GIBBS ENERGY OF MIXING FUNCTION: TOPOLOGICAL ANALYSIS IN AZEOTROPIC SYSTEMS

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Introduction

Thermodynamic models have been used for decades to formulate the activity coefficients of the components of non-ideal liquid mixtures in phase equilibrium calculations. Additionally, the use of topological analysis and constrains have been applied with success in the characterization and simultaneous correlation of complex phase equilibrium including condensed phases: Liquid-Liquid, Liquid-Solid, Liquid-Liquid-Solid and Liquid-Liquid-Hydrated Solid [1-6]. In a recent paper [7], we presented the results of a systematic topological study of the Gibbs energy of mixing (G^M) as a function of composition and showed that the NRTL model exhibits "gaps" or regions where solutions of the NRTL model for miscible binaries do not exist. But what is more important is that the gaps themselves are responsible for the poor correlation of the LLE and VLE data of many systems.

GOAL: To analyze the topology of the Gibbs energy of mixing and the behavior of its composition derivatives, in relation to the corresponding VL and LL phase equilibrium conditions such as the minor common tangent plane, and the existence and characteristics of azeotropic points and distillation boundaries

Mathematical restrictions for homogeneous azeotropic compositions:
$$\frac{\partial y_i}{\partial x_i}(x_{i,az}) = \frac{\partial^2 y_i}{\partial x_i^2}(x_{i,az}) = \frac{\partial T}{\partial x_i}(x_{i,az}) = \frac{\partial T}{\partial y_i}(y_{i,az}) = \frac{\partial G^{M,L}}{\partial x_i}(x_{i,az}) = \frac{\partial G^{M,V}}{\partial y_i}(y_{i,az}) = \frac{\partial G^{E,L}}{\partial x_i}(x_{i,az}) = \frac{\partial G^{E,V}}{\partial y_i}(y_{i,az}) = 0 \quad (eq.1)$$

According to their definition, the partial derivatives of the G^{EL}/RT and G^{EV}/RT vs. temperature are almost constant. On the other hand, the derivatives of the ideal Gibbs energy vs. temperature for the liquid and vapor phase are zero. Moreover, the partial derivatives of the G^{EV}/RT vs. composition are constant. Additionally, from the point of view of the common tangent plane criterion the existence of azeotropic points produces a cero value ternary pathways in the ternary space when calculating the following corrected difference functions Ψ_{ij}, where we have multiplied the difference of G^E derivatives by $x_i \cdot x_j$ in order to allow a clearer observation of the distillation regions in a single graph when combining the three possible functions Ψ_{ij}:
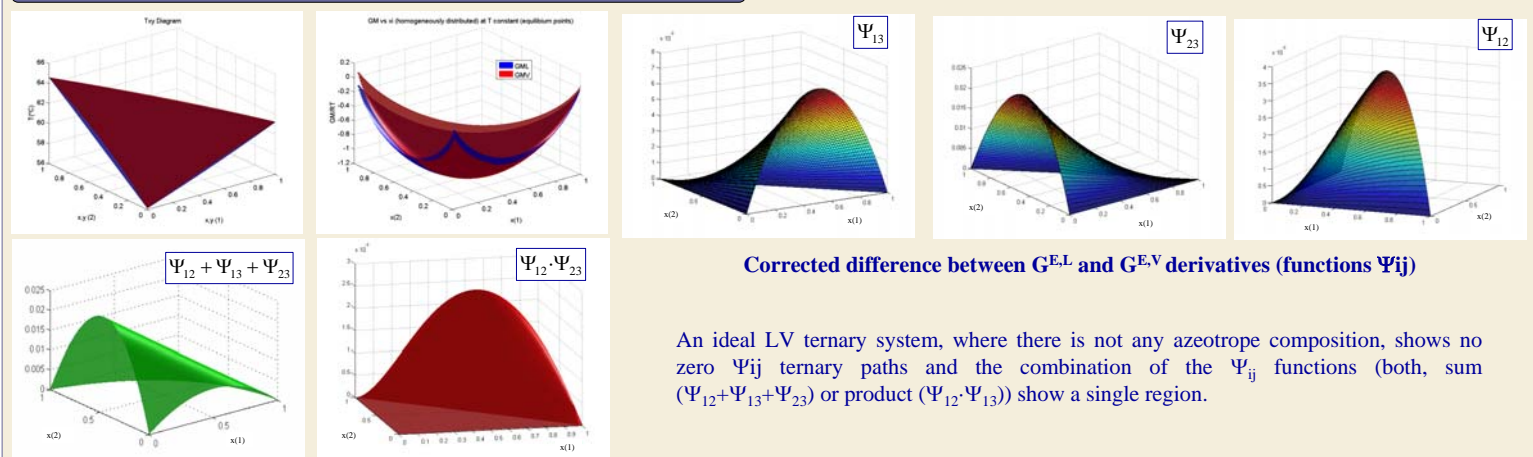
$$\Psi_{12} = \left[\left(\frac{\partial G^{E,L}(x_{1,2,3})}{\partial x_1} - \frac{\partial G^{E,L}(x_{1,2,3})}{\partial x_2} \right) - \left(\frac{\partial G^{E,V}(y_{1,2,3})}{\partial y_1} - \frac{\partial G^{E,V}(y_{1,2,3})}{\partial y_2} \right) \right] \cdot x_1 \cdot x_2$$

$$\Psi_{23} = \left[\left(\frac{\partial G^{E,L}(x_{1,2,3})}{\partial x_2} - \frac{\partial G^{E,L}(x_{1,2,3})}{\partial x_3} \right) - \left(\frac{\partial G^{E,V}(y_{1,2,3})}{\partial y_2} - \frac{\partial G^{E,V}(y_{1,2,3})}{\partial y_3} \right) \right] \cdot x_2 \cdot x_3$$
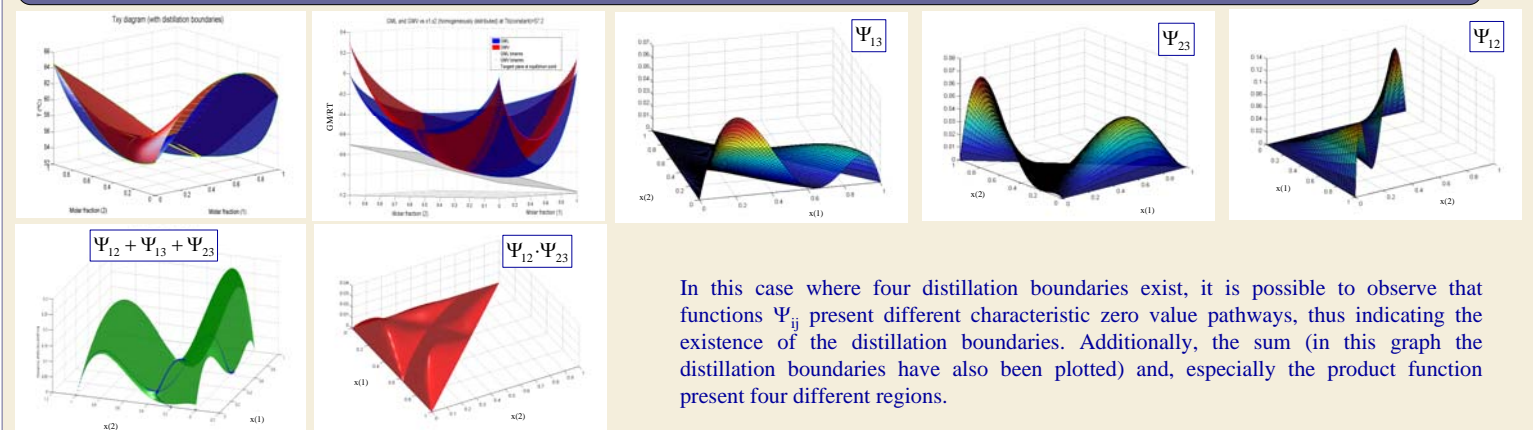
$$\Psi_{13} = \left[\left(\frac{\partial G^{E,L}(x_{1,2,3})}{\partial x_1} - \frac{\partial G^{E,L}(x_{1,2,3})}{\partial x_3} \right) - \left(\frac{\partial G^{E,V}(y_{1,2,3})}{\partial y_1} - \frac{\partial G^{E,V}(y_{1,2,3})}{\partial y_3} \right) \right] \cdot x_1 \cdot x_3$$

Since trajectories must exist where the conditions expressed in eq.(1) are fulfilled for at least one component if any azeotropic point exists. Thus the analysis of the evolution of such functions may provide interesting information on the type of equilibrium according to the existence of different distillation regions.

Example1: Ideal ternary system (no azeotropes, type #001 [8])

Corrected difference between $G^{E,L}$ and $G^{E,V}$ derivatives (functions Ψ_{ij})

An ideal LV ternary system, where there is not any azeotrope composition, shows no zero Ψ_{ij} ternary paths and the combination of the Ψ_{ij} functions (both, sum ($\Psi_{12}+\Psi_{13}+\Psi_{23}$) or product ($\Psi_{12}\cdot\Psi_{13}$)) show a single region.

Example: Ternary system with 3 binary azeotropies (2 of minimum temperature and one of maximum temperature), 1 ternary azeotropy (saddle) and 4 distillation boundaries (type #105 [8])

In this case where four distillation boundaries exist, it is possible to observe that functions Ψ_{ij} present different characteristic zero value pathways, thus indicating the existence of the distillation boundaries. Additionally, the sum (in this graph the distillation boundaries have also been plotted) and, especially the product function present four different regions.

References

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➢ The analysis of the topology of the excess functions has revealed interesting features that may help in the understanding of the phase equilibrium behaviour as well as in their calculation. In a future work we will extend this study to the 125 different possible behaviours of the ternary LV equilibrium (according to classification shown in Perry Handbook of Chemical Engineering [8]), in order to obtain the relations among the functions defined and the distillation regions.