

VAPOR-LIQUID EQUILIBRIA

Using the Gibbs Energy and the Common Tangent Plane Criterion

MARÍA DEL MAR OLAYA, JUAN A. REYES-LABARTA, MARÍA DOLORES SERRANO, ANTONIO MARCILLA
University of Alicante • Apdo. 99, Alicante 03080, Spain

Phase thermodynamics is often perceived as a difficult subject with which many students never become fully comfortable. It is our opinion that the Gibbsian geometrical framework, which can be easily represented in Excel spreadsheets, can help students to gain a better understanding of phase equilibria using only elementary concepts of high school geometry.

Phase equilibrium calculations are essential to the simulation and optimization of chemical processes. The task with these calculations is to accurately predict the correct number of phases at equilibrium present in the system and their compositions. Methods for these calculations can be divided into two main categories: the equation-solving approach (K-value method) and minimization of the Gibbs free energy. Isofugacity conditions and mass balances form the set of equations in the equation-solving approach. Although the equation-solving approach appears to be the most popular method of solution, it does not guarantee minimization of the global Gibbs energy, which is the thermodynamic requirement for equilibrium. This is because isofugacity criterium is only a necessary but not a sufficient equilibrium condition. Minimization of the global Gibbs free energy can be equivalently formulated as the stability test or the common tangent test.

The Gibbs stability condition is described and has been used extensively in many references.^[1, 2] It has been more frequently applied in liquid-liquid equilibrium rather than vapor-liquid equilibrium calculations. Gibbs showed that a necessary and sufficient condition for the absolute stability of a binary mixture at a fixed temperature, pressure, and overall composition is that the Gibbs energy of mixing (g^M) curve at no point be below the tangent line to the curve at the given

overall composition. This is the case with the binary system in **Figure 1(a)**; it is homogeneous for all compositions. The g^M vs. composition curve is concave down, meaning that no split occurs in the global mixture composition to give two liquid phases. Geometrically, this implies that it is impossible to find two different points on the g^M curve sharing a common tangent line. In contrast, the change of curvature in the g^M function as shown in **Figure 1(b)** permits the existence of two conjugated points (I and II) that do share a common tangent line and which, in turn, lead to the formation of two equilibrium liquid phases (LL). Any initial mixture, as for example z_1 in **Figure 1(b)**, located between the inflection points s on the g^M curve, is *intrinsically unstable* ($d^2g^M/dx_1^2 < 0$) and splits

Antonio Marcilla is a professor of chemical engineering at Alicante University. He has presented courses in Unit Operations, Phase Equilibria, 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 Technology-CSIC (Spain), he is now a full-time lecturer in Separation Processes and Molding Design.

María Dolores Serrano is a recent chemical engineering graduate of the University of Alicante. She is currently a post-graduate student, working on different aspects of phase equilibria.

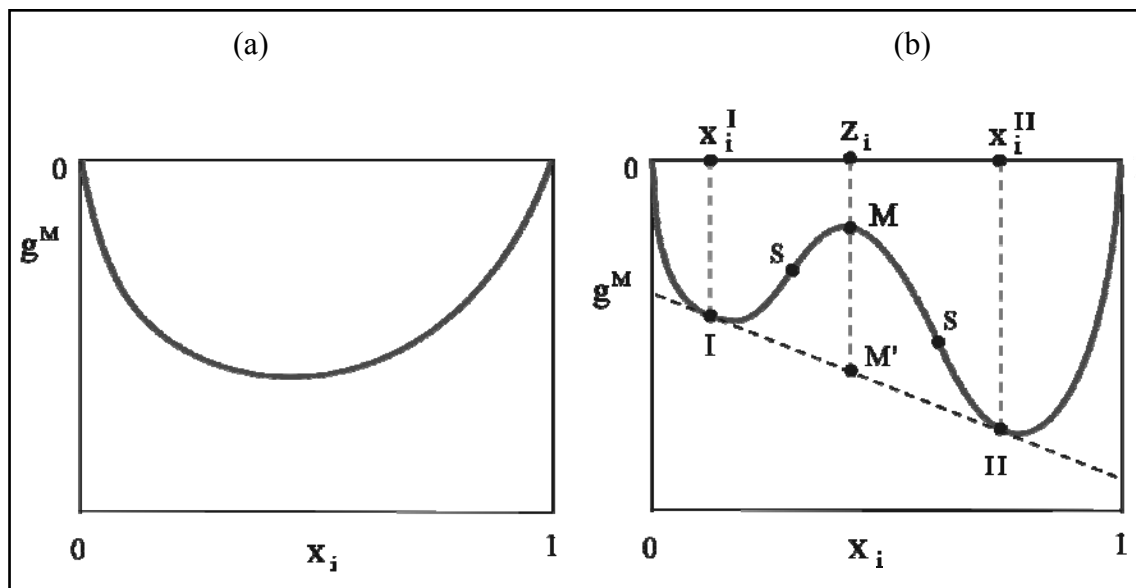


Figure 1. Dimensionless Gibbs energy of mixing (g^M) for a binary liquid mixture as a function of the molar fraction of component i (x_i): (a) for a homogeneous system, and (b) for a heterogeneous system (LL).

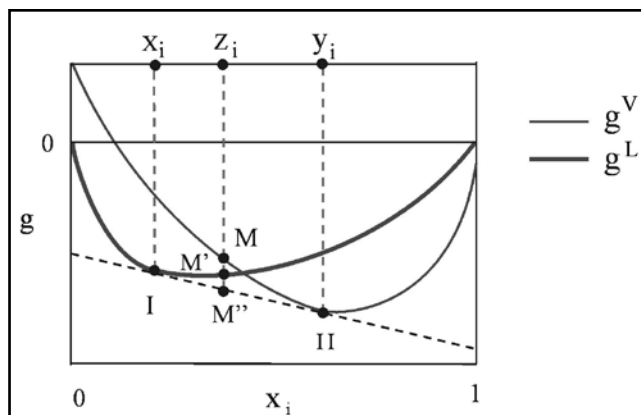


Figure 2. Dimensionless Gibbs energy curves (g^V , g^L) for a binary mixture with a VLE region at constant T and P as a function of the molar fraction of component i .

into two liquid phases having compositions x_i^I and x_i^{II} , and a lower value for the overall Gibbs energy of mixing ($M' < M$). Global mixtures located between points I and s or s and II are *metastable* or *locally stable* ($d^2g^M/dx_i^2 > 0$). Therefore, the inflection points separate the metastable equilibrium region from the definitely unstable region.^[3]

Of course, the Gibbs stability criteria can be extended to ternary or multicomponent systems, where the g^M curve is replaced by the g^M surface or g^M hyper-surface and the common tangent line by the common tangent plane or hyper-plane, respectively.

The analytical expression for the Gibbs energy in LLE calculations is the same for both phases (let it be denoted by g^L). This is not the case for equilibria involving different aggregation state phases such as vapor-liquid equilibria (VLE), where different expressions for the Gibbs energy must be used for each phase, yielding two possible Gibbs energy curves: g^V

and g^L . Obviously, a common reference state must be used for each of the components in the calculations, and for both of the phases involved (for example the pure component as liquid at the same P and T). VLE exists at a given T and P , whenever any initial mixture, such as z_i in **Figure 2**, is thermodynamically unstable and splits into a vapor and liquid phases having compositions y_i and x_i , respectively, with a common tangent line to both g^V and g^L curves and a lower value for the overall Gibbs energy of mixing ($M'' < M' < M$).

The geometrical perspective of the Gibbs energy minimization is not new and there are interesting papers dealing with this topic in depth. The paper of Jolls, et al.,^[4] for instance, presents images of thermodynamic fundamental and state functions for pure binary and ternary systems. These authors discuss the relationship between the model geometry and stability criteria. This geometrical perspective, however, is not usually considered in practice when dealing with VLE using local composition models for the liquid phases, although it clearly illustrates the conditions for stable equilibrium vs. other possible unstable situations. The goal of the present paper is to show an example of the visualization of the VLE from a Gibbs perspective for teaching purposes.

EDUCATIONAL ASPECTS

Our objective is to propose an exercise to analyze the VLE using the Gibbs common tangent plane criterion using Excel and Matlab. In the engineering education literature, a number of papers concerning the use of spreadsheets have been described.^[5, 6] Excel spreadsheets are used mainly due to their simplicity and built-in graphics capabilities. Matlab software, which has more powerful graphical tools, can be used to represent 3-D diagrams that support the graphical interpretation of equilibrium since plots can be easily rotated and manipulated to facilitate their understanding.

This activity is framed in the subject of Principals of Separation Processes in Chemical Engineering in a fourth-year course of a five-year program of chemical engineering. This task takes place during the first part of the course and consists of:

- A lecture of the theoretical fundamentals of VLE, presentation and analysis of T-x,y diagrams and sketch of Gibbs stability criterion.
- A guided classroom solution of different VLE problems with increasing difficulty. Previous presentation of a simple non-azeotropic VLE binary system, and consequent solution of a binary homogenous azeotropic mixture, where students work on their own computers using Excel and Matlab.
- Development of a project in groups of students where an analogous analysis of VLE, but also of LLE, must be done for a heterogeneous azeotropic binary mixture.
- As optional projects, VLE for ternary or more complicated mixtures could also be considered, but the visualization becomes more complicated.

THEORY

The equilibrium condition for component i being simultaneously present as a liquid and vapor equilibrium phase can be written as the isofugacity condition

$$f_i^v = f_i^L \quad (1)$$

$$\varphi_i^v \cdot P \cdot y_i = p_i^{ol} \cdot \varphi_i^{ol} \cdot \exp\left(\int_{p_i^o}^P \frac{v_i^c}{RT} dP\right) \cdot \gamma_i \cdot x_i \quad (2)$$

where φ_i^v is the fugacity coefficient for the vapor phase, P is the total pressure, y_i and x_i are the molar fractions of component i in the vapor and liquid phases, respectively, p_i^{ol} is the vapor pressure of component i , φ_i^{ol} is the fugacity coefficient for the liquid phase at p_i^o , γ_i is the activity coefficient, defined by the selected model, and v_i^c is the molar volume of the condensed phase as a function of pressure. The exponential correction is the *Poynting* factor which takes into account that the liquid is at a pressure P different from the liquid saturation pressure p_i^o .^[7]

At moderate pressures, φ_i^v , φ_i^{ol} , and the *Poynting* factor are near unity, and Eq. (2) can be rewritten as

$$P \cdot y_i = p_i^o \cdot \gamma_i \cdot x_i \quad (3)$$

The constant pressure T-x,y diagram can be obtained by calculating the bubble temperatures (T_b) of the various liquid mixture compositions (x_i), and also by calculating the composition of the equilibrium vapor phase (y_i). The calculation is to be carried out according to the flow chart in **Figure 3**.

On the other hand, the Gibbs energy of mixing (dimensionless) is the sum of two contributions, the ideal and excess Gibbs energies:

$$g^M = g^{id} + g^E \quad (4)$$

Gibbs Energy for the Liquid Phase

For liquid mixtures the ideal Gibbs energy of mixing (dimensionless) is

$$g^{id,L} = \sum_i x_i \cdot \ln x_i \quad (5)$$

where the reference state for each component i is the pure liquid at the temperature and pressure of the system.

Many equations have been proposed to model the excess Gibbs energy and can be found in the literature. For example, the van Laar equation for binary systems:

$$g^{E,L} = \frac{A_{12} \cdot A_{21} \cdot x_1 \cdot x_2}{A_{12} \cdot x_1 + A_{21} \cdot x_2} \quad (6)$$

where A_{12} and A_{21} are the binary interaction parameters of the model that must be obtained by equilibrium data correlation.

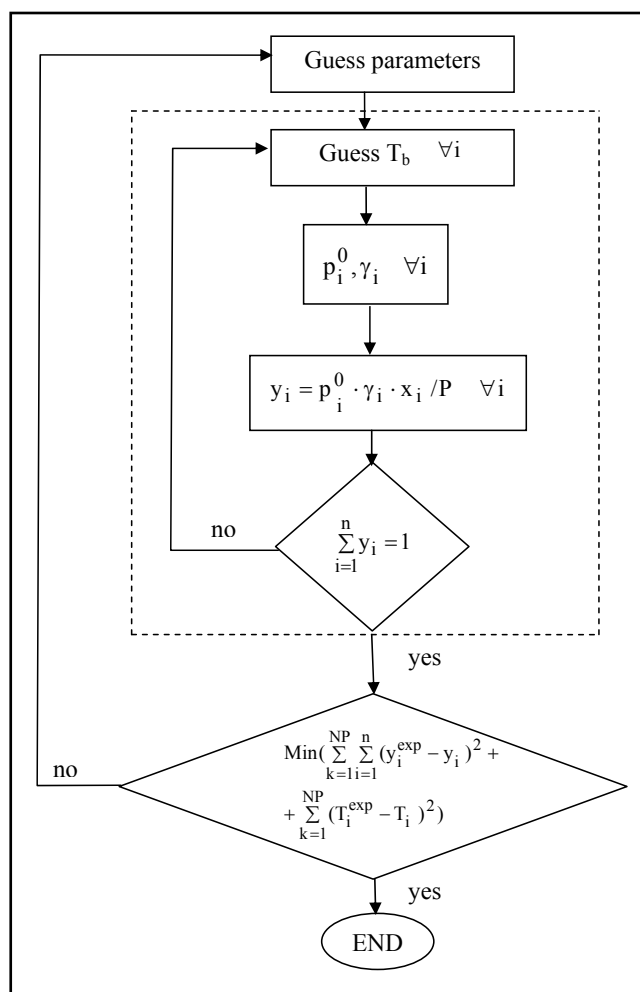


Figure 3. Flow chart for the calculation of the activity coefficient model parameters by equilibrium data regression. The discontinuous line represents the algorithm for the bubble point equilibrium calculations.

Substituting Eq. (5) and Eq. (6) into Eq. (4), and considering the selected reference state, the expression obtained for the Gibbs energy of the liquid phase at the temperature of the system T is:

$$g^L(T) = g^{M,L} = x_1 \ln x_1 + x_2 \ln x_2 + \frac{A_{12} \cdot A_{21} \cdot x_1 \cdot x_2}{A_{12} \cdot x_1 + A_{21} \cdot x_2} \quad (7)$$

Gibbs Energy for the Vapor Phase

The vapor phase is considered ideal and, therefore, the following equation is used for the Gibbs energy of mixing of the vapor phase:

$$g^{M,V} = g^{id,V} = y_1 \ln y_1 + y_2 \ln y_2 \quad (8)$$

To compare Gibbs energy curves for liquid and vapor phases both must be obtained from a common reference state. For VLE calculations at constant T and P a convenient reference state is the pure component as liquid at the same T and P of the system. In this case, the Gibbs energy of pure component i in the vapor and liquid phases are $g_i^{o,V} \neq 0$ and $g_i^{o,L} = 0$, respectively. The difference in the Gibbs energy between a pure vapor and a pure liquid can be approximated using the following equation:

$$g_i^{o,V} - g_i^{o,L} = \ln \frac{P}{p_i^o} \quad (9)$$

Consequently the following equation is used for the Gibbs energy of the vapor phase, referred to the liquid aggregation state at the temperature of the system T:

$$g^V(T) = y_1 \cdot g_1^{o,V} + y_2 \cdot g_2^{o,V} + y_1 \ln y_1 + y_2 \ln y_2 \quad (10)$$

According to Eq. (9), the sign of $g_i^{o,V}$ may be positive or negative; depending on the ratio between the total pressure of the system and the vapor pressure of component i, which, in turn, depends on the temperature:

$$\text{—If } P > p_i^o \rightarrow g_i^{o,V} - g_i^{o,L} > 0 \rightarrow g_i^{o,V} \text{ is positive}$$

$$\text{—If } P < p_i^o \rightarrow g_i^{o,V} - g_i^{o,L} < 0 \rightarrow g_i^{o,V} \text{ is negative}$$

After both the g^V and g^L isotherm curves have been calculated and represented, the Gibbs stability or common tangent plane test can be easily applied to them to ascertain which of the phases are most stable and what the equilibrium compositions are.

The reference state is defined to be arbitrary and for a system at constant T and P can be selected to be the liquid state at the temperature of the system for both components in both phases. If Gibbs energy surfaces for both p phases are generated to analyze the equilibrium as a function of temperature T, however, a reference state must be used in the calculations at a unique temperature T_0 .

$$g^p(T_0) = g^p(T) - \frac{1}{RT} \int_{T_0}^T S \cdot dT + \frac{1}{RT} \int_{T_0}^T V \cdot dP \quad (11)$$

For non-isothermal VLE, however, the Gibbs energy for both p phases (V and L) must be calculated as a function of temperature T using a reference state (*i.e.*, the pure liquid) at a unique reference temperature T_0 $g^p(T_0)$. In this case, the Gibbs energy for both vapor and liquid phases includes an entropic term from T_0 to T.

For isobaric conditions, Eq. (11) becomes:

$$g^p(T_0) = g^p(T) - \frac{1}{RT} \int_{T_0}^T \int_{T_0}^T \frac{C_{pL}}{T} \cdot dTdT \quad (12)$$

where C_{pL} is the heat capacity of the liquid. In the above expression $g^p(T)$ is calculated with Eq. (7) for $p=L$ or with Eq. (10) for $p=V$.

PROBLEM STATEMENT

For the binary homogeneous azeotropic system ethanol (1) + benzene (2) at $P=1$ atm:

- Calculate the parameters for the selected thermodynamic model regressing T-x,y experimental data.
- Build the temperature vs. composition (T-x,y) diagram with an Excel spreadsheet.
- Represent graphically in a 3-D diagram (for example, using Matlab) the g (vapor and liquid) vs. composition and temperature surfaces for this system.
- For a more precise analysis of the above 3-D figure, plot g curves in Excel for the vapor and liquid mixtures of the following isotherms: 90.0 °C, 79.0 °C, 72.0 °C, temperature of the calculated azeotrope, and 60.0 °C. The number of phases present and their compositions must be deduced using the Gibbs common tangent test.
- Show that the results obtained using the Gibbs stability criteria are consistent with those obtained using the T-x,y diagram.

The Van Laar equation can be used to represent the excess Gibbs energy (g^E) and the activity coefficient (γ_i) of the liquid mixtures. The vapor phase can be considered as ideal.

SOLUTION

The A_{ij} parameters for the Van Laar model [Eq. (6)] calculated for the ethanol (1) + benzene (2) binary system have been calculated by fitting VLE data^[8-10] according to the diagram flow shown in Figure 3. Figure 4 (next page) shows an example of the possible spreadsheet distribution to obtain the model parameter values and the T-x,y diagram by successive bubble temperature calculations with Solver function in Excel using various liquid mixture compositions (x_i) and calculating the equilibrium vapor phase composition. The parameter values obtained are $A_{12}=1.965$ and $A_{21}=1.335$ (dimensionless). As can be seen in Figure 4, a homogeneous azeotropic point occurs for this system at a minimum boiling temperature.

Figure 4 (right). Spreadsheet example of the Van Laar parameters calculation regressing T-x,y experimental data for the ethanol (1) + benzene (2) binary system at P=760 mmHg.

	A	B	C	D	E	F	G	H	I
27	Guess A ₁₂	Guess A ₂₁							
28	1.9649	1.3348							
29	T exp (°C)	x ₁ exp	y ₁ exp	Guess Tb	P* ₁ (mmHg)	P* ₂ (mmHg)	x ₂	γ ₁ (van Laar)	γ ₂ (van Laar)
30	80.09	0	0	80.05	815.82	760.94	1.000	7.1340	10.000
31	70.61	0.086	0.296	70.95	564.75	570.01	0.914	4.5534	10.200
32	68.52	0.258	0.392	68.41	507.43	523.97	0.742	2.3623	1.653
33	68.26	0.325	0.41	68.18	502.52	519.98	0.675	1.9600	1.2581
34	68.24	0.448	0.448	68.06	500.03	517.95	0.552	1.5037	1.4852
35	68.06	0.438	0.446	68.03	499.39	517.43	0.562	1.5314	1.4638
36	68.61	0.64	0.515	68.56	510.67	526.61	0.360	1.1621	2.0112
37	70.17	0.788	0.608	70.23	547.89	556.58	0.212	1.0480	2.5965
38	73.87	0.917	0.778	73.91	638.02	627.38	0.083	1.0066	3.2695
39	78.29	1	1	78.27	760.39	720.07	0.000	1.0000	3.7992
40	g ₁ calc (eq. 3)	g ₂ calc (eq. 3)	g ₁ cal-g ₂ cal	(Σg ₁ cal-l) ²	(T cal-T exp) ²	Σ(g ₁ cal-g ₁ exp) ²	Σ(Σg ₁ cal-l) ²	Σ(T cal-T exp) ²	Σ(Σg ₁ cal-g ₁ exp) ²
41	0.000	1.001	1.0012	1.51E-06	0.00144	0.00E-00	1.23E-04	1.82E-01	8.27E-04
42	0.291	0.699	0.9902	9.66E-05	0.11844	2.51E-05			
43	0.407	0.596	1.0031	9.38E-06	0.01300	2.23E-04			
44	0.421	0.581	1.0022	4.96E-06	0.00694	1.25E-04			
45	0.443	0.559	1.0019	3.74E-06	0.03295	2.29E-05			
46	0.441	0.560	1.0008	6.87E-07	0.00093	2.77E-05			
47	0.500	0.502	1.0014	2.02E-06	0.00286	2.33E-04			
48	0.595	0.403	0.9985	2.31E-06	0.00339	1.60E-04			
49	0.775	0.224	0.9989	1.16E-06	0.00175	9.56E-06			
50	1.001	0.000	1.0005	2.64E-07	0.00042	2.64E-07			
51	azeotrope calculation								
52	Guess x ₁	g ₁ exp	Guess Tb	P* ₁ (mmHg)	P* ₂ (mmHg)				
53	0.4409	0.4480	68.0075	498.8214	517.0483				
54	x ₂	γ ₁ (van Laar)	γ ₂ (van Laar)	g ₁ calc (eq. 3)	g ₂ calc (eq. 3)				
55	0.5591	1.5233	1.4699	0.4409	0.5591				
56	g ₁ cal-g ₂ cal	(Σg ₁ cal-l) ²	(x ₁ -y ₁) ² +(x ₂ -y ₂) ²						
57	1.0000	1.45E-12	7.23E-13						

Figure 5 (below). Gibbs energy surfaces for vapor V_g (ideal) and liquid L_g (Van Laar) mixtures as a function of the temperature and composition for the ethanol (1) + benzene (2) binary system at P=1 atm.

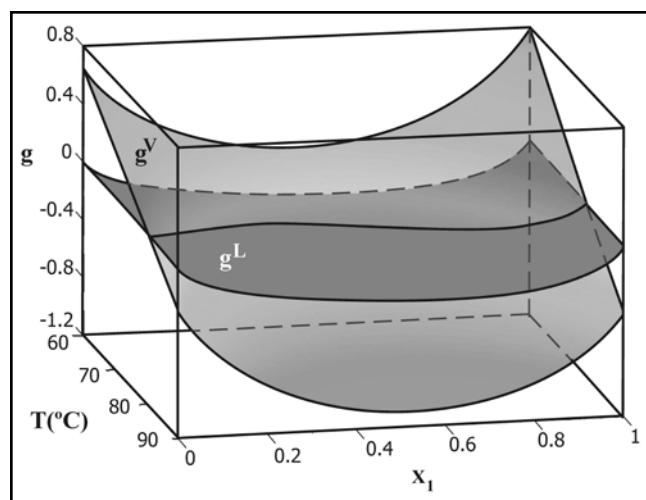


Figure 5 shows the 3D graph used to represent the Gibbs energy surfaces of the liquid (g^L) and vapor phases (g^V) as a function of temperature and composition. The selected reference state for each one of the components is the liquid state at the azeotrope boiling point (T_0). The Gibbs energy surfaces for L and V have been calculated using Eq. (12) where $g^p(T)$ when p =liquid is calculated with Eq. (7) and when p =vapor is calculated with Eq. (10). The values for $g_i^{o,V}$ are calculated with Eq. (9), where the vapor pressures for ethanol and benzene have been obtained using the Antoine equation, with the constants given in Table 1.^[11] The entropy changes of Eq. (12) are calculated with $C_p(T)$ given in Table 2.^[12]

As can be seen in Figure 5, the g surfaces cross each other so that the vapor phase is the stable phase at high temperatures

(g^V lower than g^L) and the liquid phase the stable aggregation state at lower temperatures (g^L lower than g^V). For a more detailed analysis of this figure some sectional planes have been selected, corresponding to the following isotherms: 90 °C, 79 °C, 72 °C, 68.01 °C (calculated azeotrope), and 60 °C.

Figure 6 shows the Gibbs energy curves plotted for the vapor and the homogeneous liquid mixtures at each one of these temperatures. After students have completed these representations, an analysis of Figure 6 is done, taking into account the Gibbs stability criteria:

- For $T=90$ °C, $P=1\text{atm} < p_2^o < p_1^o$; therefore, taking into account Eq. (9), $g_1^{o,V} < g_1^{o,L}$ for $i=1, 2$, and the entire g^V vs. composition curve is lower than g^L [Figure 6(a)], showing that the vapor phase is the stable aggregation state over the entire composition space at this temperature.
- For $T=79$ °C, $p_2^o < P=1\text{atm} < p_1^o$; therefore, for the ethanol component, $g_1^{o,V} < g_1^{o,L}$, but for benzene, $g_2^{o,V} > g_2^{o,L}$. The g^V and g^L curves have two points sharing a common tangent line, corresponding to the VL equilibrium $y_1=0.0355$ and $x_1=0.00497$. At molar fractions below $z_1=0.00497$ the liquid is the stable aggregation state, and at values higher than $z_1=0.0355$ the vapor is the stable phase [Figure 6(b)]. Any global mixture between those values will split in the VLE.
- For $T=72$ °C, $p_2^o < p_1^o < P=1\text{atm}$; therefore, $g_2^{o,V} > g_2^{o,L}$ for both ethanol and benzene components. Two regions of the g^V and g^L curves each contain one point of VL equilibrium: $[y_1=0.269, x_1=0.0708]$ and $[y_1'=0.681, x_1'=0.861]$ having common tangent lines that connect

the conjugated y-x equilibrium compositions, as can be seen in Figure 6(c). The vapor is the stable aggregation state at intermediate concentrations and the liquid is the stable phase near each pure component.

- The g^V curve rises as the temperature decreases until the azeotropic temperature (68.01 °C) is reached. Here, both g^V and g^L curves are tangent in one point [Figure 6(d)]. This point corresponds to the homogeneous azeotrope, for which the vapor and liquid phases in equilibrium have identical compositions ($y_1 = x_1 = 0.441$).
- For $T = 60$ °C, the g^L curve lies below the g^V curve over the entire composition space, demonstrating that a homogeneous liquid phase is the most stable aggregation state for any global mixture composition [Figure 6(e)].

It must be highlighted that all of the above, deduced from the Gibbs energy curves, is obviously consistent with the T-x,y diagram shown in Figure 4. Treatment of the VLE calculation using the Gibbs common tangent plane criteria provides students with a deeper understanding of the problem, however, because the insight into the reasons for the V or L phase stability or the VLE splitting is much more evident than with using the isofugacity condition. Although solving the isofugacity condition together with the mass balance equations (K-value method) constitutes the most popular method of calculation, our experience has shown that the Gibbsian geometrical framework is a very useful tool for educational purposes. Students state that the geometric analysis of chemical equilibrium, with an available and easy to use program such as Excel, permits a clear understanding of the VLE splitting in terms of Gibbs energy minimization.

EXTENSION TO HETEROGENEOUS AZEOTROPIC MIXTURES

An extension of this exercise is proposed where the VLE is studied for a heterogeneous instead of a homogeneous azeotropic system. The binary system

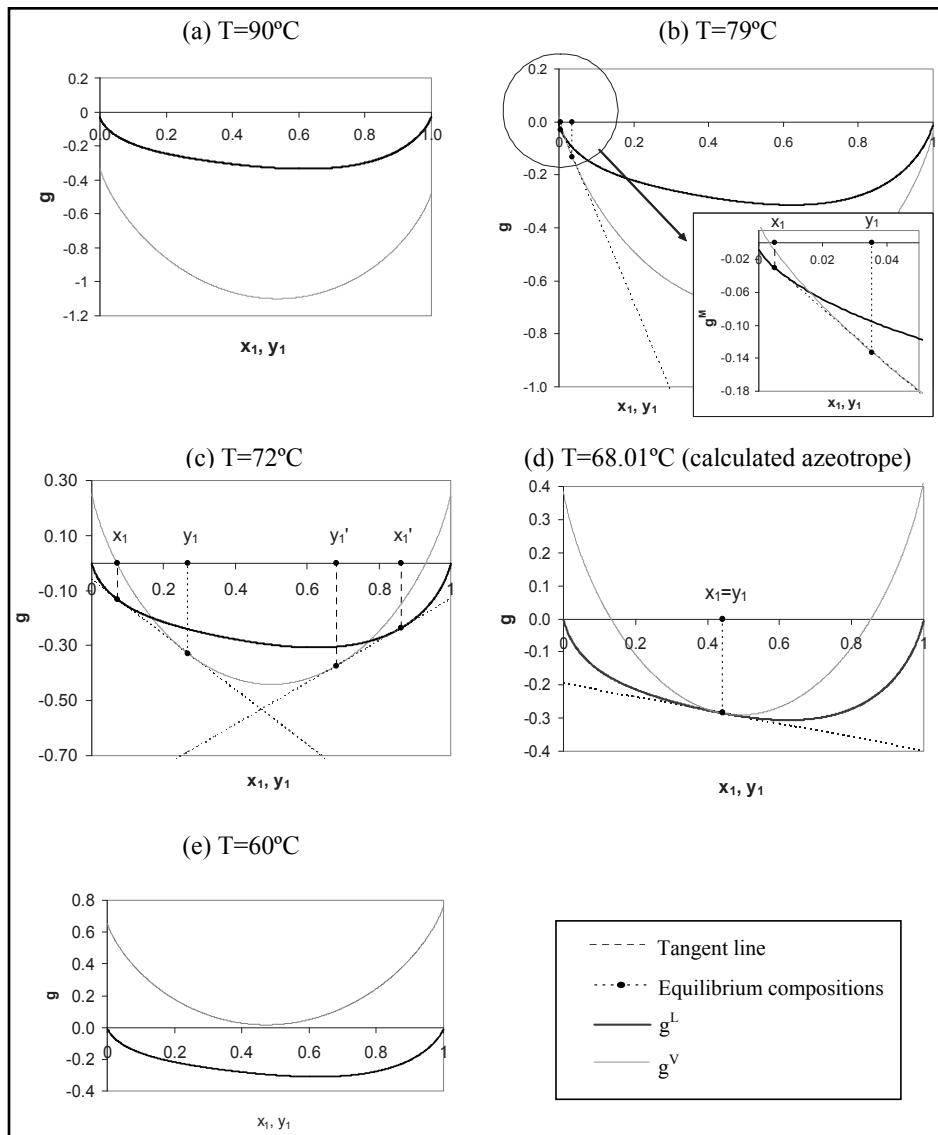


Figure 6. Analysis of the Gibbs energy curves for vapor (g^V) and liquid (g^L) mixtures at different temperatures for the ethanol (1) + benzene (2) binary system at $P=1$ atm showing the common tangent equilibrium condition.

TABLE 1 Antoine Equation Constants for Ethanol and Benzene ⁽¹⁰⁾			
	$\log(p^\circ) = A - B / (T + C)$ (p° in bar, T in °C)		
	A	B	C
Ethanol	5.33675	1648.220	230.918
Benzene	3.98523	1184.240	217.572

TABLE 2 Heat Capacity Constants of Liquid for Ethanol and Benzene ⁽¹²⁾				
	$C_p L = A + BT + CT^2 + DT^3$ (J/mol/K, T in K)			
	A	B	C	D
Ethanol	59.342	0.36358	-0.0012164	1.803·10 ⁻⁶
Benzene	-31.662	1.3043	-0.0036078	3.8243·10 ⁻⁶

water-n-butanol at $P = 1$ atm is an example of a heterogeneous azeotrope. The vapor phase can be considered ideal as in the previous example. The NRTL equation can be used to represent the excess Gibbs energy (g^E) and the activity coefficient (γ_i) of the liquid mixtures. The equation parameters can be obtained by fitting the VLE and VLLE data at 1 atm^[10,13,14] following the same calculation algorithm shown in the previous section. The values obtained for these binary NRTL interaction parameters are: $A_{12} = 1256.9$ K, $A_{21} = 374.86$ K, and $\alpha_{12} = 0.476$.

Figure 7 shows the T-x,y diagram of the system under consideration. Figure 8 shows the 3-D graph used to represent the Gibbs energy surfaces for the vapor and liquid phases, as functions of the temperature and composition. The selected reference state for each one of the components is the liquid state at the boiling point of the azeotrope (T_0). The g surfaces cross each other, as in the previous example shown in Figure 5, but the existence of a heterogeneous azeotrope implies that one vapor and two different liquid phases must coexist in equilibrium at a unique temperature. The isotherm of the azeotrope ($T = 92.7$ °C) has been included in Figure 8. To provide a better understanding of this 3-D graph, some sectional planes corresponding to the following isotherms—91 °C, 94 °C, and 92.7 °C (calculated azeotrope)—have been shown in Figure 9:

- For all temperatures below the azeotrope, g^L is lower than g^V over the entire the composition space. According to the Phase Rule constraint, for $n=2$ components and $p=2$ phases, there are two degrees of freedom: $f=n+2-p=2$. Consequently, when the pressure is fixed, a temperature

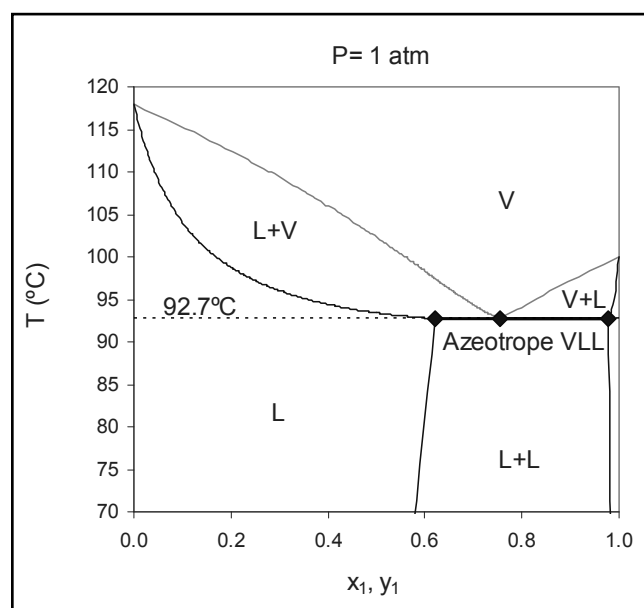


Figure 7. Temperature versus liquid (x) and vapor (y) molar fractions for the binary system water (1) + n-butanol (2) at $P=1$ atm, including the azeotropic isotherm line.

must be specified to calculate the LL equilibrium compositions. Figure 9(a) shows the isotherm corresponding to $T=91$ °C where two points of the g^L curve ($x_1^{L1} = 0.623$, $x_1^{L2} = 0.978$) have a common tangent line, demonstrating that a liquid phase splitting is the most stable situation for any global mixture composition z comprised between them, $x_1^{L1} < z_1 < x_1^{L2}$.

- For temperatures above the azeotrope, the g^V curve twice intersects the g^L curve giving two regions of VL equilibrium since there are two common tangent lines. When the pressure is fixed, a temperature must be specified to calculate the corresponding equilibrium compositions in the two VL regions. Figure 9(b) shows the isotherm $T=94$ °C where there are two common tangents to the g^V and g^L curves, each one defining a VL equilibrium: $[y_1 = 0.710, x_1 = 0.435]$ and $[y_1' = 0.795, x_1' = 0.986]$. The vapor is the stable aggregation state at intermediate concentrations and the liquid is the stable phase near each pure component.
- It is obvious that between the above situations, there must be a temperature, which is the azeotrope temperature, where the g^V and g^L curves have a unique common tangent line. According to the Phase Rule, for $n=2$ components and $p=3$ phases, there is only one degree of freedom: $f=n+2-p=1$. Consequently, when the pressure is fixed, only the azeotrope temperature describes the VLL equilibrium. Figure 9(c) shows the $T=92.7$ °C isothermal section where one point on the g^V curve ($y_1=0.756$) and two points on the g^L curve ($x_1^{L1}=0.622$, $x_1^{L2}=0.978$)

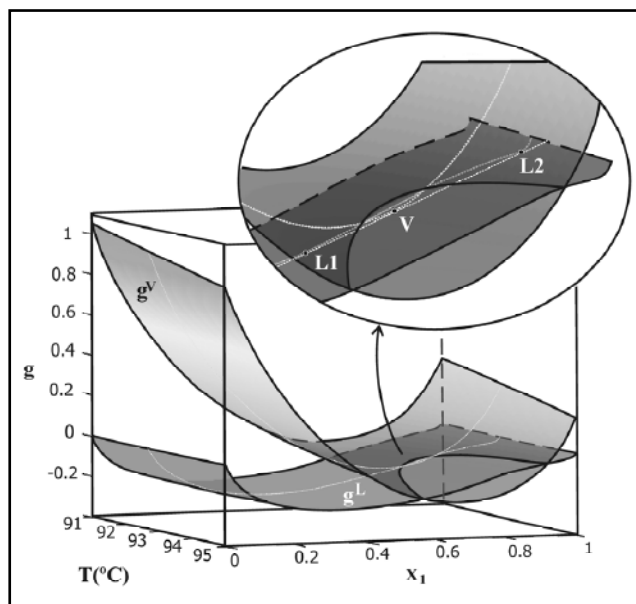


Figure 8. Gibbs energy surfaces for vapor (Vg) and liquid (Lg) mixtures as a function of the temperature and composition for the water (1) + n-butanol (2) binary system at $P=1$ atm. The isotherm curves ($T=92.7$ °C) of the azeotrope have also been included on the surfaces.

have a common tangent line. The existence of this VLL equilibrium is consistent with the T-x,y representation of this system (Figure 7).

With this example, the students demonstrate the reason for the VLL splitting in terms of stability or the minimum Gibbs energy of the system.

CONCLUSIONS

Dealing with the VLE calculation in terms of the Gibbs common tangent criteria provides students with a deeper understanding of the problem than using the isofugacity condition.

An exercise of application of the Gibbs common tangent criteria to VLE has been proposed for a homogeneous azeotropic binary system at a constant pressure using simple tools such as Excel spreadsheets and Matlab graphics. The Gibbs energy surface and curves at different temperatures have been analyzed to compare distinct situations that are consistent with

the T-x,y diagrams. This graphical analysis proves that the vapor is the stable phase at high temperatures, the liquid phase is the stable aggregation state for lower temperatures, and that the azeotrope (VLE) corresponds to a temperature where both liquid and vapor Gibbs energy curves are tangent in one point. Students use this previous spreadsheet to develop an extension to consider the VLLE of a heterogeneous azeotropic system, which is tackled as a project in groups. Their reports of results show that the reasons for the V or L phase stability or the VLE and VLLE splitting is much more evident with the Gibbsian framework than using the isofugacity condition.

NOMENCLATURE

- f_i^F Fugacity of component i in phase F
- P Pressure
- p phase
- f Degrees of freedom (Phase Rule)

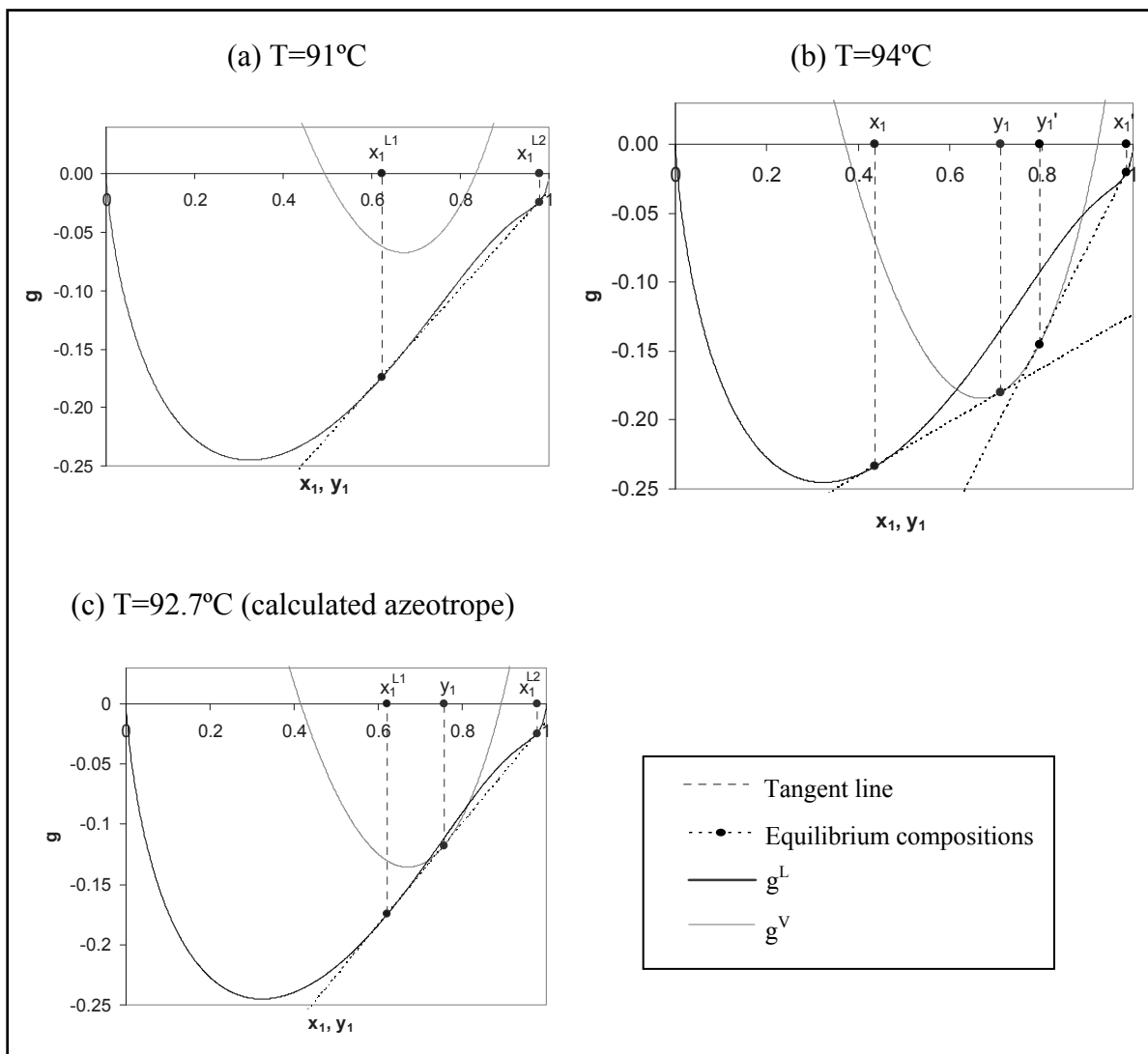


Figure 9. Analysis of the Gibbs energy curves for vapor (V_g) and liquid (L_g) mixtures at different temperatures for the water (1) + n-butanol (2) binary system at $P=1$ atm, showing the common tangent equilibrium condition.

T_b	Boiling temperature
n	Number of components
φ_i^V	Fugacity coefficient for the vapor phase
φ_i^{oL}	Fugacity coefficient for the liquid phase at oip
V_i^c	Molar volume of the condensed phase as a function of pressure
P_i^o	Vapor pressure of component i
y_i	Molar fraction of component i in the vapor phase
x_i	Molar fraction of component i in the liquid phase
γ_i	Activity coefficient of component i in the liquid phase
A_{ij}	Binary interaction parameter between species i and j (van Laar or NRTL equation)
α_{ij}	Non-randomness factor (NRTL equation)
g^{id}	Ideal Gibbs energy of mixing (dimensionless)
g^E	Excess Gibbs energy (dimensionless)
g^M	Gibbs energy of mixing (dimensionless)
g	Gibbs energy (dimensionless)
g^V, g^L	Gibbs energy (dimensionless) of the vapor and liquid phase, respectively.
$g_i^{o,V}, g_i^{o,L}$	Gibbs energy of pure component i (dimensionless) in the vapor and liquid phase, respectively.

Superscripts

id	Ideal
E	Excess
M	Mixture
L, L1, L2	Liquid phase, Liquid phase 1, Liquid phase 2
V	Vapor phase

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REFERENCES

1. Wasylkiewicz, S.K., S.N. Sridhar, M.F. Doherty, and M.F. Malone, "Global Stability Analysis and Calculation of Liquid-Liquid equilibrium in Multicomponent Mixtures," *Ind. Eng. Chem. Res.*, **35**, 1395-1408 (1996)
2. Baker, L.E., A.C. Pierce, and K.D. Luks, "Gibbs Energy Analysis of Phase Equilibria," *Soc. Petrol. Eng. AIME.*, **22**, 731-742 (1982)
3. Sandler, S.I., *Models for Thermodynamic and Phase Equilibria Calculations*, Marcel Dekker, New York (1994)
4. Jolls, K.R., and D.C. Coy, "Visualizing the Gibbs Models," *Ind. Eng. Chem. Res.*, **47**, 4973-4987 (2008)
5. Castier, M., "XSEOS—an Open Software for Chemical Engineering Thermodynamics," *Chem. Eng. Ed.*, **42**(2) 74 (2008)
6. Lwin, Y., "Chemical Equilibrium by Gibbs Energy Minimization on Spreadsheets," *Int. J. Eng. Ed.*, **16**(4) 335-339 (2000)
7. Prausnitz, J.M., R.N. Lichtenthaler, and E. Gomes De Azevedo, *Molecular Thermodynamics of Fluid-Phase Equilibria*, 3rd Ed., Prentice Hall PTR, Upper Saddle River (1999)
8. Gmehling, J., and U. Onken, *Vapor-Liquid Equilibrium Data Collection. Alcohols, ethanol and 1, 2-Ethandiol, Supplement 6*, Chemistry Data Series, DECHEMA (2006)
9. Wisniak, J., "Azeotrope Behaviour and Vapor-Liquid Equilibrium Calculation", AICHE M.I. Series D. Thermodynamics, V.3, AICHE, 17-23 (1982)
10. Lide, D.R., *CRC Handbook of Chemistry and Physics 2006-2007: A Ready-Reference Book Of Chemical and Physical Data*, CRC Press (2006)
11. Poling, B.E., J.M. Prausnitz, and J.P. O'Connell, *The Properties of Gases and Liquids*, McGraw Hill (2001)
12. Yaws, C.L., *Chemical Properties Handbook: Physical, Thermodynamic, Environmental, Transport, Safety, and Health-Related Properties for Organic and Inorganic Chemicals*, McGraw-Hill (1999)
13. Gmehling, J., and U. Onken, *Vapor-Liquid Equilibrium Data Collection. Aqueous System*, Supplement 3. Vol. I, part 1c. Chemistry Data Series, DECHEMA, (2003)
14. Iwakabe, K., and H. Kosuge, "A Correlation Method For Isobaric Vapor-liquid and Vapor-liquid-liquid Equilibria Data of Binary Systems," *Fluid Phase Equilib.*, **192**, 171- 186 (2001) □