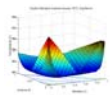
Universitat d'Alacant
Universidad de Alicante



Numerical Determination of Distillation Boundaries for Multicomponent Homogeneous and Heterogeneous Azeotropic Systems

Juan A. Reyes-Labarta*, **J.A. Caballero, A. Marcilla**
(ja.reyes@ua.es)

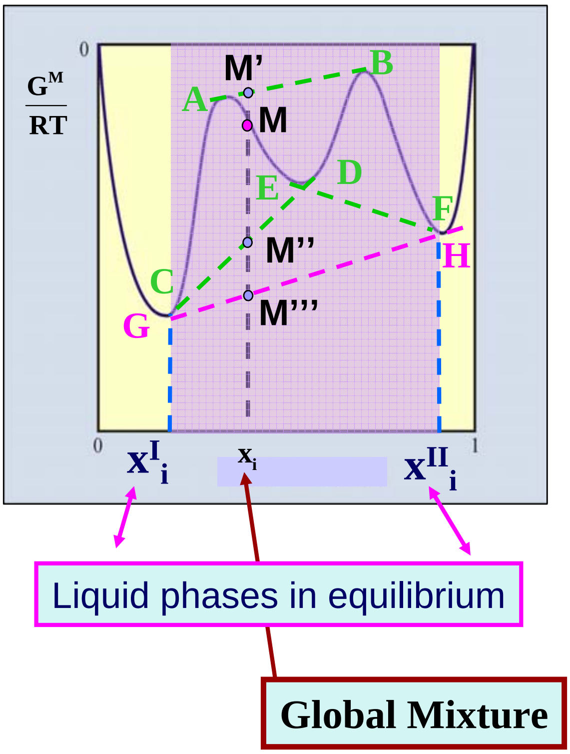
Assistant Professor
Chemical Engineering Department
Institute of Chemical Process Engineering
University of Alicante. Spain
(http://iq.ua.es/gcef.htm)

outlines

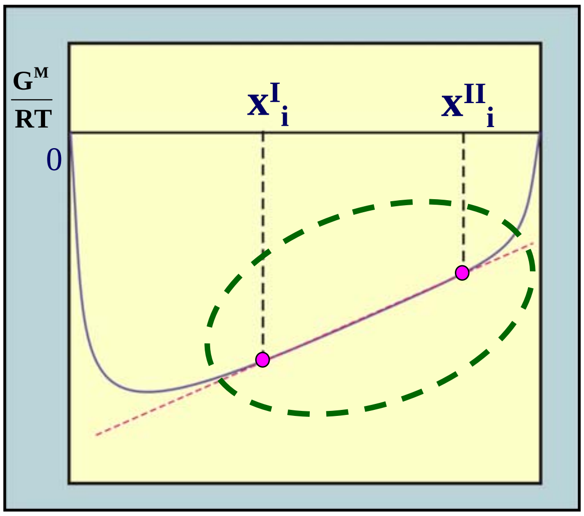
- Introduction
  - ✓ Relevance of the topological analysis:
    - ✓ Topology of the Gibbs Energy Function (LLE, LLSE, LLShE)
    - ✓ Topology of azeotropic LV Equilibrium Surfaces
- Distillation Boundary Condition
- Mathematical algorithm
- Numerical examples
- Conclusions

1) Possibility of different false solutions

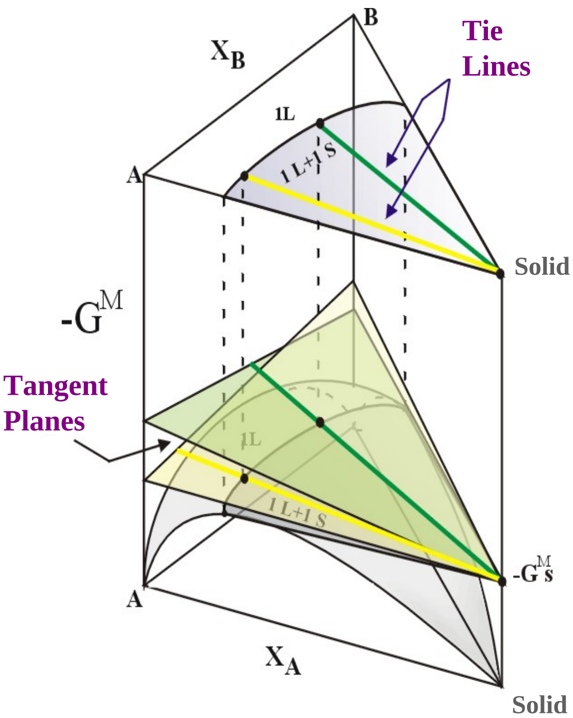
TYPICAL PROBLEMS!!

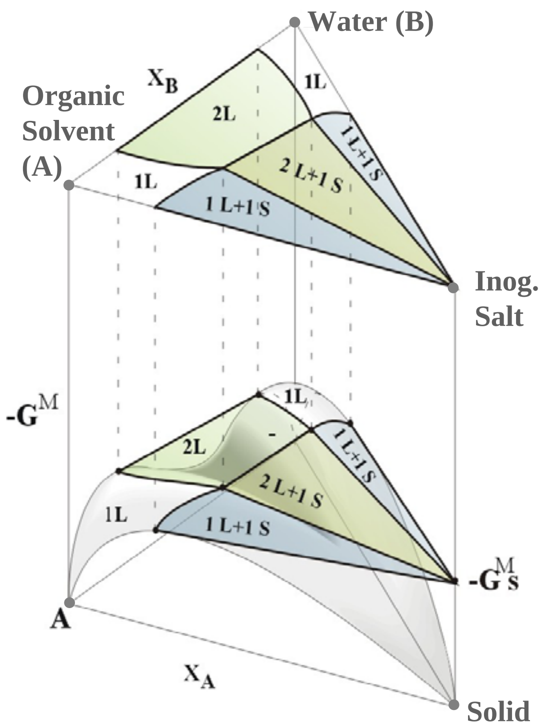


2) Uncertainty in the final solution

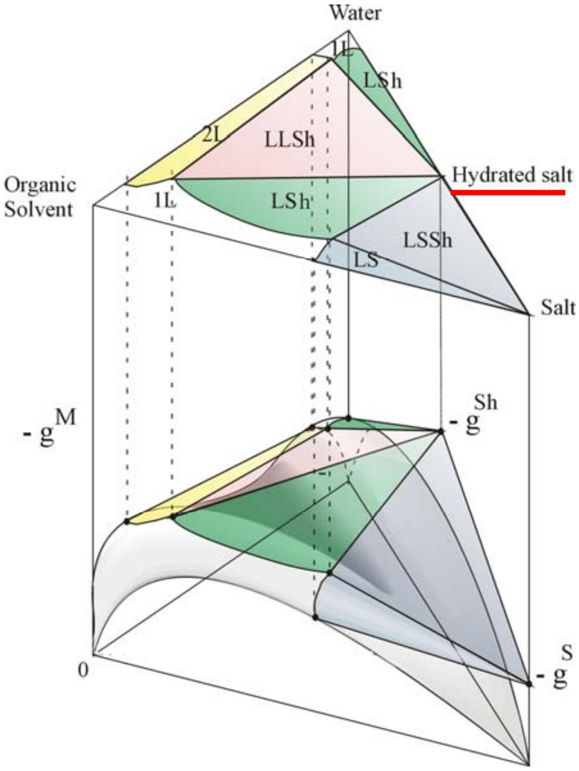


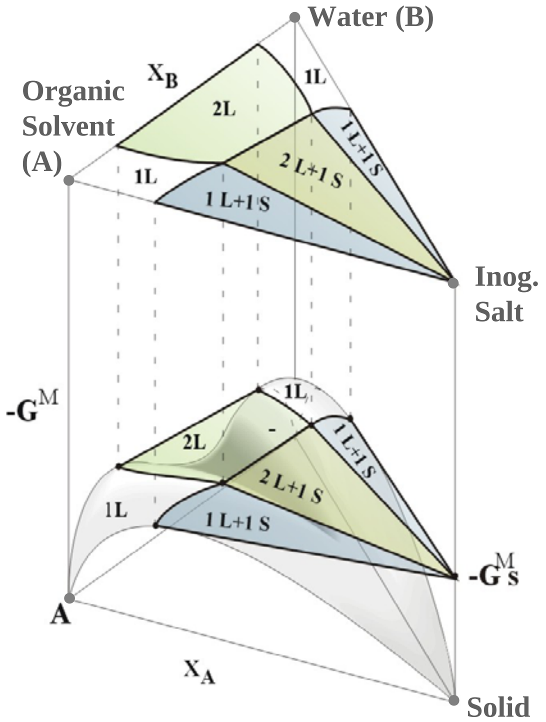
(minor common tangent plane criterion)



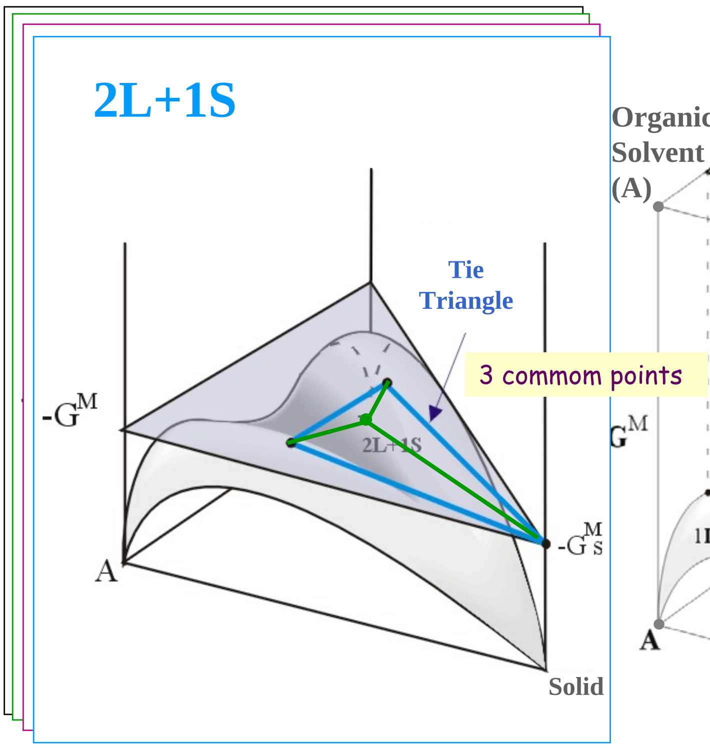


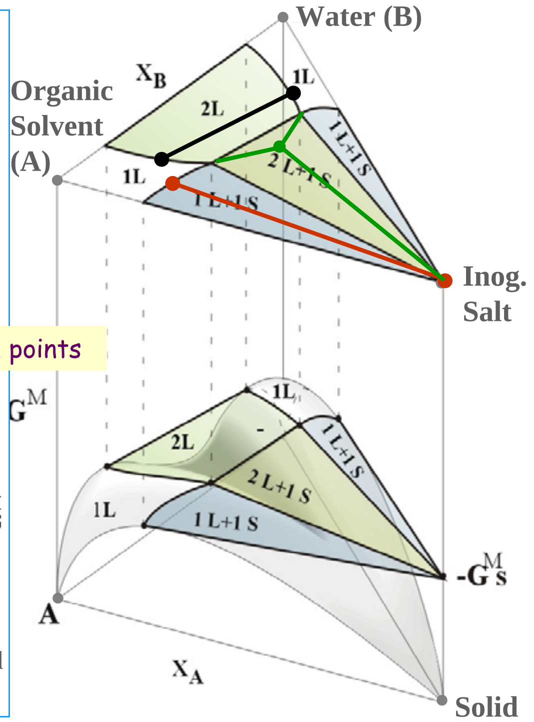
(minor common tangent plane criterion)





(minor common tangent plane criterion)





NEW STRATEGIES

♦ **Limit the equilibrium composition space for the LLE root determination**

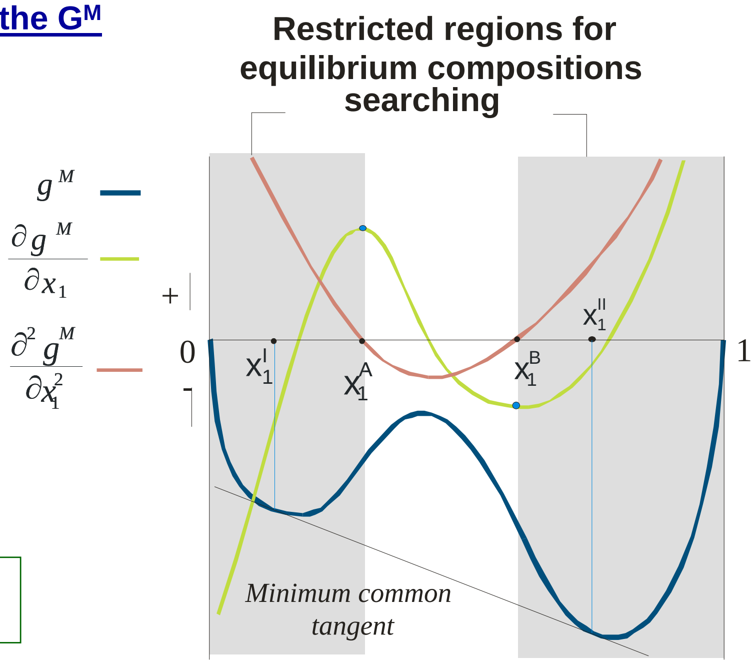
a) Using the second derivative of the G^M

Advantages:

✓ Less time consuming

✓ Trivial solution is avoided

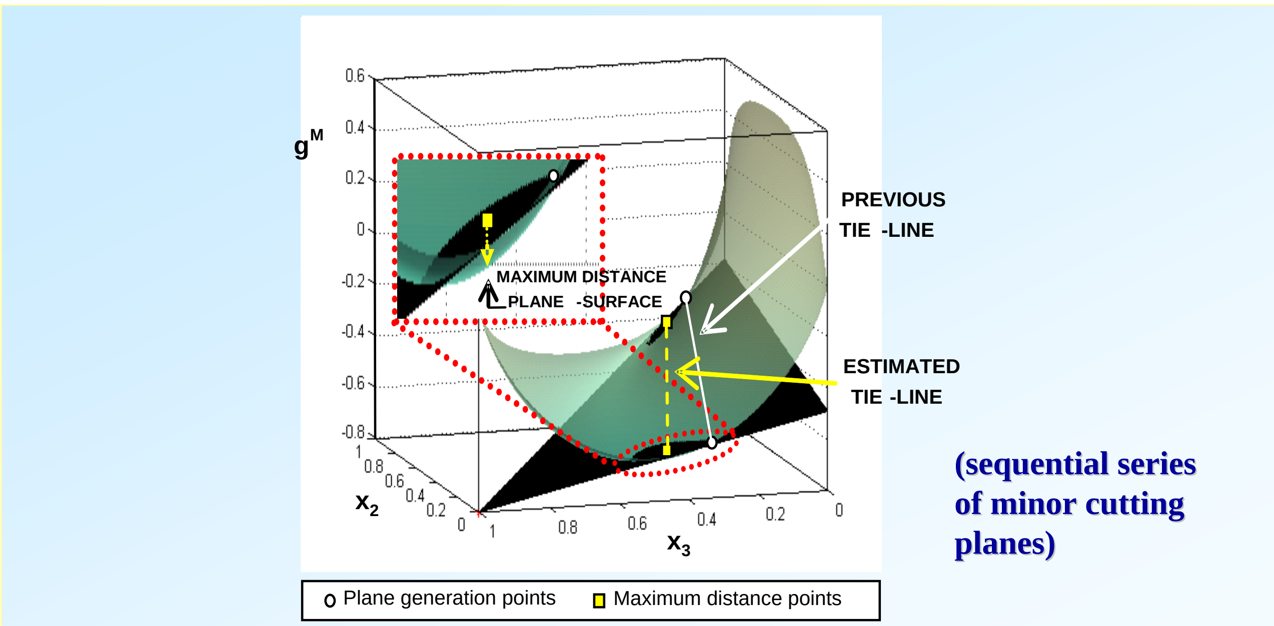
Marcilla et al. Fluid Phase Equilibria (2010)
http://dx.doi.org/10.1016/j.fluid.2009.12.026



NEW STRATEGIES

♦ **Limit the equilibrium composition space for the LLE root determination**

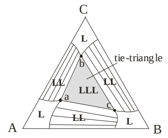
b) Using a geometrical approach → very good approximation to the ELL solution

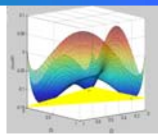


Introduction: Topology of the Gibbs Energy Surface (ternary LLE)

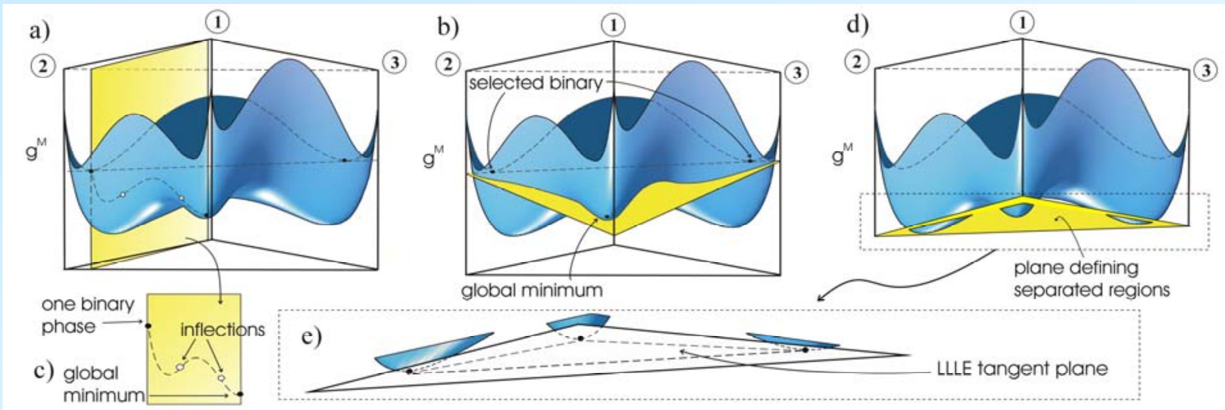
NEW STRATEGIES

♦ **Limited composition space for the LLLE root determination**





b) Using a geometrical approach → very good approximation to the ELLL solution



(sequential series of minor cutting planes)

Marcilla et al. Fluid Phase Equilibria 281, 87-95 (2009)

Introduction: Topology of the Gibbs Energy Surface (ternary LLSE)

NEW STRATEGIES

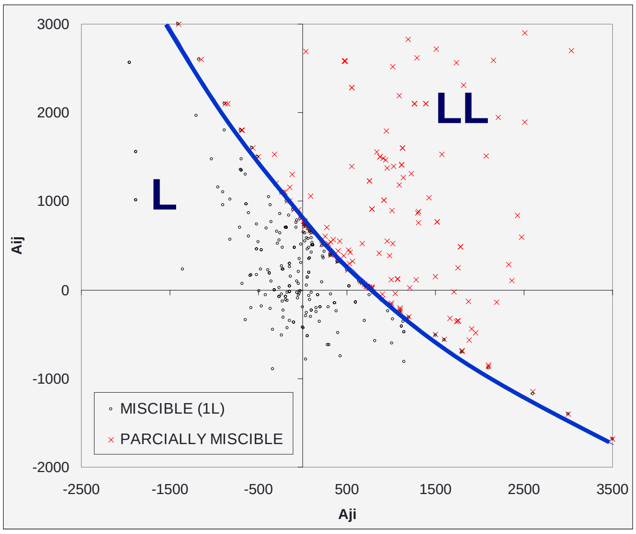
♦ **Mathematical constraints for binary parameters**

Border line between L and LL regions for the NRTL model

$$A_{ij} = f(A_{ji}) = -4.46564\cdot10^{-8} A_{ji}^{3} + 2.95745\cdot10^{-4} A_{ji}^{2} + 1.20662\, A_{ji} + 766.908$$

Homogeneous (L) $A_{ij} < f(A_{ji})$

Heterogeneous (LL) $A_{ij} > f(A_{ji})$



Type island ternary systems:

A12+ A21<0 (dissimilar binary pair)
A13+ A31>0
A23+ A32>0

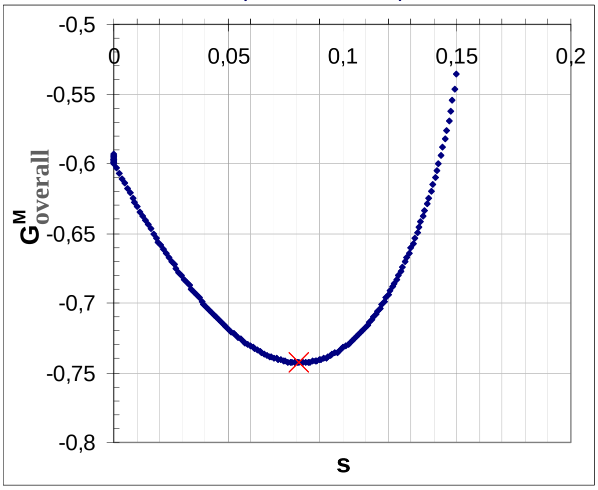
NEW STRATEGIES

♦ Different objective functions

a) Minimum of the overall Gibbs Energy of mixing

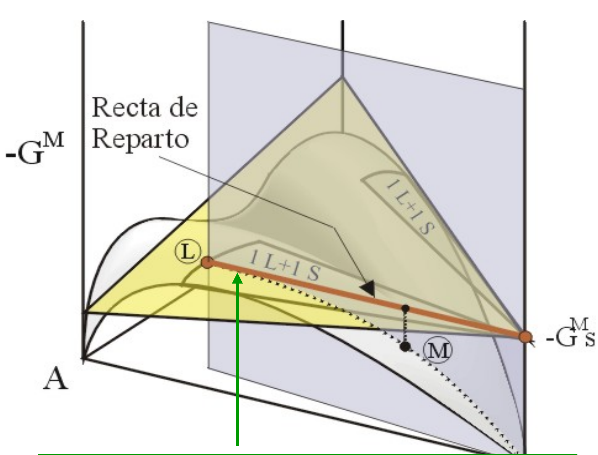
$$\frac{G^M_{overall}}{RT} = \frac{G^S}{RT} + \frac{G^M_{liquid}}{RT} = s \cdot \frac{\Delta\mu^S}{RT} + (1-s) \cdot \sum_{i=1}^{c} x_i^L \cdot \frac{\Delta\mu_i^L}{RT}$$

Calculation of the Minimum of the overall Gibbs Energy of mixing, along a concrete line* for each experimental point.



Reyes et al. IEC&R 40,902-907 (2001)

1L+1S



*Line defined by a constant ratio $x_{OrganicSolvent}/x_{water}$

NEW STRATEGIES

Olaya et al. Chem.Eng.Education 41(3), 218-224 (2007)

♦ Different objective functions

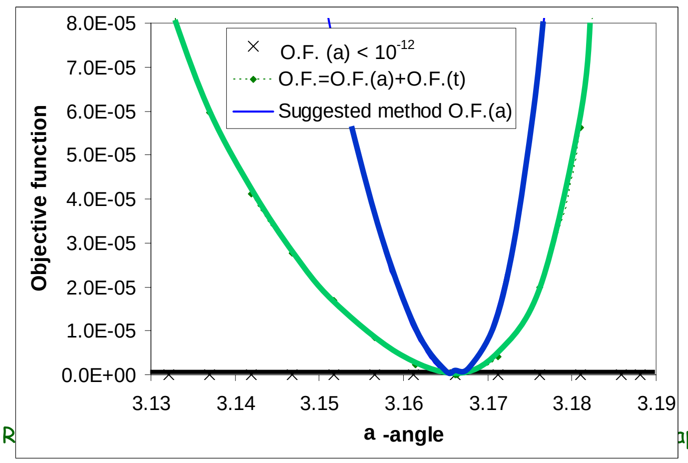
a) Minimum of the overall Gibbs Energy of mixing

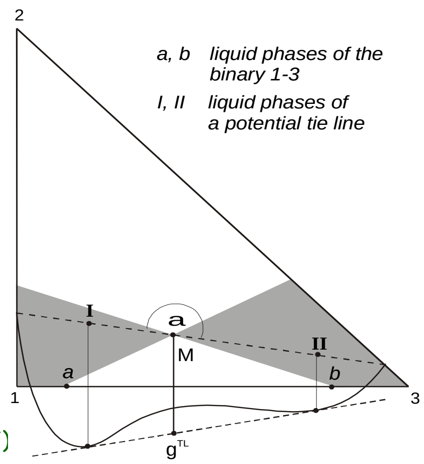
$$\frac{G^M_{overall}}{RT} = \frac{G^S}{RT} + \frac{G^M_{liquid}}{RT} = s \cdot \frac{\Delta\mu^S}{RT} + (1-s) \cdot \sum_{i=1}^{c} x_i^L \cdot \frac{\Delta\mu_i^L}{RT}$$

b) Isoactivity criterium $O.F.(a) = \sum_{i=1}^{3}\left(a_i^I - a_i^{II}\right)^2 = 0$

c) Isoactivity + Minor common tangent condition (Iglesias Silva et al., 2003)

d) A modification of the initial vector method of Eubank et al., 1992 (Olaya et al., 2007)



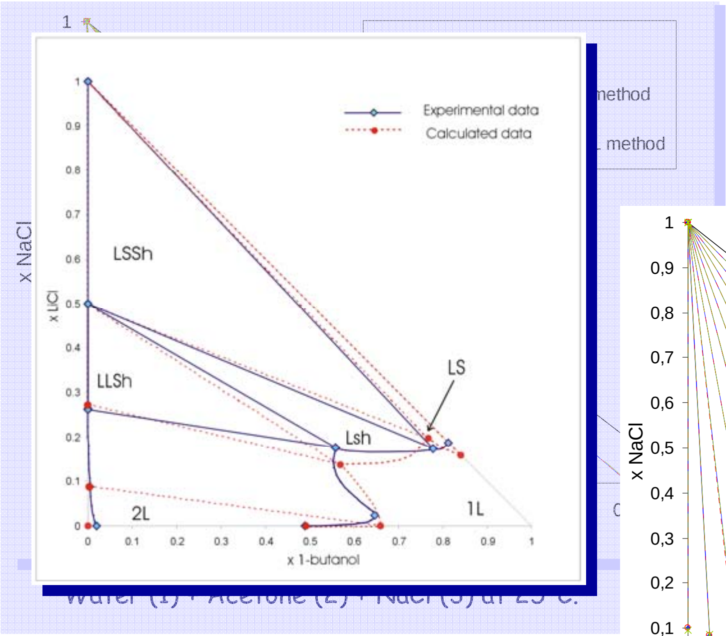


NEW STRATEGIE RESULTS:

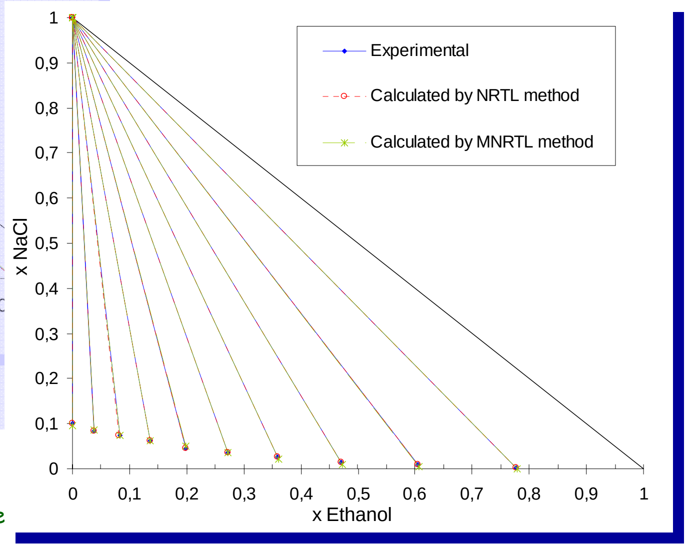
•SIMULTANEOUS CORRELATION (including all equilibrium regions) OF LLS SYSTEMS (NRTL and E-NRTL)

Olaya et al. IEC&R 46, 7030-7037 (2007)

Marcilla et al. IEC&R 47, 2100-2108 (2008)



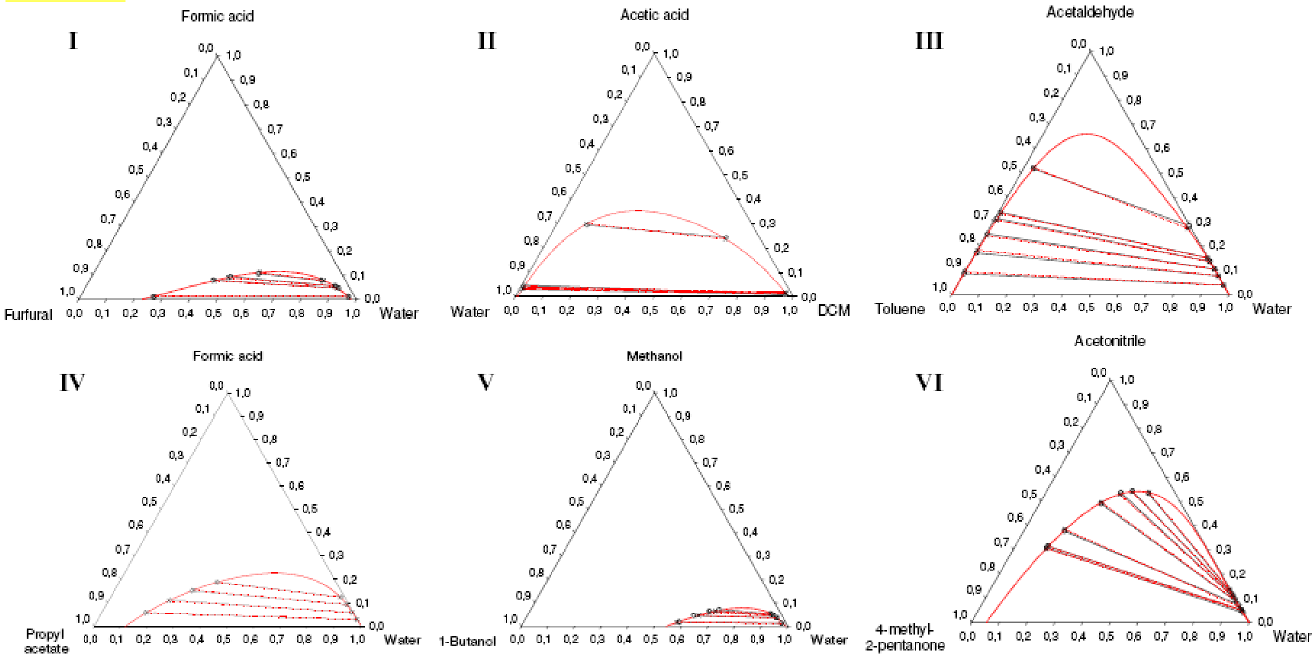
•Water(1) + Ethanol (2) + NaCl (3) at 25°C.



NEW STRATEGIE RESULTS:

• CORRELATION OF (uncorrelated) COMPLEX LL SYSTEMS (NRTL)

TYPE I



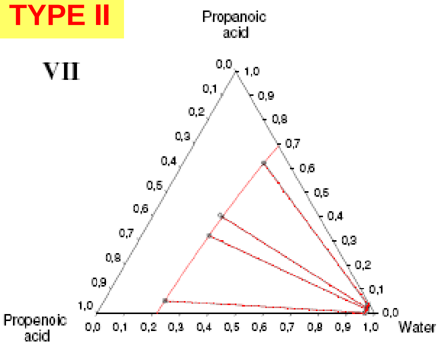
Reyes-Labarta et al. Fluid Phase Equilibria 278, 9-14 (2009)

NEW STRATEGIE RESULTS:

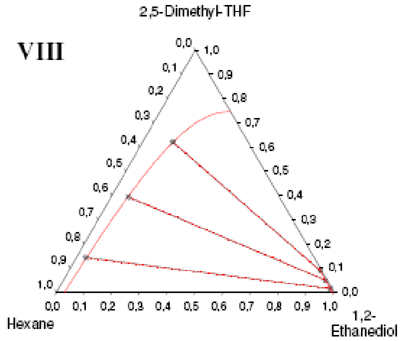
•CORRELATION OF(uncorrelated) COMPLEX LL SYSTEMS (NRTL)

TYPE II

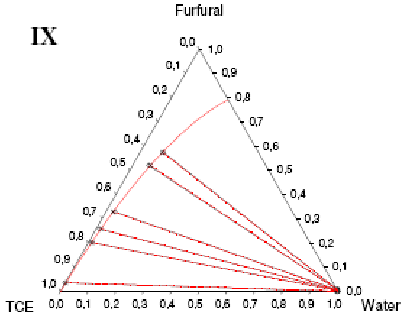
VII



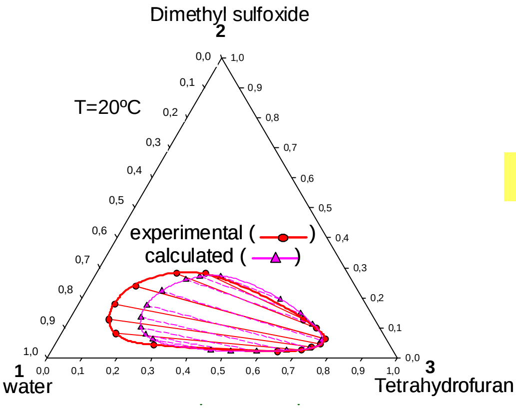
VIII



IX

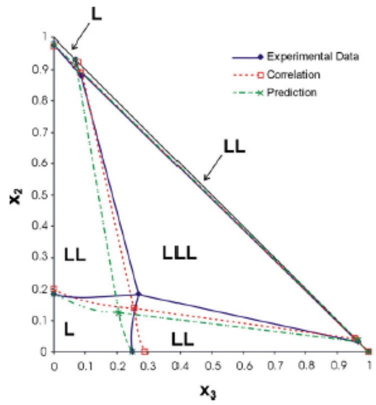


TYPE 0



Olaya et al. Fluid Phase Equilibria 265, 184-191 (2008)

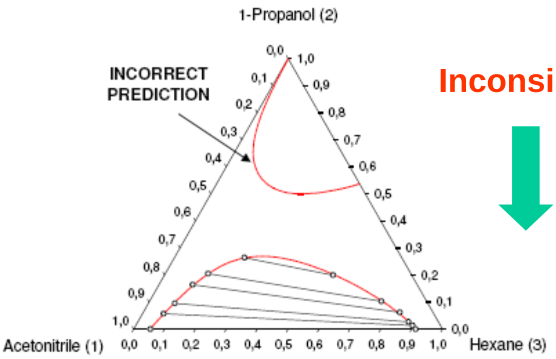
TYPE III



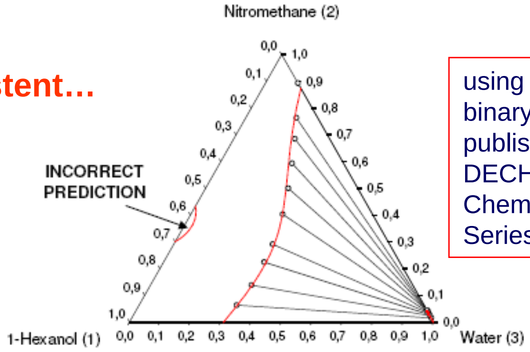
Marcilla et al. Fluid Phase Equilibria 281, 87-95 (2009)

NEW STRATEGIE RESULTS:

• CORRECTION OF SOME (NRTL) INCONSISTENT IN LL (type I-II) SYSTEMS

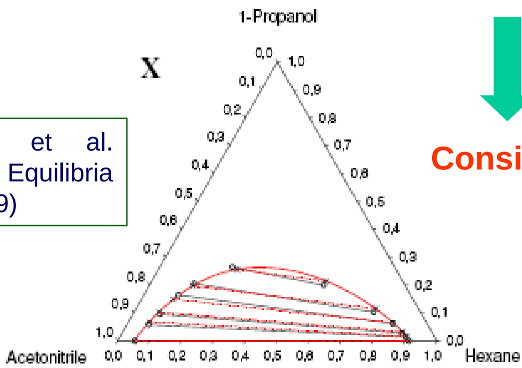


Inconsistent…



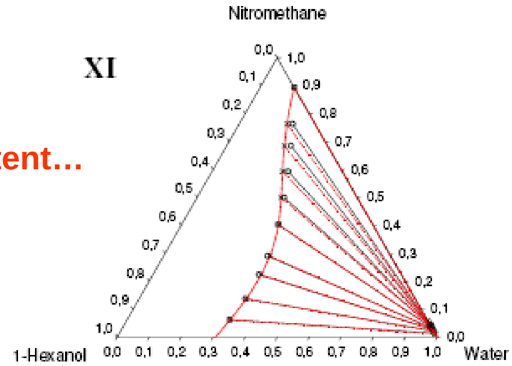
using the NRTL binary parameters published in the DECHEMA Chemistry Data Series

X



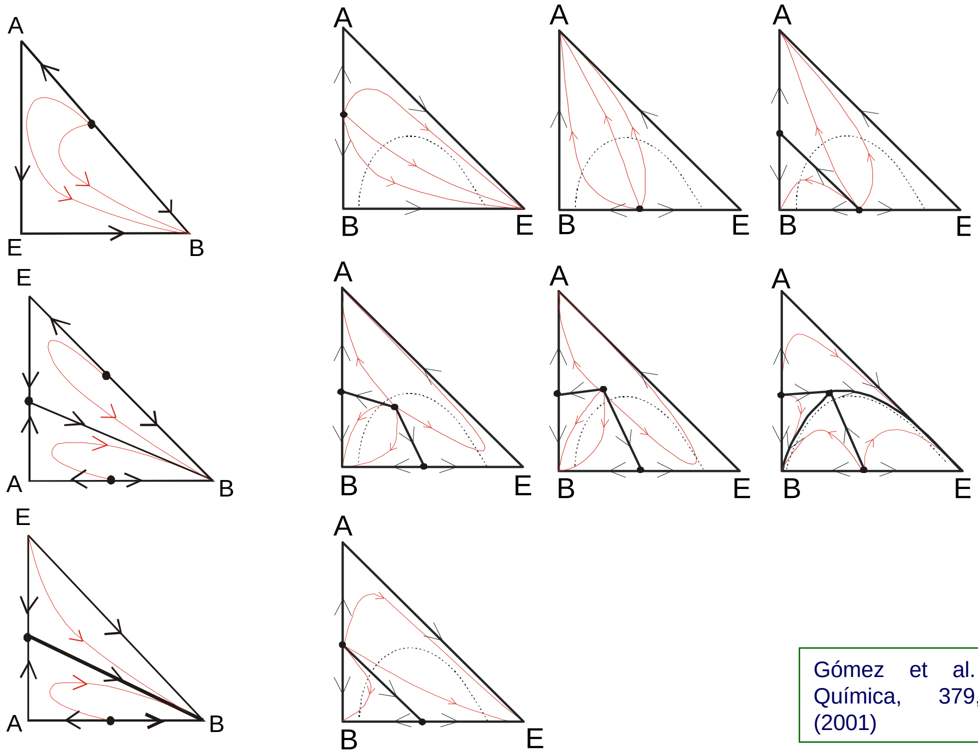
Consistent…

XI



Reyes-Labarta et al. Fluid Phase Equilibria 278, 9-14 (2009)

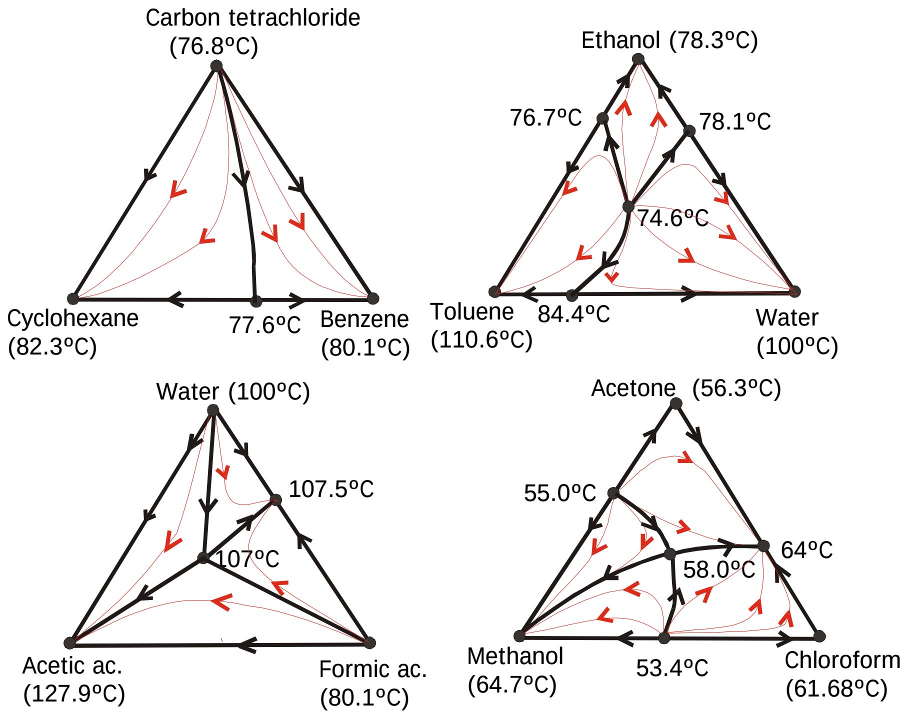
• **LV Equilibria (P = cte). Homogeneous Ternary Azeotropic Systems**



Gómez et al. Ingeniería Química, 379, 253-262 (2001)

Introduction: Topology Azeotropic Liquid-Vapour Equilibrium

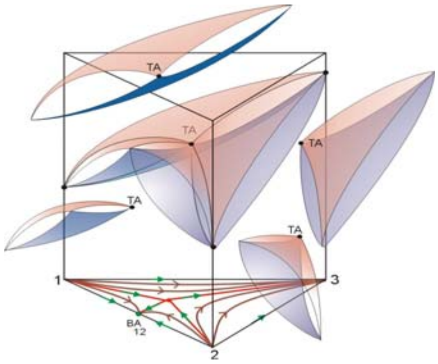
• **LV Equilibria (P = cte). Homogeneous Ternary Azeotropic Systems**



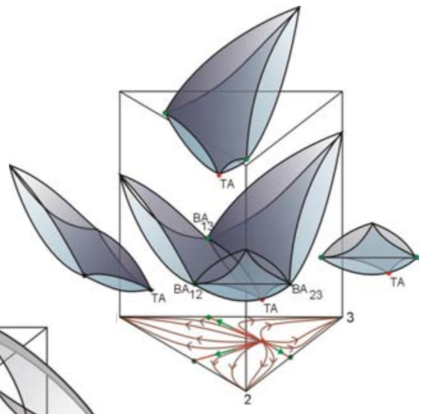
Gómez et al. Ingeniería Química, 379, 253-262 (2001)

- **LV Equilibria (T vs. x,y at P = cte). Homogeneous Ternary Azeotropic Systems**

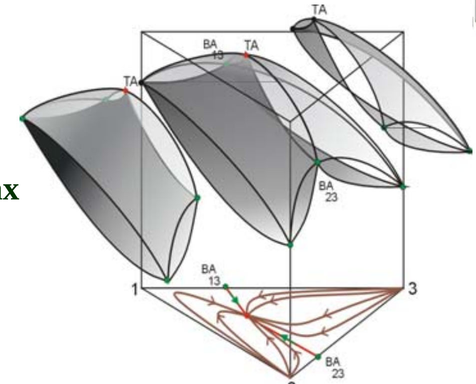
1 BAMax + 1 TAsaddle



3 BAmin + 1TAmin



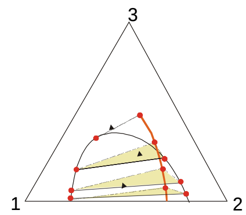
2 BAMax + 1 TAMax

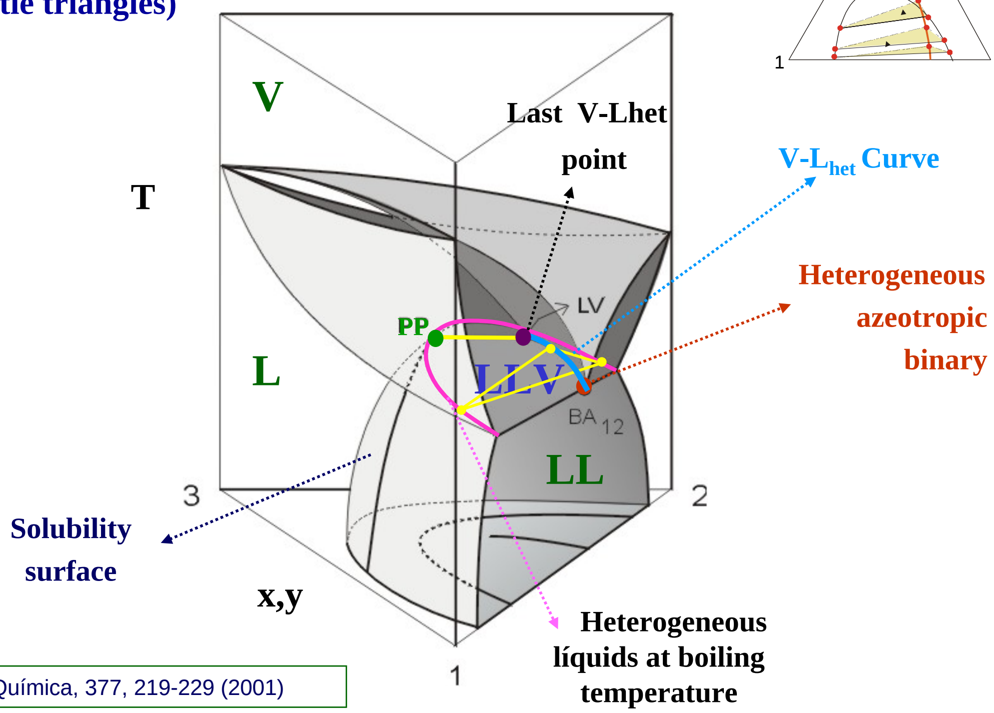


Gómez et al. Ingeniería Química, 377, 219-229 (2001)

Ternary system with:

- **1 heterogeneous binary azeotrope**
- **1 LLV region (tie triangles)**



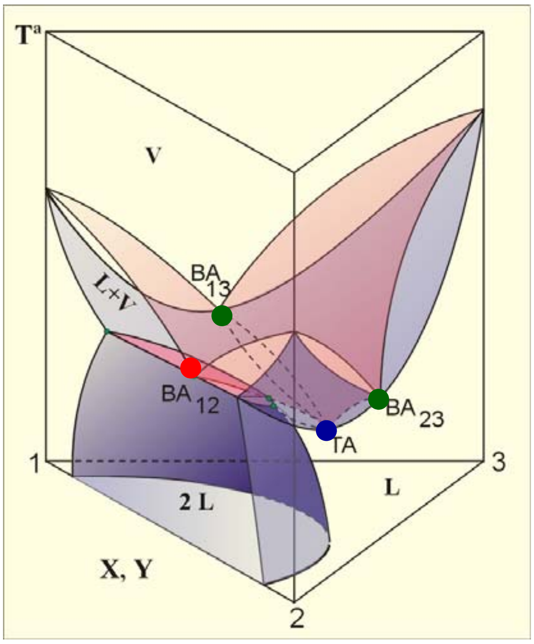


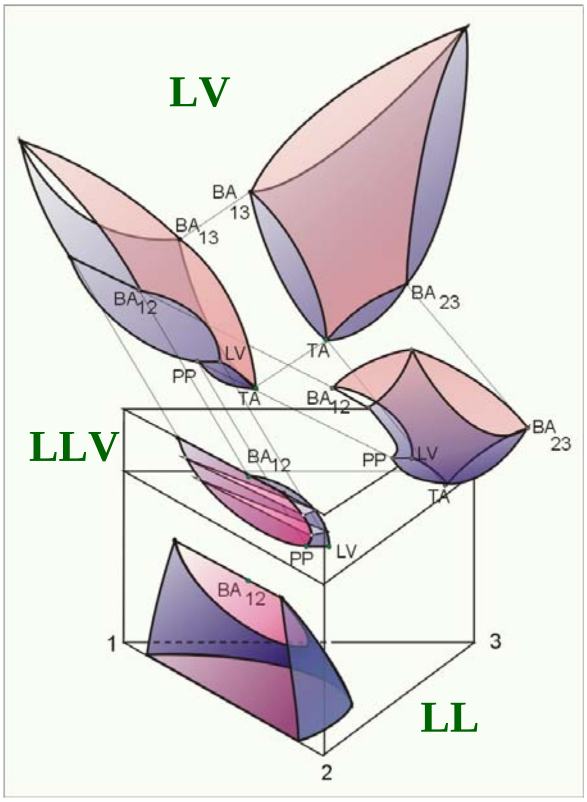
Gómez et al. Ingeniería Química, 377, 219-229 (2001)

Introduction: Topology Azeotropic Liquid-Vapour Equilibrium

Ternary system with:

- **1 heterogeneous binary azeotrope**
- **2 homogeneous binary azeotrope**
- **1 homogeneous ternary azeotrope**



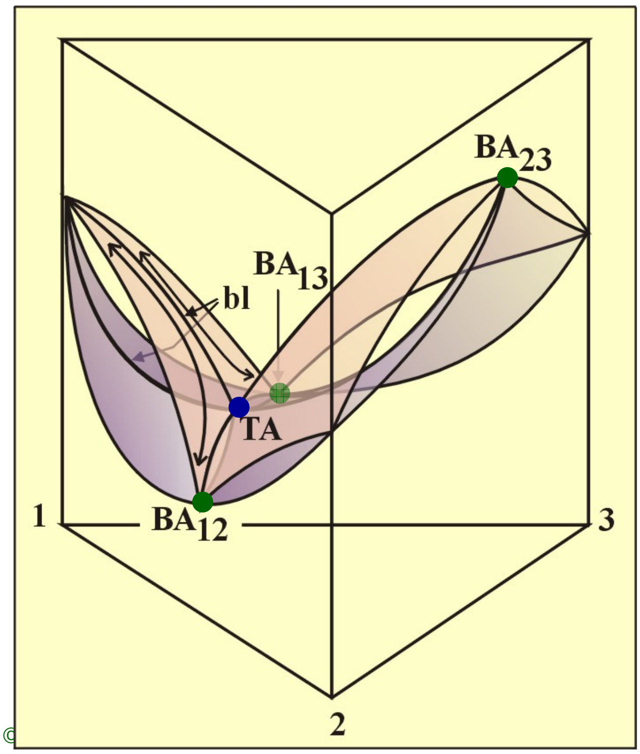


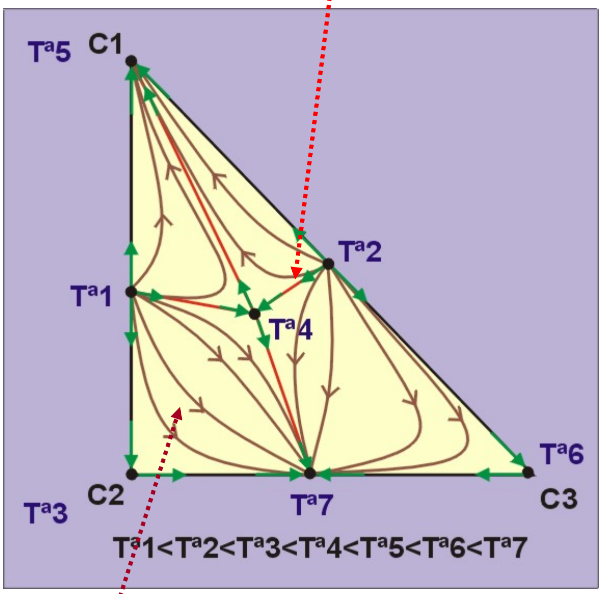
Introduction: Topology Azeotropic Liquid-Vapour Equilibrium

Ternary system with:

- **3 azeotropic binary compositions (2 min, 1 max)**
- **1 azeotropic ternary composition**

Distillation Boundary

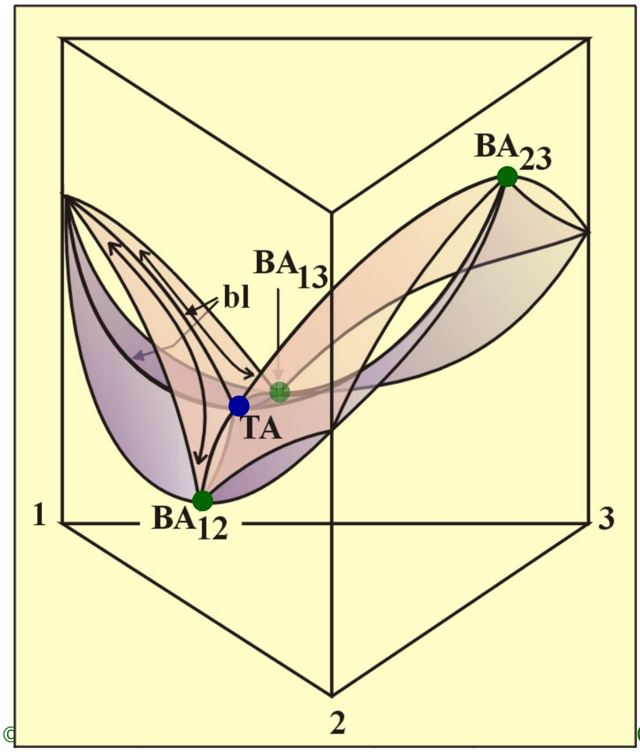


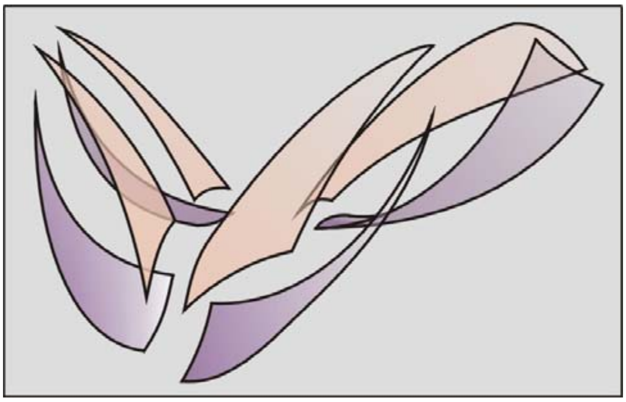


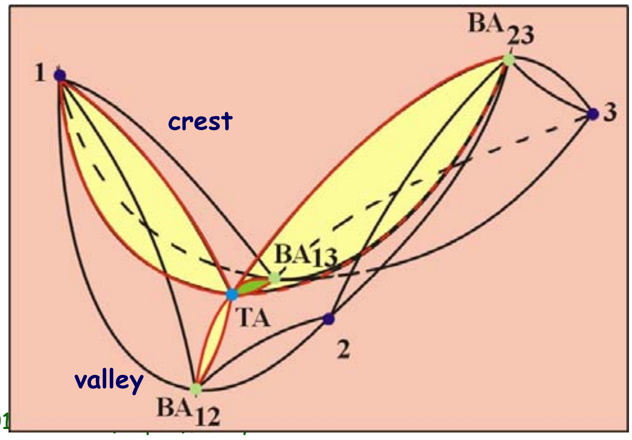
Trajectory distillation

Ternary system with:

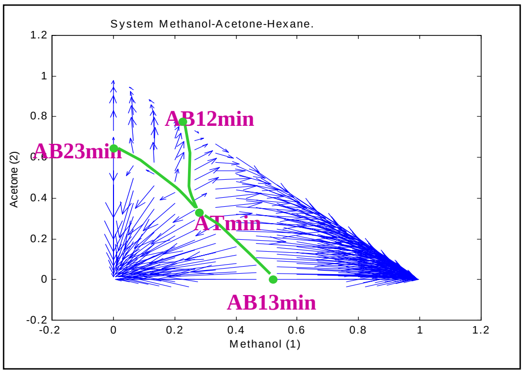
- 3 azeotropic binary compositions
- 1 azeotropic ternary composition

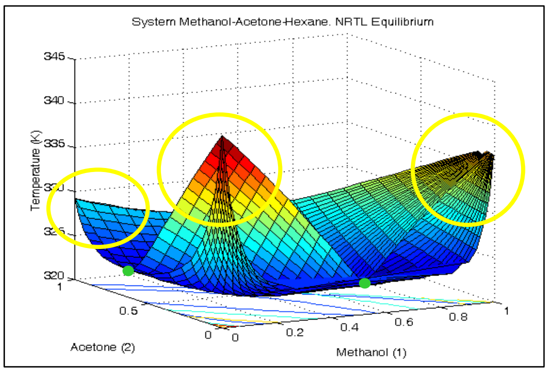


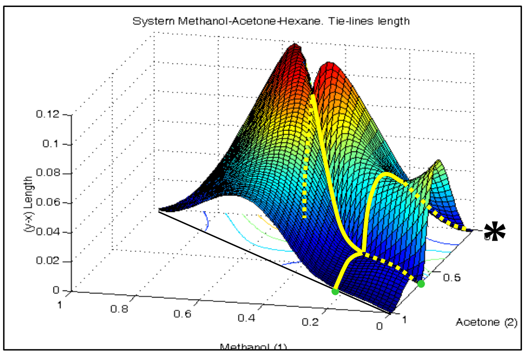


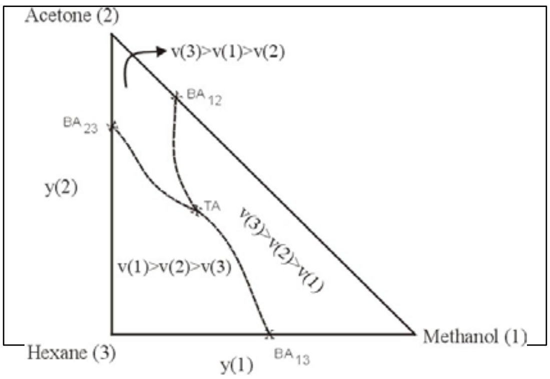


•e.g. Methanol-Acetone-Hexane System (3 ABmin+1ATmin)



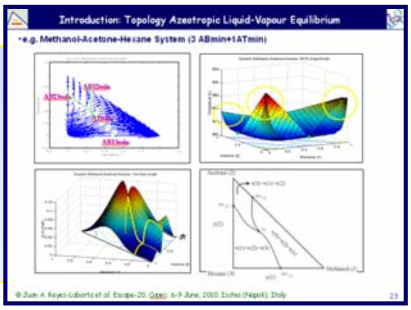






- **A Distillation boundary needs:**

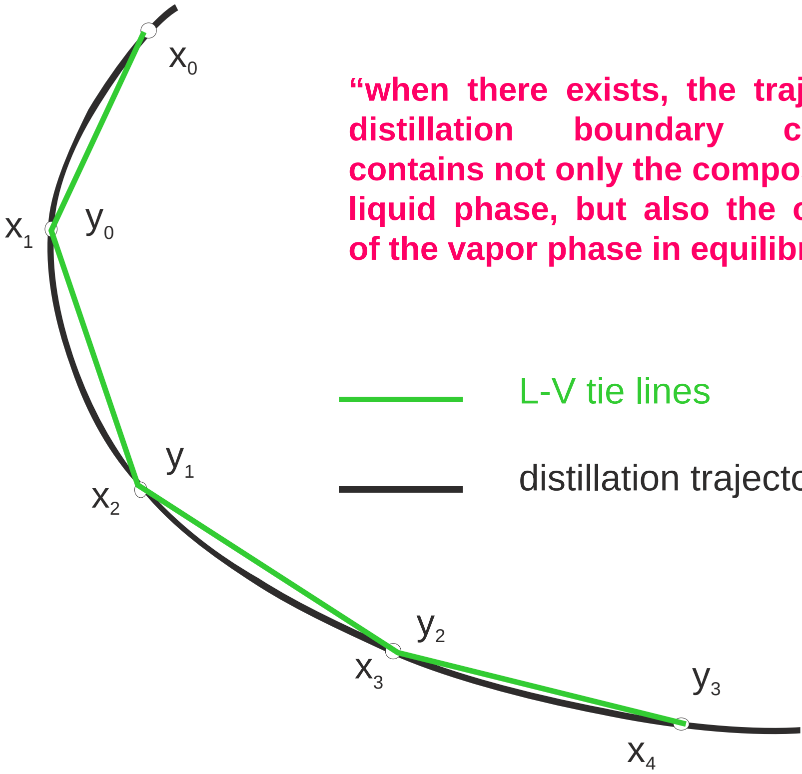
  - **A valley or crest in the T vs x,y diagram**
  - **A minimum in the LV tie line size**
  - **Inversion at least of one relative volatility**



➢ Any of these conditions is sufficient by itself.

➢ The simultaneous inversion of two relative volatilities seems to guarantee the existence of a distillation boundary.

•Topological concept used:

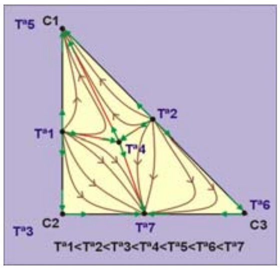


"when there exists, the trajectory of a distillation boundary continuously contains not only the composition of the liquid phase, but also the composition of the vapor phase in equilibrium"

L-V tie lines

distillation trajectory

•Mathematical algorithm:



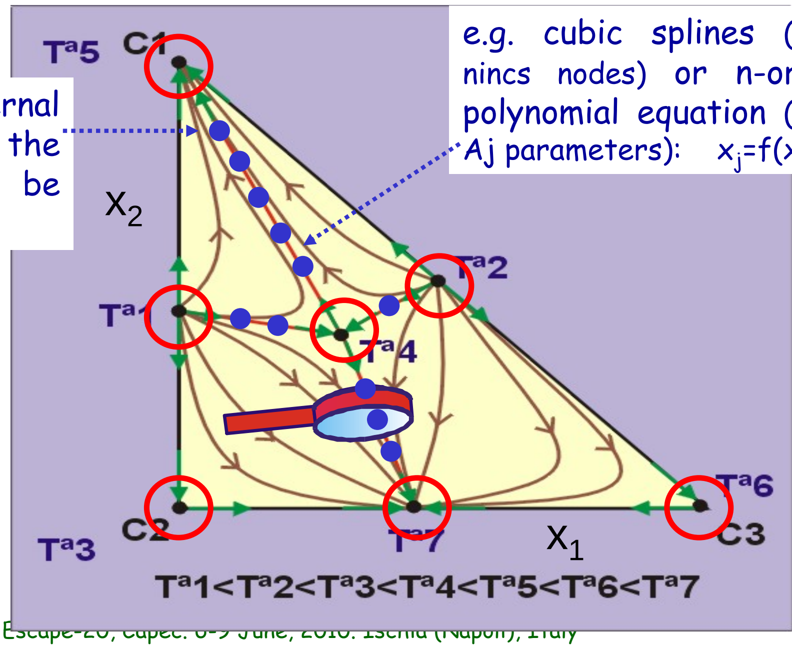
Singular points
↓
Trajectories: extremes, nipt, and function (nincs or n)
↓
Independent variable (e.g. x_2)
↓
Compositions: $x_{2,k}$($k=1,2,\ldots,nipt$)
↓
Initial values for parameters A_j (or cs nodes, $x_{1,k'}$)
↓
Compositions: $x^{cal}_{1,k}$($k=1,2,\ldots,nipt$)
↓
Compositions: $y^{eq}_{1,k}$($k=1,2,\ldots,nipt$)
↓
Compositions: $y^{cal}_{1,k}$($k=1,2,\ldots,nipt$)
↓
¿$y^{cal}_{1,k}=y^{ceq}_{1,k}$?
yes → End
no ↓
New values for parameters A_j (or cs nodes: $x_{1,k'}$ $k'=1,2,\ldots,$ *nincs*) → back to Compositions: $x^{cal}_{1,k}$

•Mathematical algorithm:

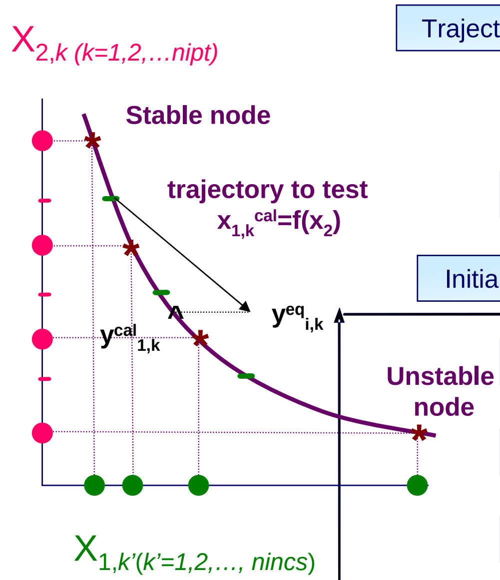
Singular points
↓
Trajectory: origin/end , nipt and function (nincs or n)
↓
Independent variable (e.g. x_2)

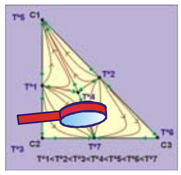
nipt = number of internal points along the trajectory k to be calculated

e.g. cubic splines (with nincs nodes) or n-order polynomial equation (with Aj parameters): $x_j=f(x_i)$



•Mathematical algorithm:

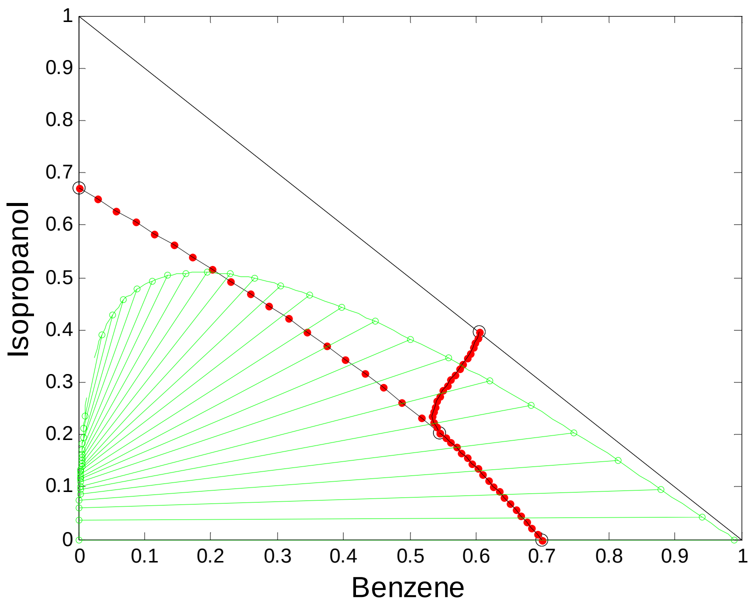




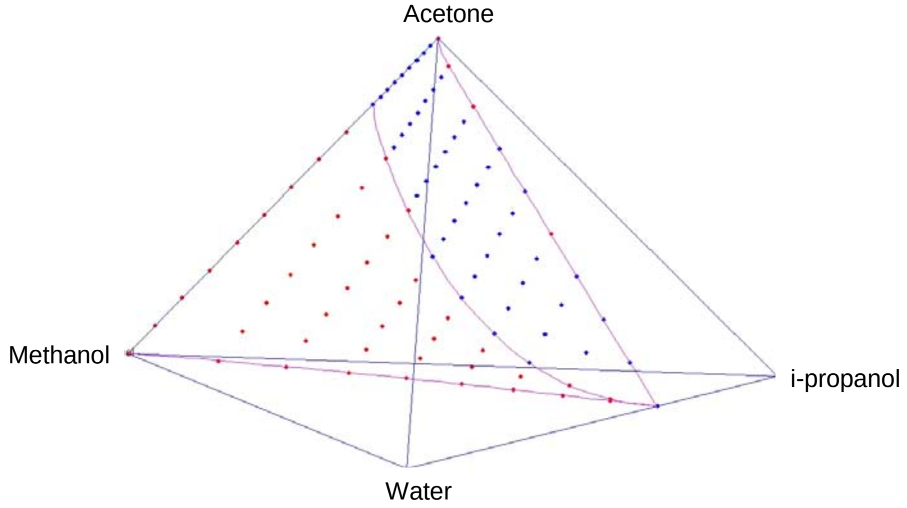
- Singular points
- Trajectory: origin/end, nipt and function (nincs or n)
- Independent variable (e.g. x_2)
- Compositions: $x_{2,k}$ (k=1,2,…,nipt)
- Initial values for parameters A_j (or cs nodes, $x_{1,k'}$)
- Compositions: $x^{cal}_{1,k}$ (k=1,2,…,nipt)
- Compositions: $y^{eq}_{1,k}$ (k=1,2,…,nipt)
- Compositions: $y^{cal}_{1,k}$ (k=1,2,…,nipt) — $y_{1,k}^{cal}=f(y_2)$
- ¿$y^{cal}_{1,k}=y^{ceq}_{1,k}$? — yes → End; no ↓
- New values for parameters Aj or (cs nodes: $x_{1,k'}$ k'=1,2,…, nincs)

Heterogeneous ternary system with:

- **1 heterogeneous azeotropic binary composition**
- **2 homogeneous azeotropic binary compositions**
- **1 homogeneous azeotropic ternary composition**



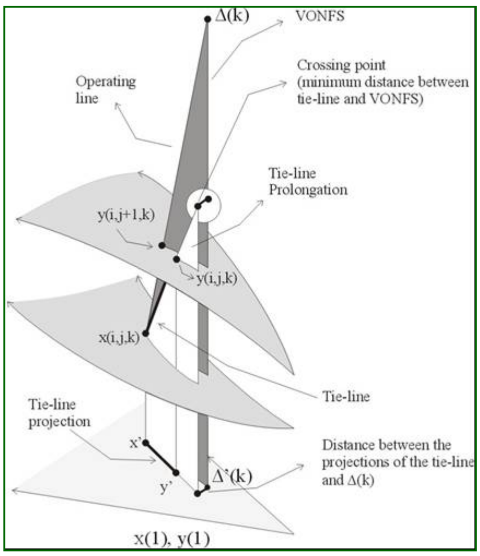
Homogeneous quaternary system with:
2 homogeneous azeotropic binary compositions

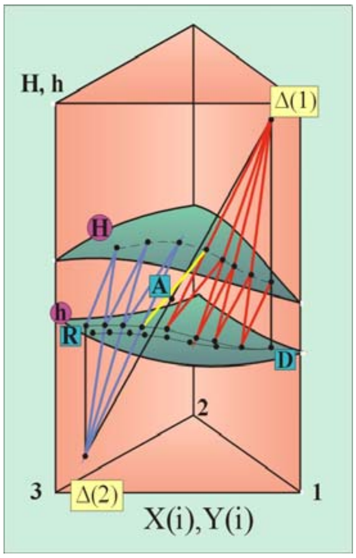


➢ In this case, the distillation boundary is formed by the two different surfaces, that intersect in one curve.

•Conclusions

✓ Topological analysis can really help to equilibrium calculations in complex systems, and therefore in the calculation of unit operation such as multicomponent distillation columns (including minimum reflux calculation)



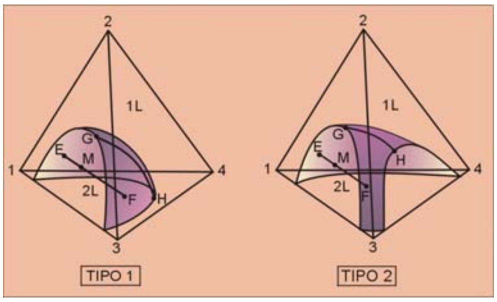


Reyes-Labarta et al. IEC&R 39(10),3912-3919 (2000)

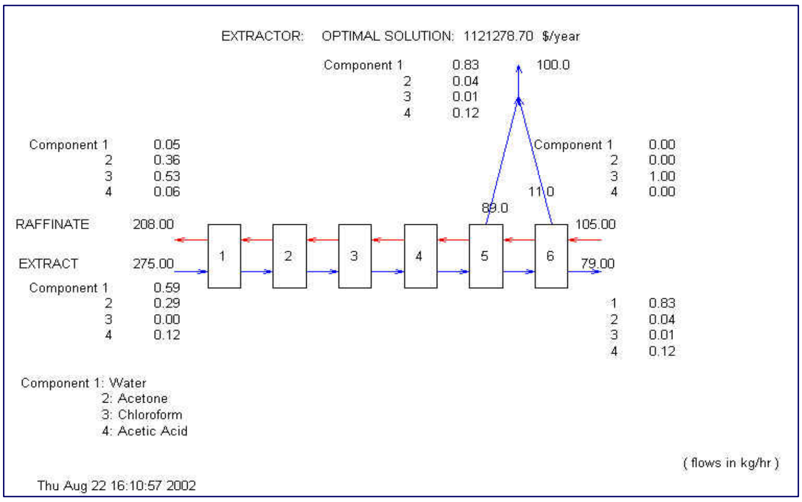
Marcilla et al. Latin American Applied Research and International Journal of Chemical Engineering, 27, 51-60 (1997)

•Conclusions

✓ Topological analysis can really help to equilibrium calculations in complex systems, and therefore in the calculation of unit operation such as multicomponent distillation columns (including minimum reflux calculation) or extraction columns…



Marcilla et al. IEC&R, 38, 3083-3095 (1999)



Reyes-Labarta & Grossmann, AIChE 47(10), 2243-2252 (2001)

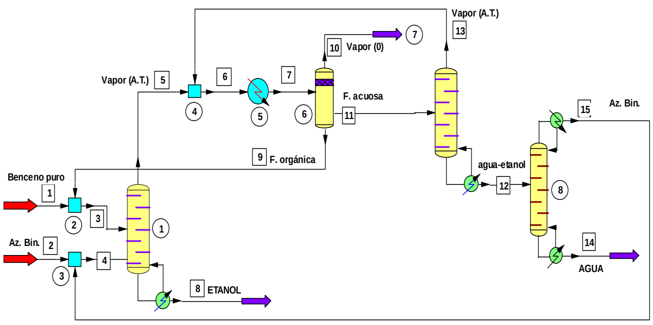
Universitat d'Alacant
Universidad de Alicante
Numerical Determination of Distillation Boundaries

•Conclusions

✓ Topological analysis can really help to equilibrium calculations in complex systems, and therefore in the calculation of unit operation such as multicomponent distillation or extraction columns…

✓ The proposed new method is very easy to model, gives very good results and has also the possibility of using different equilibrium equations (thermodynamical or empirical)

✓ The prediction of distillation boundaries is essential in the design and simulation of complex chemical processes, including distillation column sequences, etc.



Biography (I. Unit operations)

-Reyes-Labarta, J.A. "Diseño de Columnas de Rectificación Y Extracción Multicomponentes". Biblioteca Virtual Miguel de Cervantes (Universidad de Alicante), 1998.

http://www.cervantesvirtual.com/FichaObra.html?Ref=4845&ext=pdf

-A. Marcilla, A. Gómez, J.A. Reyes, M.M. Olaya.; New Method for Quaternary Systems Liquid-liquid Extraction Tray to Tray Design. Industrial & Engineering Chemistry Research, 38, 3083-3095 (1999).

-A. Marcilla, A. Gómez, J.A. Reyes; New Methods for Designing Distillation Columns of Multicomponent Mixtures. Latin American Applied Research and International Journal of Chemical Engineering, 27, 51-60 (1997).

-Reyes, J.A.; Gomez, A.; Marcilla, A. Graphical concepts to orient the minimum reflux ratio calculation on ternary mixtures distillation. Industrial & Engineering Chemistry Research 39(10),3912-3919 (2000).

-J.A. Reyes-Labarta, I.E. Grossmann; Disjunctive Programming Models for the Optimal Design Of Liquid-liquid Multistage Extractors And Separation Sequences. AIChE Journal. 2001, 47 (10), 2243-2252.

-J.A. Reyes-Labarta y I.E. Grossmann. Optimal Synthesis of Liquid-liquid Multistage Extractors. Escape-11 (European Symposium of Computer Aided Process Engineering), Capec (Computer Aided Process Engineering Center). ISBN: 0-444-50709-4 (Dinamarca, 2001).

Biography (II. Phase equilibria)

-Marcilla, A.; Reyes-Labarta, J.A.; Olaya, M.M.; Serrano M.D. Simultaneous Correlation of LL, LS and LLS Equilibrium Data for Water + Organic Solvent + Salt Ternary Systems. Hydrated Solid Phase Formation. Industrial & Engineering Chemistry Research, 47, 2100-2108 (2008).

-Olaya, M.M.; Marcilla, A.; Serrano,M.D.; Botella A.; Reyes-Labarta, J.A. Simultaneous Correlation of LL, LS and LLS Equilibrium Data for Water + Organic Solvent + Salt Ternary Systems. Anhydrous Solid Phase. Industrial & Engineering Chemistry Research, 46, 7030- 7037 (2007).

-Reyes, J.A.; Conesa, J.A.; Marcilla, A.; Olaya, M.M. Solid-Liquid Equilibrium Thermodinamics: checking stability in multiphase systems using Gibbs Energy Function. Industrial & Engineering Chemistry Research, 40, 902-907 (2001).

-Reyes-Labarta, J.A.; Olaya, M.; Velasco, R.; Serrano M.D.; Marcilla, A. Correlation of the Liquid-Liquid Equilibrium Data for Specific Ternary Systems with One or Two Partially Miscible Binary Subsystems. Fluid Phase Equilibria 278, 9-14 (2009).

-Marcilla, A; Olaya, M.; Serrano M.D.; Velasco, R.; Reyes-Labarta, J.A. Gibbs Energy Based Procedure for the Correlation of Type 3 Ternary Systems Including a Three-Liquid Phase Region. Fluid Phase Equilibria 281, 87-95 (2009).

-Olaya, M.M.; Reyes-Labarta, J.A.; Velasco, R.; Ibarra, I.; Marcilla A. Modelling Liquid-Liquid Equilibria for Island Type Ternary Systems. Fluid Phase Equilibria 265, 184-191 (2008).

-Marcilla, A; Olaya, M.; Serrano M.D.; Reyes-Labarta, J.A. Methods for Improving Models for Condensed Phase Equilibrium Calculations. Fluid Phase Equilibria (2010). http://dx.doi.org/10.1016/j.fluid.2009.12.026

-Reyes, J.A.; Olaya, M.M.; Gómez, A.; Marcilla, A. Calculation of liquid-vapor and liquid-liquid equilibrium in multicomponent systems using correlations of equilibrium data. V Iberoamerican Conference on Phase Equilibria and Fluid Properties for Process Design. EQUIFASE 99 Book of Abstracts. http://hdl.handle.net/10045/2687

-Olaya, M.M.; Reyes-Labarta, J.A.; Serrano, M.D.; Marcilla, A. Vapor-Liquid Equilibria using the Gibbs Energy and the Common Tangent Plane Criterion. Chemical Engineering Education (in press 2010)

-Olaya, M.M.; Ibarra, I.; Reyes-Labarta, J.A.; Serrano, M.D.; Marcilla, A. Computing Liquid-Liquid Phase Equilibria: An exercise to understand the nature of false solutions and how to avoid them. Chemical Engineering Education 41 (3), 218-224 (2007).

-Gómez, A.; Ruiz, F.; Marcilla, A.;Reyes, J.; Menargues, S. Diseño de la separación de mezclas ternarias (I). Conceptos gráficos del equilibrio entre fases . Ingeniería Química, 377, 219-229 (2001).

-Gómez, A.; Ruiz, F.; Marcilla, A.;Reyes, J.; Menargues, S. Diseño de la separación de mezclas ternarias (II). Aplicación de conceptos gráficos a la separación de mezclas azeotrópicas. Ingeniería Química, 379, 253-262 (2001).

-Marcilla, A.; Olaya, M.M.; Reyes, J.; Gómez, A. Graphical analysis of the phase equilibria diagram. V Iberoamerican Conference on Phase Equilibria and Fluid Properties for Process Design. EQUIFASE 99 Book of Proceedings, pag. : 3 – 10. Vigo (España), 1999 (http://hdl.handle.net/10045/2482).

GENERALITAT VALENCIANA

ACKNOWLEDGMENTS

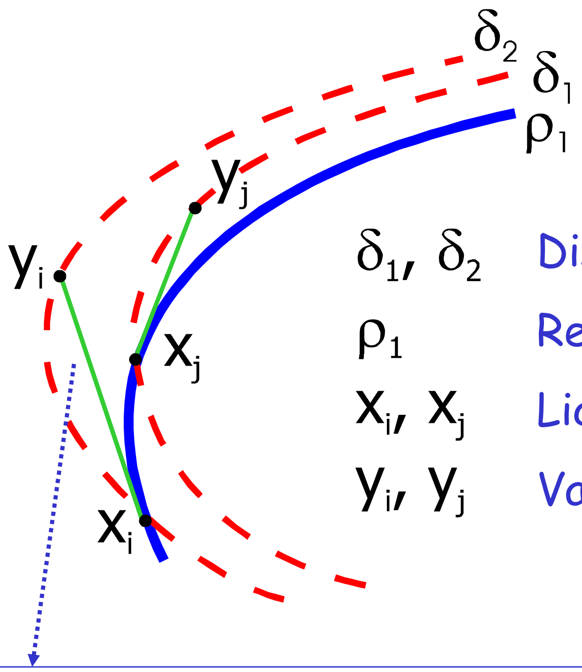
For financial support the authors wish to thank the Generalitat Valenciana of Spain (project GV/2007/125, Consellería de Empresa Universidad y Ciencia)

Numerical Determination of Multicomponent Distillation Boundaries

Juan A. Reyes-Labarta
e-mail: ja.reyes@ua.es
web: http://iq.ua.es/gcef.htm
web: http://iq.ua.es/~jareyes/

Campus Sostenible agenda 21

UA Universitat d'Alacant
Universidad de Alicante



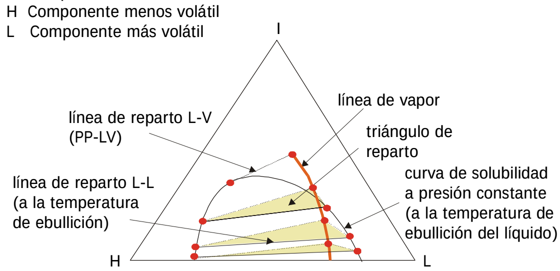
δ_1, δ_2	Distillation trajectory
ρ_1	Residue curve
x_i, x_j	Liquid phase composition
y_i, y_j	Vapour phase composition

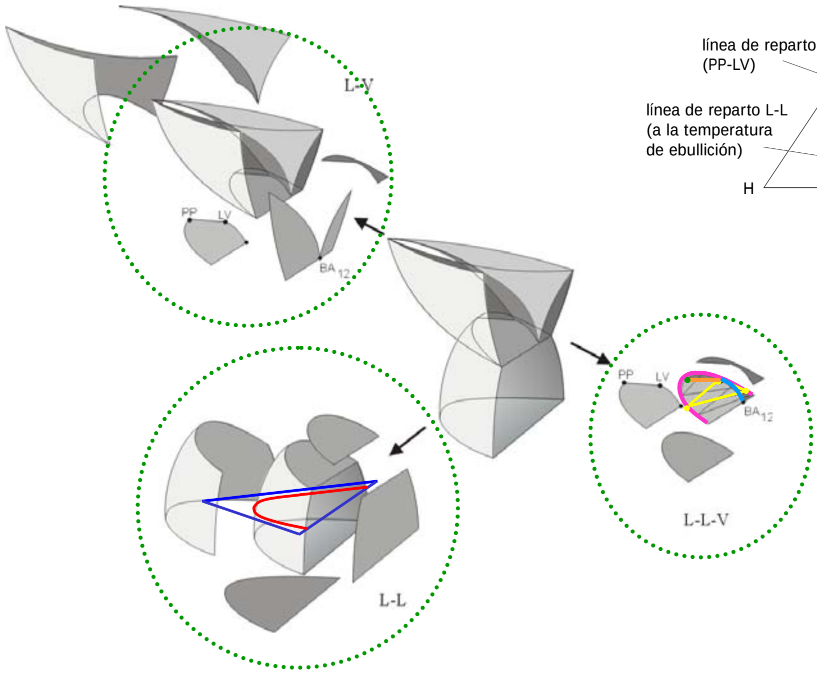
LV tie line (tangent to the residue curve)

Gómez et al. Ingeniería Química, 377, 219-229 (2001)

Ternary system with:

1 heterogeneous azeotropic binary composition

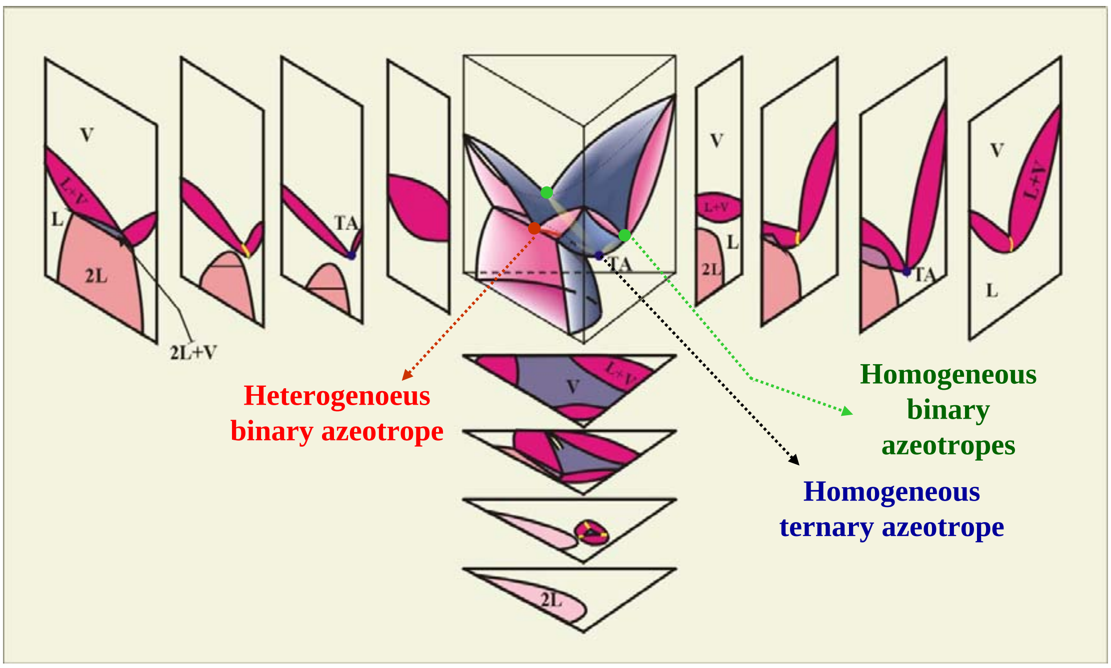




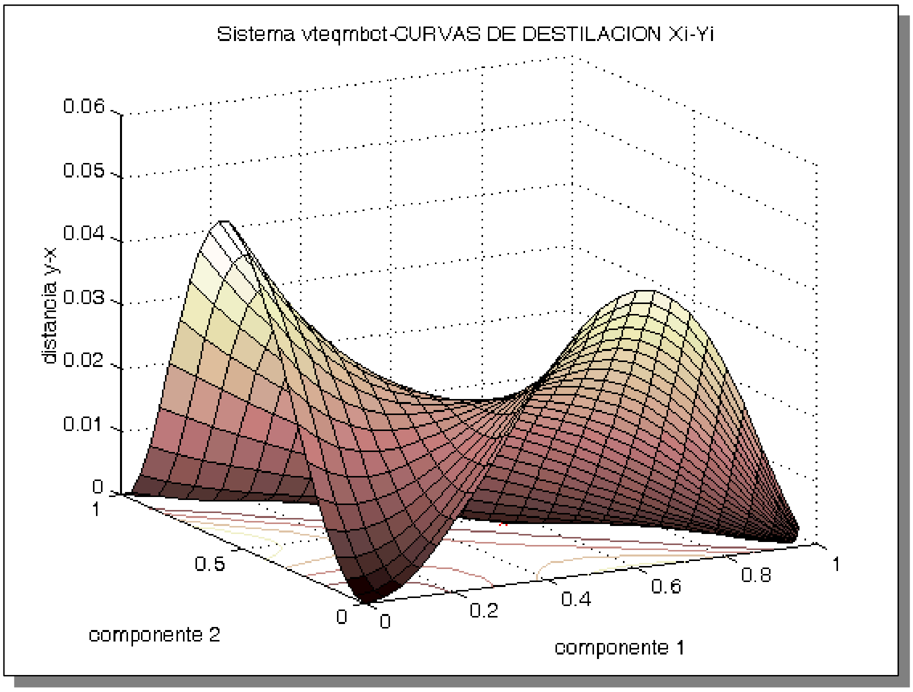
Gómez et al. Ingeniería Química, 377, 219-229 (2001)

Ternary system with:

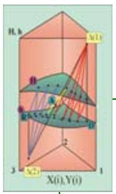
- 1 heterogeneous azeotropic binary composition
- 2 homogeneous azeotropic binary compositions
- 1 homogeneous azeotropic ternary composition

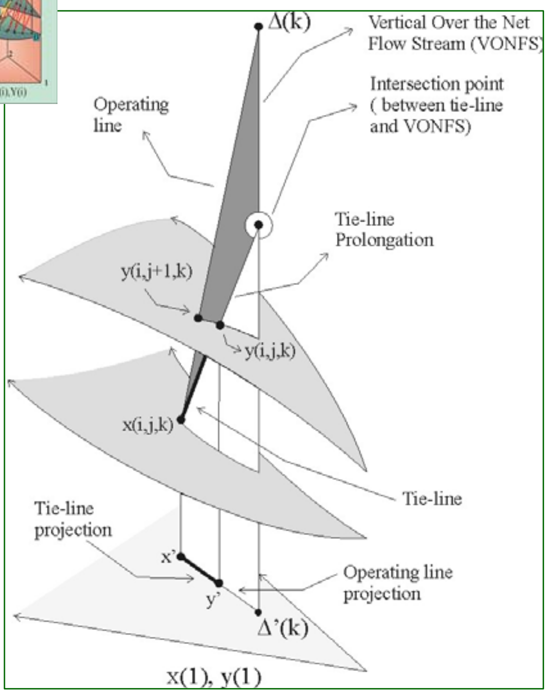


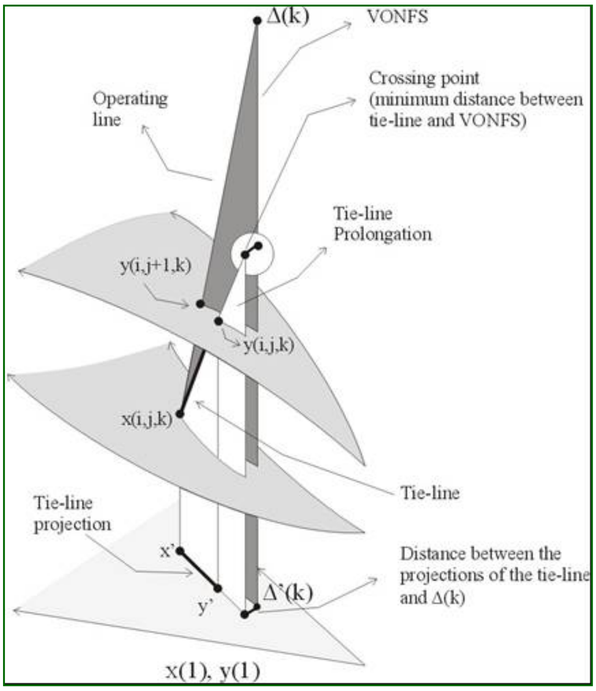
•e.g. Bencene-Ciclohexane-Toluene System (1 ABmin)



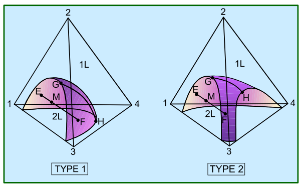
• GRAPHICAL CONCEPTS TO ORIENT THE MINIMUM REFLUX RATIO CALCULATION ON TERNARY MIXTURES DISTILLATION







Reyes-Labarta et al. IEC&R 39(10),3912-3919 (2000)



• **EMPIRICAL CORRELATIONS**

Marcilla et al. IEC&R 38(8), 3083-3095 (1999)

$$\log\left(\frac{y'_k}{y'_p}\right) = \left\{\left[a_{k,p} + b_{k,p}\cdot\left(\frac{x'_4}{x'_2}\right) + c_{k,p}\cdot\left(\frac{x'_4}{x'_2}\right)^2\right] + \left[d_{k,p} + e_{k,p}\cdot\left(\frac{x'_4}{x'_2}\right) + f_{k,p}\cdot\left(\frac{x'_4}{x'_2}\right)^2\right]\cdot\log\left(\frac{x'_2}{x'_1}\right) + \left[g_{k,p} + h_{k,p}\cdot\left(\frac{x'_4}{x'_2}\right) + i_{k,p}\cdot\left(\frac{x'_4}{x'_2}\right)^2\right]\cdot\left[\log\left(\frac{x'_2}{x'_1}\right)\right]^2\right\}$$

$$\log\left(\frac{y'(3)}{y'(2)}\right) = k_1 \qquad \log\left(\frac{y'(2)}{y'(1)}\right) = k_2 \qquad \log\left(\frac{y'(4)}{y'(3)}\right) = k_3$$

$$y'(1) + y'(2) + y'(3) + y'(4) = 1 + 4\cdot C$$

$$\Downarrow$$

$$y'(i) = y(i) + C$$

Four equations with four variables !!

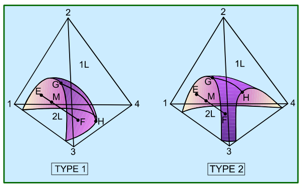
If you have:

- **a concrete multicomponent azeotropic system,**
- **a specified separation and/or recovery of solutes in the product streams (for the distillation process).**

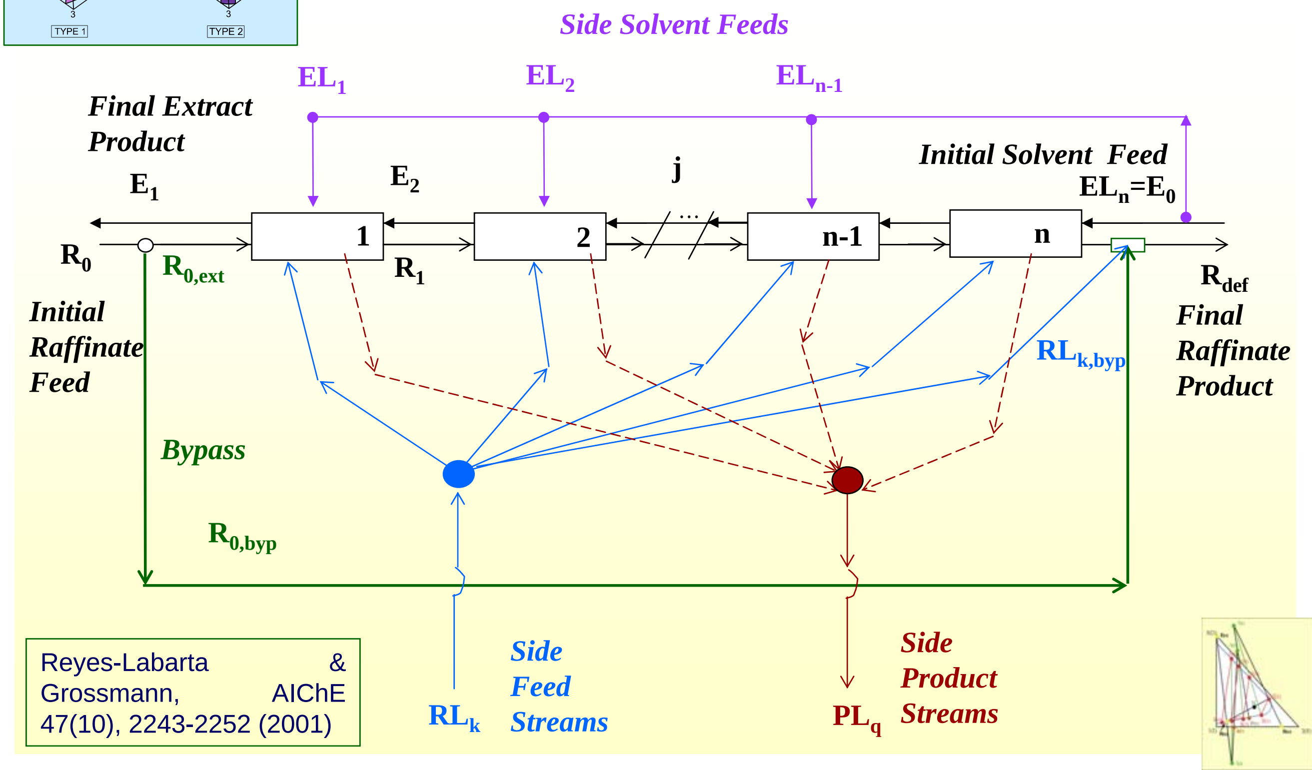
The design problem needs the determination of:

- **possible distillation boundaries and distillation regions present in the system,**

The objective is to make the correct design of the distillation column (that can not work in different distillation regions)



• **COMPLEX EXTRACTOR DESIGN**
General Disjunctive Programming



Reyes-Labarta & Grossmann, AIChE 47(10), 2243-2252 (2001)

• **COMPLEX EXTRACTOR DESIGN (GDP)**

http://newton.cheme.cmu.edu/interfaces/extractor/main.html