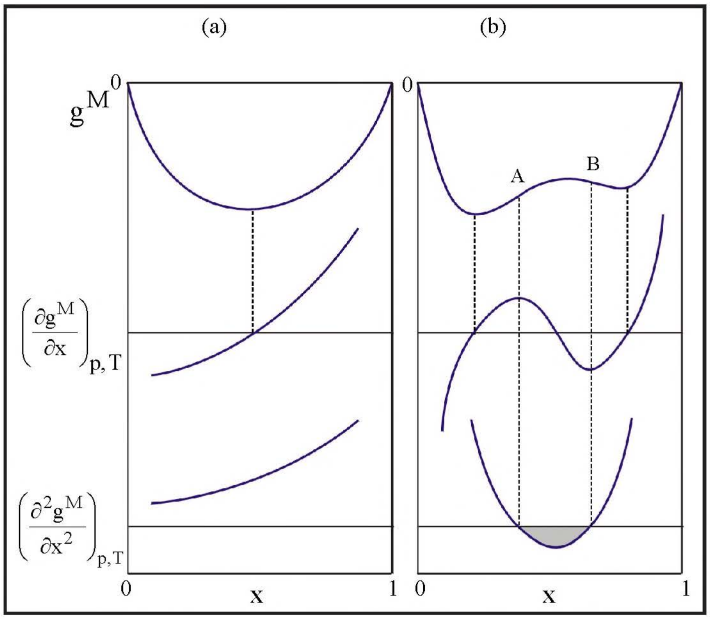

Figure 8. *Variation of g^M, $(\partial g^M / \partial x)_{p,T}$ and $(\partial^2 g^M / \partial x^2)_{p,T}$ with composition for a binary system: (a) completely miscible binary, and (b) partially miscible.*

Considering all the information previously presented, students construct the LLE diagram of the methanol (1) + diphenylamine (2) + cyclohexane (3) ternary system at 25 °C, used to illustrate all the different parts discussed here. The results obtained are available on the Web (<http://iq.ua.es/~gcef/SM_TF1S.pdf>) as supplementary data to this paper, in Table 1S. Furthermore, sectional planes passing through the calculated tie-lines in Table 1S are represented in Figure 1S for the best view of the g^M function, and also to validate the results obtained from the common tangent line criterion viewpoint. For all sectional planes that contain the ten calculated tie-lines, the equilibrium points have a common tangent line to the g^M curve. This is a necessary, but not sufficient condition, for ternary LLE and can be helpful to reject false solutions.

Also, in the evolution of tie-lines 1 to 10, students can observe how the cavity between the Gibbs energy curve and the common tangent line is decreasing [lined area in Figure 1(a), showing how the LL region is disappearing, the limit situation being similar to that represented in Figure 1(b)]. The difficulties found in calculating tie-lines very close to the plait-point are explained in this context.

CONCLUSIONS

An exercise to compute LLE data and to construct the phase diagram for ternary systems is presented. The NRTL equation is used to model the activity coefficient, but any other model can be used and the same conclusions would be made. Some problems are illustrated that arise when the isoactivity equilibrium condition is used in the LLE calculations. A much more efficient condition is obtained when isoactivity is combined with the common tangent line criterion, avoiding false solutions that correspond with very low values of the activity objective function. The Solver optimization tool included in the Excel worksheet can be used by students to solve this LLE exercise. The successive calculation of tie-lines allows the students to obtain the ternary composition diagram. Also, 3D figures are represented to discuss the topological aspects of the dimensionless Gibbs energy of mixture function (g^M) and to validate the results obtained from checking the common tangent line criterion. Two ideas should be emphasized:

1. *The isoactivity condition must be used very carefully for LLE to avoid false solutions.*
2. *The topological concepts related with the equilibrium condition formulated on the basis of the G^M/RT function are very useful to validate the obtained solutions.*

ACKNOWLEDGMENTS

The authors wish to thank the Generalitat Valenciana and the University of Alicante for financial support of projects GV05/191 and GRE04-17, respectively.

REFERENCES

1. Eubank, P.T., A.E. Elhassan, M.A. Barrufet, W.B. Whiting, *Ind. Eng. Chem. Res.*, **31**, 942-949 (1992)
2. Iglesias-Silva, G.A., A. Bonilla-Petriciolet, P.T. Eubank, J.C. Holste, and K.R. Hall, *Fluid Phase Equilibria,* **210**, 229-245 (2003)
3. Sorensen, J.M., and W. Arlt, *Chemistry Data Series* DECHEMA, Franckfurt (1980)
4. Michelsen, M.L. *Fluid Phase Equilibria* 9, 1-20, 21-35 (1982)
5. Elhassan, A.E., S.G. Tsvetkov, R.J.B. Craven, R.P. Stateva, and W.A. Wakeham, *Ind. Eng. Chem. Res.*, **37**, 1483-1489 (1998)
6. Eubank, P.T., and K.R. Hall, *AIChE J.*, **41**, 924-927 (1995) ❐