APPLICATION OF THE DOUBLE-TANGENT CONSTRUCTION OF COEXISTING PHASES to Any Type of Phase Equilibrium For Binary Systems Modeled With the Gamma-Phi Approach

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Phase equilibrium calculations are essential to the simulation and optimization of chemical processes. The success of such calculations depends on correct predictions of the number and compositions of phases present at a given temperature, pressure, and overall fluid composition. Equality of chemical potentials for each component in all phases is, however, only a necessary but not a sufficient condition to reach a thermodynamically stable equilibrium. As a consequence, if a stability analysis is not performed, it is not possible to ascertain that the calculated equilibrium state is the one having the lowest Gibbs energy and consequently, an incorrect number of phases or incorrect phase compositions may be predicted.

The double-tangent construction of coexisting phases is an elegant approach to visualizing all the multiphase systems that satisfy the equality of chemical potentials and to select the stable state. This paper shows how the molar Gibbs energy change on mixing ($\Delta G^\text{mix}$) can be used to easily perform the double-tangent construction of coexisting phases for binary systems modeled with the gamma-phi approach.

Many examples of instances where incorrect predictions (false two-phase states) may be made will be described. The mathematical equations to handle are simple and can easily be used by the students during class exercises. Two binary systems involving vapor-liquid (VL), liquid-liquid (LL), vapor-liquid-liquid (VLL), solid-liquid (SL), solid-solid (SS), and solid-solid-liquid (SSL) equilibria are discussed in detail.

THE GIBBS DOUBLE-TANGENT CONSTRUCTION OF COEXISTING PHASES

This section is devoted to recalling how to properly perform the Gibbs double-tangent construction of coexisting phases that makes it possible to graphically determine the composition of the phases in equilibrium in a system of known temperature, pressure, and overall composition.

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From basic thermodynamics,[1] it is well known that by plotting, at constant temperature and pressure, any molar property $m$ of a binary system vs. $z_i$ (the overall composition), and by adding the tangent line for a composition $z_i'$, the tangent intercepts (at $z_i = 1$ and $z_i = 0$) directly give the values of the two molar partial properties: $\overline{m}_1(T, P, z'_i)$ and $\overline{m}_2(T, P, z'_i)$. This graphical technique can be used to determine the composition of the coexisting phases by plotting $g$ (the molar Gibbs energy) as a function of $z_i$ at constant $T$ and $P$. Indeed, for a binary system, the equilibrium condition between two phases $\alpha$ and $\beta$ is:

$$
\begin{align*}
\overline{g}_\alpha(T, P, z_{\alpha}^1) &= \overline{g}_\beta(T, P, z_{\beta}^1) \\
\overline{g}_\alpha(T, P, z_{\alpha}^2) &= \overline{g}_\beta(T, P, z_{\beta}^2)
\end{align*}
$$
(1)

where $\overline{g}$ denotes the chemical potential of component $i$. As a consequence, the presence of a double tangent—in a $g$ vs. $z_i$ plot—allows defining two phases, the composition of which are $z_{\alpha}^i$ and $z_{\beta}^i$, which satisfy Eq. (1). Let us recall, however, that Eq. (1) is a necessary but not a sufficient condition to reach a stable equilibrium. This means that the graphically determined compositions do not necessarily correspond to a stable equilibrium.

It is nevertheless impossible to plot $g$ vs. $z_i$ since the molar Gibbs energy cannot be defined absolutely by the classical thermodynamics, and an elegant way to bypass this limitation is to plot instead:

$$
\Delta g(T, P, z) = g(T, P, z) - \sum_{i=1}^2 z_i \cdot \overline{g}_{i, pure}^{ref.\ state}(T, P)
$$
(2)

The corresponding partial molar properties are given by:

$$
\Delta \overline{g}_i(T, P, z) = \overline{g}_i(T, P, z) - \overline{g}_{i, pure}^{ref.\ state}(T, P)
$$
(3)

Eq. (1) thus writes:

$$
\begin{align*}
\Delta \overline{g}_\alpha(T, P, z_{\alpha}^1) &= \Delta \overline{g}_\beta(T, P, z_{\beta}^1) \\
\Delta \overline{g}_\alpha(T, P, z_{\alpha}^2) &= \Delta \overline{g}_\beta(T, P, z_{\beta}^2)
\end{align*}
$$
(4)

We can thus assert that the presence of a double tangent on an isothermal and isobaric $\Delta g(T, P, z)$ vs. $z_i$ plot allows defining two phases that satisfy Eq. (1). In Eq. (2), the pure component reference state can be chosen freely and can, for instance, be the pure liquid, the pure gas, or the stable (actual) state.

In this study, the selected reference state is the stable (actual) state of the pure component at the pressure and temperature of the studied system so that $\Delta g(T, P, z)$ is simply the Gibbs energy change on mixing $g^m$. Let us indeed recall that the property change on mixing $M^m$, of any extensive property $M$, is by definition the difference between the property $M$ of the actual mixture and the sum of the properties of the pure components that make it up—all at the same temperature and pressure as the mixture.[2,3] We want to emphasize that such a quantity is called "change on mixing" because it is the change that would be measured if the mixing took place in a mixing device of a laboratory. As an example, the enthalpy change on mixing can be measured using a calorimeter; two streams—one of pure fluid 1 and the second of pure fluid 2, both at a temperature $T$ and at pressure $P$—enter a mixing device, and a single mixed stream, also at $T$ and $P$, leaves. Heat is added or removed to maintain the temperature of the outlet stream. This quantity of heat is by definition the enthalpy change on mixing. This well-known example was selected to emphasize that all the states are physically realizable: The obtained mixture (liquid, gaseous, solid, or in the two-phase area) and the two pure fluids (either liquid, gaseous, or solid) are in their stable state at $T$ and $P$. We can thus define the molar Gibbs energy change on mixing $g^m$ by the following equation:

$$
g^m(T, P, z) = g(T, P, z) - \sum_{i=1}^2 z_i \cdot \overline{g}_{i, pure}^{stable}(T, P)
$$
(5)

We believe it was necessary to recall the proper definition of the molar Gibbs energy change on mixing because in many textbooks in which the double-tangent construction of coexisting phases is explained, $\Delta g(T, P, z)$ defined in Eq. (2) is mistakenly called Gibbs energy change on mixing when the pure-component reference state is the pure liquid or the pure gas.

When the different phases in equilibrium are in the same aggregation state, e.g., liquid-liquid equilibrium (LLE), a single expression of $g^m$ must be considered ($\overline{g}_{liquid}$ for an LLE). On the other hand when the phases in equilibrium are in different aggregation states, e.g., vapor-liquid equilibrium (VLE), solid-liquid equilibrium (SLE), etc., it is necessary to plot as many $g^m$ curves as aggregation states ($\overline{g}_{liquid}$ and $\overline{g}_{gas}$ for a VLE, $\overline{g}_{liquid}$ and $\overline{g}_{solid}$ for an SLE, $\overline{g}_{gas}$ and $\overline{g}_{solid}$ for an SVE). $\overline{g}_{liquid}$, $\overline{g}_{gas}$, and $\overline{g}_{solid}$ are, respectively, the $g^m$ expressions of the one-phase liquid or gas or solid postulated system. For a given value of the overall composition $z_i$, only the smallest value between $\overline{g}_{liquid}$, $\overline{g}_{gas}$, and $\overline{g}_{solid}$ that identifies the most stable homogeneous system must be reported in the $g^m$ vs. $z_i$ plot (this requirement is a statement of the second law of thermodynamics: when several homogeneous states are possible at a given $T$, $P$, and overall composition only the transformation from high to low Gibbs energy levels is authorized thus justifying why the stable state is associated to the lowest Gibbs energy change on mixing value).

The molar Gibbs energy change on mixing of the one-phase system is thus defined by:

$$
g^m(T, P, z) = \min\{\overline{g}_{liquid}(T, P, z), \overline{g}_{gas}(T, P, z), \overline{g}_{solid}(T, P, z)\}
$$
(6)

The next section explains how to calculate such a property change on mixing regardless of the aggregation state.
For a binary system, \( g^m \) is defined by:

\[
\hat{g}^m(T,P,z) = \frac{\text{given agg. state (T,P,z)}}{RT} = \sum_{i=1}^{2} z_i \cdot \frac{\hat{g}^m_i(T,P,z)}{RT}
\]

(7)

In order to calculate \( g^m \), it is thus necessary to know the mathematical expression of the chemical potential change on mixing, \( \hat{g}^m \), whatever the considered aggregation state (liquid, gas or solid):

\[
\hat{g}^m_{\text{solid}}(T,P,z) = \ln \left[ \frac{\hat{g}^m_{\text{liquid}}(T,P,x)}{f^m_{\text{gas}}(T,P)} \right]
\]

(8)

**Special attention to \( g^m_{\text{solid}} \)**

The type of solid-liquid equilibrium (SLE) mainly depends on the mutual solubility of the components in the solid phase. In this paper, we will assume total immiscibility in the solid phase (a solid phase is assumed to be one pure component) since it is the widest spread SLE behavior in the case of organic compounds. More complicated cases could obviously be imagined and analyzed. By formulating this hypothesis, the \( g^m_{\text{solid}}(T,P,z) \) quantity can only be calculated for \( z_i = 1 \) and becomes composition-independent. Consequently, the curve reduces to a single point.

**Basic thermodynamics relations**

In order to use Eq. (8), the basic thermodynamic relations between the fugacity, the fugacity coefficients, and the activity coefficients must be known. For clarity, let us thus recall that:

- the fugacity \( \hat{f}_i \) and the fugacity coefficient \( \gamma_i \) of a component \( i \) in a multi-component phase are related through:

\[
\hat{f}_i(T,P,x) = x_i \cdot \gamma_i
\]

(12)

- The fugacity of a pure component changes with pressure according to:

\[
f_{\text{pure}}(T,P) = f_{\text{pure}}(T,P) \exp \left[ \frac{1}{RT} \int_{P_1}^{P} f_{\text{pure}}(T,P) \cdot dP \right]
\]

(11)

- The activity coefficient \( \gamma_i \) of a component \( i \) in a liquid solution satisfies:

\[
\hat{f}_{\text{liquid}}(T,P,x) = x_i \cdot \gamma_i
\]

(12)

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\[
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\]

(11)

**General expressions of \( g^m \)**

In Eq. (8), the aggregation state of the stable pure component depends on temperature and pressure and three different cases must be considered.

- **CASE 1**: pure component \( i \) is gaseous, i.e., \( T > T_{b,i}(P) \) where \( T_{b,i}(P) \) is the boiling temperature of pure \( i \) at the selected pressure. From Eqs. (8) to (13), we obtain:

\[
\hat{f}_i(T,P,z) = P \cdot z_i \cdot \hat{\phi}_i(T,P,z)
\]

(9)

- For a pure component, Eq. (9) is written:

\[
f_{\text{pure}}(T,P) = f_{\text{pure}}(T,P) \exp \left[ \frac{1}{RT} \int_{P_1}^{P} f_{\text{pure}}(T,P) \cdot dP \right]
\]

(10)

- The fugacity of a pure component changes with pressure according to:

\[
f_{\text{pure}}(T,P) = f_{\text{pure}}(T,P) \exp \left[ \frac{1}{RT} \int_{P_1}^{P} f_{\text{pure}}(T,P) \cdot dP \right]
\]

(11)

- The activity coefficient \( \gamma_i \) of a component \( i \) in a liquid solution satisfies:

\[
\hat{f}_{\text{liquid}}(T,P,x) = x_i \cdot \gamma_i
\]

(12)

- The Gibbs energy of fusion (melting), defined as

\[
\Delta g_{m,i} = g^m_{\text{liquid}}(T,P) - g^m_{\text{solid}}(T,P)
\]

(13)

- The Gibbs energy of sublimation (melting), defined as

\[
\Delta g_{m,i} = g^m_{\text{liquid}}(T,P) - g^m_{\text{pure}}(T,P) - \Delta g_{m,i}(T)
\]

(13)

In Eq. (14):

\[
\hat{\phi}_i = \frac{\hat{\phi}_{\text{pure}}(T,P_{Sat})}{\hat{\phi}_{\text{gas}}(T,P)} \exp \left[ \frac{1}{RT} \int_{P_1}^{P} \frac{\hat{f}_{\text{liquid}}(T,P,x) \cdot dP}{RT} \right]
\]

(14a)
This quantity is close to unity under low or moderate pressure and is usually neglected.

• CASE 2: pure component \( i \) is liquid, \( i.e., T_{m,i}(P) < T < T_{b,i}(P) \). We thus obtain:

\[
\frac{e^{n}_{i,\text{liquid}}(T,P,x)}{RT} = \ln \left[ \frac{\hat{f}_{i,\text{liquid}}(T,P,x)}{f_{i,\text{pure}}(T,P)} \right] = \ln(\chi_i) + \frac{\Delta G_{m,i}(T)}{RT} \]

\[
\frac{e^{n}_{i,\text{gas}}(T,P,y)}{RT} = \ln \left[ \frac{\hat{f}_{i,\text{gas}}(T,P,y)}{f_{i,\text{pure}}(T,P)} \right] = \ln \left[ \frac{P \cdot y_i \cdot C_i}{P_{i}^{\text{sat}}(T)} \right] + \frac{\Delta G_{m,i}(T)}{RT} \]

\[
\frac{e^{n}_{i,\text{solid}}(T,P)}{RT} = \ln \left[ \frac{\hat{f}_{i,\text{solid}}(T,P)}{f_{i,\text{pure}}(T,P)} \right] = \ln \left[ \frac{\gamma_{i} \cdot P_{i}^{\text{sat}}(T)}{P_{i}^{\text{sat}}(T)} \right] = 0 \quad (16)
\]

In Eq. (15):

\[
C_i = \frac{\phi_{\text{state}}(T,P,y)}{\phi_{\text{pure}}(T,P_{i}^{\text{sat}})} \exp \left[ \frac{1}{RT} \int_{P}^{P_{i}^{\text{sat}}(T)} \gamma_{i}(T,P) \cdot dP \right] \quad (15a)
\]

This quantity is close to unity under low or moderate pressure and is usually neglected.

• CASE 3: pure component \( i \) is solid, \( i.e., T < T_{m,i}(P) \). We thus obtain:

\[
\frac{e^{n}_{i,\text{liquid}}(T,P,x)}{RT} = \ln \left[ \frac{\hat{f}_{i,\text{liquid}}(T,P,x)}{f_{i,\text{pure}}(T,P)} \right] = \ln(\chi_i) + \frac{\Delta G_{m,i}(T)}{RT} \]

\[
\frac{e^{n}_{i,\text{gas}}(T,P,y)}{RT} = \ln \left[ \frac{\hat{f}_{i,\text{gas}}(T,P,y)}{f_{i,\text{pure}}(T,P)} \right] = \ln \left[ \frac{P \cdot y_i \cdot C_i}{P_{i}^{\text{sat}}(T)} \right] + \frac{\Delta G_{m,i}(T)}{RT} \]

\[
\frac{e^{n}_{i,\text{solid}}(T,P)}{RT} = \ln \left[ \frac{\hat{f}_{i,\text{solid}}(T,P)}{f_{i,\text{pure}}(T,P)} \right] = \ln \left[ \frac{\gamma_{i} \cdot P_{i}^{\text{sat}}(T)}{P_{i}^{\text{sat}}(T)} \right] = 0 \quad (16)
\]

Our personal experience

We believe that relations given in Eqs. (14) to (16) are of the highest importance because they are unknown by most of the students, including the smartest ones. We indeed asked the following question to 50 of our best graduate students: “What is the mathematical expression of the Gibbs energy change on mixing of a vapor phase that can be considered as perfect?” Ninety percent of them answered:

\[
\frac{g^{n}_{\text{perfect gas}}(T,y)}{RT} = y_1 \cdot \ln y_1 + y_2 \cdot \ln y_2 \quad (17)
\]

Unfortunately, in spite of what is written in too many chemical engineering thermodynamics textbooks, this is not always correct. Eq. (17) is only true when the obtained perfect-gas mixture (after mixing of 2 stable pure components) and the 2 pure components are all in the gaseous state. However, a perfect gas mixture can be obtained by mixing a pure gas and a pure liquid or even two pure liquids. As an example by mixing at \( t = 20 \, ^{\circ\text{C}} \) and \( P = 2 \, \text{kPa} \), 9 mol of gaseous toluene(1) and 1 mol of liquid ethylbenzene(2), we obtain a gas mixture that can be considered as a perfect-gas mixture since the pressure is low. For such a case, according to Eqs. (14) and (15):

\[
\frac{g^{n}_{\text{perfect gas}}(T,y)}{RT} = y_1 \cdot \ln y_1 + y_2 \cdot \ln y_2 + y_2 \cdot \ln \left[ \frac{P}{P_{i}^{\text{sat}}(T)} \right] \quad (18)
\]

Moreover, in such a case, the molar enthalpy change on mixing is far from zero. \(^{[3]}\) One has:

\[
h^{m}_{\text{perfect gas}} = y_2 \cdot \Delta h_{\text{vaporization,1}}(20 \, ^{\circ\text{C}}) = +4 \, \text{kJ} \cdot \text{mol}^{-1} \quad (19)
\]

In return, the molar excess enthalpy \( h^{e} \), is obviously null since a perfect-gas mixture is a particular ideal solution.

Be sure that our students open their eyes wide when they are told that the mixing enthalpy of a perfect-gas mixture can be different from zero. A similar amazement arises when we add that for a perfect-gas mixture, the excess enthalpy is necessarily zero, so that \( h^{e} \) may be different from \( h^{n} \).

APPLICATIONS

The goal of this section is to highlight that the Gibbs double-tangent construction of coexisting phases is not only a very useful tool to visualize all the solutions of Eq. (1) but also to study the stability of a binary system of known temperature, pressure, and overall composition. In advanced textbooks of thermodynamics,\(^{[5]}\) such a stability analysis is generally performed with the help of an equation of state capable of representing the liquid and the gas phases. In this case, the obtained mathematical equations are, however, complex and not easy to handle.\(^{[6,7]}\) We here want to show that the same kind of analysis can be performed with less effort using the gamma-phi approach.\(^{[8,9]}\)

**Application 1**

In this section, it was decided to study the phase behavior of the binary system butan-2- one(1) + water(2) under atmospheric pressure. For this system, experimental data show the simultaneous existence of liquid-liquid equilibrium and positive azeotropy. Such a complexity is thus propitious to underline the usefulness of the double-tangent construction. Since the pressure is low, the gas phase was assumed to be a perfect-gas mixture. The non-ideality of the liquid phase was accounted through the NRTL equation\(^{[10]}\) with the following temperature-independent parameters:

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∆\(g\)\(_{12}\) = 4490.17 J \(\cdot\) mol\(^{-1}\) \(\Delta g\)\(_{21}\) = 10337.2 J \(\cdot\) mol\(^{-1}\) \(\alpha\)\(_{12}\) = 0.4893

The vapor pressures of the two pure components were correlated with the Antoine equation and the resulting expressions are:

\[
\begin{align*}
\log (P_{1\text{sat}} / \text{bar}) &= 4.1885 - \frac{1261.3}{T \ ^{\circ} \text{C} + 221.97} \\
\log (P_{2\text{sat}} / \text{bar}) &= 5.1962 - \frac{1730.6}{T \ ^{\circ} \text{C} + 233.43}
\end{align*}
\]

(21)

Our first task was thus to build the liquid-liquid and the liquid-vapor phase diagrams. The first one was classically calculated by varying the temperature \(T\). For each temperature, the following two-equation system was solved in order to determine the composition \((x_{1\alpha} , \ x_{1\beta})\) of the two liquid phases \(L_{\alpha} \text{ and } L_{\beta}\) in equilibrium:

\[
\begin{align*}
x_{1\alpha} \cdot \gamma_{1 T,x_{1\alpha}}(T) &= x_{1\beta} \cdot \gamma_{1 T,x_{1\beta}}(T) \\
x_{1\alpha} \cdot \gamma_{2 T,x_{1\alpha}}(T) &= x_{1\beta} \cdot \gamma_{2 T,x_{1\beta}}(T)
\end{align*}
\]

(22)

The vapor-liquid phase diagram was calculated with a so-called bubble-T algorithm: the pressure is fixed at \(P = 1\) atm and the composition of the liquid phase \(x_{1}\) is varied between zero and one. Knowing \(P\) and \(x_{1}\), the temperature \(T\) is the solution of the equation:

\[
P - P_{1\text{sat}}(T) \cdot x_{1} \cdot \gamma_{1 T,x_{1}}(T) - P_{2\text{sat}}(T) \cdot x_{2} \cdot \gamma_{2 T,x_{1}}(T) = 0
\]

(23)

and the gas phase composition \(y_{1}\) is given by:

\[
y_{1} = \frac{P_{1\text{sat}}(T) \cdot x_{1} \cdot \gamma_{1 T,x_{1}}(T)}{P}
\]

(24)

The corresponding phase diagrams can be seen in Figure 1. The liquid-liquid phase diagram in Figure 1a shows that the studied binary system exhibits an upper critical point (UCP), the coordinates of which are: \(T_{\text{UCP}} = 492.8\) K and \(x_{1,\text{UCP}} = 0.188\). As expected from the experimental data, Figure 1b highlights that the studied system also exhibits a positive homogeneous azeotrope,\(^{[11]}\) the coordinates of which are: \(T_{\text{aze}} = 347.51\) K and \(x_{1,\text{aze}} = 0.714\). The liquid-vapor phase diagram shown in Figure 1b was built by solving Eqs. (23) and (24)—that is, by assuming that VLE could exist in the whole composition range. As a result, we notice the existence of a closed loop on the dew-point curve that characterizes a metastable gaseous phase. Moreover, it is observable that in a certain composition range, the bubble-point curve is an increasing function of \(x_{1}\), meanwhile the

**Figure 1.** Isobaric phase diagrams \((P = 1\) atm\) of the binary system butan-2-one(1) + water(2).

a) Liquid-liquid phase diagram. (∗) upper critical point.

b) Liquid-vapor phase diagram as directly obtained using a bubble-T algorithm (without testing the stability). (+) positive homogeneous azeotrope.

c) Superimposition of the two previous phase diagrams in order to highlight the three-phase LLV line. Dashed lines: non-stable parts (meta-stable and unstable parts) of the dew and bubble curves.

d) Correct (stable) phase diagram obtained after removing all the non-stable parts. (∗) phases involved in a 3-phase equilibrium.
dew-point curve is a decreasing function of \( y_1 \). Such a behavior breaks the Gibbs-Konovalow theorem and indicates that this increasing part of the bubble-point curve is an unstable liquid phase. An easy way to locate the three-phase line that is the consequence of the overlapping of both the LL and the LV phase diagrams is to superimpose them. This is what has been done in Figure 1c. By the end, after removing all the non-stable parts of the resulting diagram, the correct (stable) isobaric phase diagram obtained is shown in Figure 1d.

In order to perform the stability analysis of the considered system with the help of the double-tangent construction of coexisting phases, it was decided to plot the Gibbs energy change on mixing of the previous system at \( P = 1 \) atm and at eight temperatures identifiable by horizontal lines in Figure 2. Each time, \( g^m \) for both the liquid and the gas phase was plotted on the whole composition range (the positive values of \( g^m \) were, however, in general not drawn).

- Under \( T_1 = 343.15 \) K and \( P = 1 \) atm, the two pure components are in a liquid state so that according to Eq. (15):

\[
\begin{align*}
\frac{g^m_{\text{liquid}} (T,P,x)}{RT} &= x_1 \cdot \ln (x_1 \cdot \gamma_1) + x_2 \cdot \ln (x_2 \cdot \gamma_2) \\
\frac{g^m_{\text{gas}} (T,P,y)}{RT} &= y_1 \cdot \ln \left[ \frac{P \cdot y_1}{P_{1,\text{sat}} (T)} \right] + y_2 \cdot \ln \left[ \frac{P \cdot y_2}{P_{2,\text{sat}} (T)} \right]
\end{align*}
\]

(25)

In Figure 3, it is observed that regardless of the overall composition \( z_1 \), \( g^m_{\text{liquid}} < g^m_{\text{gas}} \) so that according to Eq. (6), \( g^m_{\text{system}} (T_1,P=1 \text{ atm},z) = g^m_{\text{system}} (T_1,P=1 \text{ atm},x) \). At this temperature, the binary system is thus necessarily in the liquid state, \( i.e. \), made up of one or two liquid phases.

**Figure 2.** Highlight of the eight selected temperatures (horizontal lines) at which it was decided to perform a stability analysis under \( P=1 \) atm. \( T_1 = 343.15 \) K, \( T_2 = T_{2,\text{sat}} = 347.51 \) K, \( T_3 = 348.15 \) K, \( T_4 = 349.03 \) K is the three-phase temperature, \( T_5 = 350.15 \) K, \( T_6 = 352.73 \) K is the normal boiling temperature (\( T_{b,1} \)) of pure butan-2-one(1), \( T_7 = 373.14 \) K is the normal boiling temperature (\( T_{b,2} \)) of pure water(2), \( T_8 = 378.15 \) K.

**Figure 3.** Gibbs double-tangent construction of coexisting phases. Example of the butan-2-one(1) + water(2) binary system under \( P=1 \) atm and at \( T_1 = 343.15 \) K. The double tangent identifies a stable liquid-liquid equilibrium. The crosses (+) identify the starting and the ending point of the double tangent.
In the present case, such a liquid system is, however, not homogeneous in the whole composition range. The presence of a double tangent indicates that LL demixing occurs. The x-coordinates of the tangency points allow determining the composition of the two liquid phases in equilibrium. The determined LLE is stable since both phases satisfy the Gibbs stability condition (liquid phase compositions are thus identical to those obtained from Figure 1.d). Gibbs indeed showed that a necessary and sufficient condition for stability of a binary mixture of known temperature, pressure, and overall composition is that the tangent to the \( g^\text{m} \) curve (plotted at the mixture T and P) at the given overall composition does not lie above the curve at any composition. The mathematical expression of \( g^\text{m} \) we are talking about is obviously given by Eq. (6). In return, if we can find \( z_1 \in [0;1] \) so that the tangent to the \( g^\text{m} \) curve at the given overall composition is located above (and generally intersects) the \( g^\text{m} \) curve, the considered overall composition is non-stable. In other words, after performing a phase equilibrium calculation, the calculated equilibrium will be declared stable if the corresponding double tangent never lies above the \( g^\text{m} \) curve. This is clearly the case for the LLE shown in Figure 3.

- At \( T_2 = T_{az} = 347.51 \text{ K} \) and \( P = 1 \text{ atm} \), the two pure components are in a liquid state so that Eq. (25) still applies. The corresponding curves can be seen in Figure 4. It is noticeable that by increasing the temperature from \( T_1 \) to \( T_2 \), \( g^\text{gas} \) rapidly grows up and at \( T_2 \), the \( g^\text{gas} \) curve becomes tangent to the \( g^\text{liquid} \) curve at a unique point (see the symbol * in Figure 4).

At this point, a double tangent, the length of which is zero, can be drawn indicating that a liquid and a gas phase with the same composition are in equilibrium. For such a VLE, the Gibbs stability condition is satisfied and we are thus at the azeotropic point. In Figure 4, the stable LLE (already present at \( T_1 \)) and which is characterized by a double tangent (DT) starting and ending on the \( g^\text{liquid} \) curve, is present again. In addition, it is possible to draw two other double tangents starting on the \( g^\text{liquid} \) curve and ending on the \( g^\text{gas} \) curve (see the dashed double tangents DT2 and DT3 in Figure 4). Such VLE are, however, not stable although they satisfy Eq. (1). We indeed can find compositions for...
which the double tangent lies above the $g_m^{\text{liq}}$ curve. We thus here verify that the equality of the chemical potentials is a necessary but not a sufficient condition to ensure a stable equilibrium.

Figure 4 highlights that the double tangent DT$_2$ starts in a region where the $g_m^{\text{liq}}$ curve is concave upward (convex), which refers to a metastable homogeneous liquid phase. In Figure 2, this point is located on the decreasing part of the dashed bubble-curve. On the other hand, the double tangent DT$_3$ starts in a region where the $g_m^{\text{liq}}$ curve is concave downward, which corresponds to an unstable homogeneous liquid phase. In Figure 2, this point is located on the increasing part of the dashed bubble-curve. We can notice that these two double tangents end at the $g_m^{\text{gas}}$ curve, which is always convex. Such gas phases are thus metastable and are located on Figure 2 on the dashed closed loop.

• At $T_3$ = 348.15 K and $P$ = 1 atm, the two pure components are in a liquid state so that Eq. (25) still applies. The corresponding curves can be seen in Figure 5. It is noticeable that by again increasing the temperature, we now reach $T_4$ > $T_{az}$ and the $g_m^{\text{liq}}$ curve, which continues increasing in size, now twice crosses the $g_m^{\text{liq}}$ curve (see Figure 5). As expected, two stable VLE, located on each side of the azeotropic composition, have appeared (see double tangents DT$_4$ and DT$_5$ in Figure 5). The two double tangents DT$_2$ and DT$_3$, which represent non-stable VLE, are still present. We can, however, notice that the metastable liquid and gas phases that bound DT$_2$ have compositions that are now extremely close to stable compositions (the starting point of non-stable DT$_2$ is very close to the starting point of stable DT$_1$ and the ending point of DT$_2$ is very close to the ending point of stable DT$_4$).

• At $T_5$ = 349.03 K and $P$ = 1 atm, the two pure components are in a liquid state so that Eq. (25) still applies. The corresponding curves can be seen in Figure 6. $T_4$ is the three-phase temperature under $P$ = 1 atm. At this temperature, three out of the five double tangents that existed at temperature $T_3$ (DT$_1$, DT$_2$, and DT$_4$) merge together and give birth to a stable triple-tangent. Each of the three tangency points defines a phase of the VLLE. The metastable phases that bounded DT$_2$ at temperature $T_3$ thus become stable at $T_4$.

• At $T_5$ = 350.15 K and $P$ = 1 atm, the two pure components are in a liquid state so that Eq. (25) still applies. The corresponding curves can be seen in Figure 7. As expected, at temperature $T_5$ higher than the three-phase temperature, the LLE
becomes non-stable (see Figure 7). It is indeed possible to find compositions for which the dashed double tangent characterizing this equilibrium lies above the \( g^m \) curve. It is recalled that the \( g^m \) curve to be considered is:

\[
g^m(T,P,z) = \min \{ g^m_{\text{liquid}}(T,P,z), g^m_{\text{gas}}(T,P,z) \}.
\]  

(25a)

At this temperature and pressure, only two stable VLE located on each side of the azeotrope are observed.

• At \( T_6 = 352.73 \, \text{K} = T_{b,1} \) and \( P=1 \, \text{atm} \), pure component 1 is in VLE so that \( g^m_{\text{stable}}(T,P) = g^m_{\text{liquid}}(T,P) = g^m_{\text{gas}}(T,P) \). On the other hand, component 2 is still in a liquid state. Eqs. (14) or (15) can thus indifferently be used for component 1 whereas Eq. (15) must be applied to component 2. We thus obtain:

\[
\begin{align*}
\frac{g^m_{\text{liquid}}(T,P,x)}{RT} &= x_1 \cdot \ln \left[ \frac{P^\text{sat}(T,x_1 \cdot \gamma_1)}{P} \right] + x_2 \cdot \ln \left( x_2 \cdot \gamma_2 \right) \quad \text{Eq. (14)}
\end{align*}
\]

\[
\begin{align*}
\frac{g^m_{\text{gas}}(T,P,y)}{RT} &= y_1 \cdot \ln y_1 + y_2 \cdot \ln \left[ \frac{P \cdot y_2}{P^m(T)} \right] + y_2 \cdot \ln \left( x_2 \cdot \gamma_2 \right) \quad \text{Eq. (15)}
\end{align*}
\]

The corresponding curves can be seen in Figure 8. The double tangent representing the VLE located on the right-hand side of the azeotropic composition (\( DT_6 \) in Figure 7) disappears at \( T_6 \). Its length becomes null (see the symbol * in Figure 8) so that the \( g^m_{\text{liquid}} \) curve and the \( g^m_{\text{gas}} \) curve have a common tangent. This behavior is induced by the VLE of pure component 1 and arises therefore at a composition \( z_1 = 1 \).

• At \( T_7 = 373.14 \, \text{K} = T_{b,2} \) and \( P=1 \, \text{atm} \), pure component 2 is in VLE so that \( g^m_{\text{stable}}(T,P) = g^m_{\text{liquid}}(T,P) = g^m_{\text{gas}}(T,P) \). On the other hand, component 1 is gaseous.

Eqs. (14) or (15) can thus indifferently be used for component 2 whereas Eq. (14) must be used for component 1. We thus obtain:

\[
\begin{align*}
\frac{g^m_{\text{liquid}}(T,P,x)}{RT} &= x_1 \cdot \ln \left[ \frac{P^\text{sat}(T,x_1 \cdot \gamma_1)}{P} \right] + x_2 \cdot \ln \left( x_2 \cdot \gamma_2 \right) \quad \text{Eq. (14)}
\end{align*}
\]

\[
\begin{align*}
\frac{g^m_{\text{gas}}(T,P,y)}{RT} &= y_1 \cdot \ln y_1 + y_2 \cdot \ln \left[ \frac{P \cdot y_2}{P^m(T)} \right] + y_2 \cdot \ln \left( x_2 \cdot \gamma_2 \right) \quad \text{Eq. (15)}
\end{align*}
\]

The corresponding curves can be seen in Figure 9.

At \( T_1 \), the double tangent that highlights the VLE located on the left-hand side of the aze trope (see \( DT_1 \) in Figures 7 and 8) disappears and the \( g^m_{\text{gas}} \) curve and the \( g^m_{\text{gas}} \) curve become tangent at \( z_1 = 0 \) (the observed phenomenon is similar to the one discussed at \( T_6 \)). For all the other compositions, the system is homogeneous and gaseous.

**Figure 8.** Butan-2-one(1) + water(2) system at \( T_6 = 352.73 \, \text{K} = T_{b,1} \). Full-line double tangent: stable equilibrium. Dashed double tangent: non-stable equilibrium. (+) starting and ending points of a double tangent. (\( * \)) particular double tangent of null length.
• Under $T_8 = 378.15 \text{ K}$ and $P = 1 \text{ atm}$, both pure components are gaseous so that according to Eq. (14):

$$
\begin{align*}
\frac{g_{\text{liq}}^n(T,P,x)}{RT} &= x_1 \cdot \ln \left( \frac{p_1^{\text{sat}}(T) \cdot x_1 \cdot \gamma_1}{P} \right) + x_2 \cdot \ln \left( \frac{p_2^{\text{sat}}(T) \cdot x_2 \cdot \gamma_2}{P} \right), \\
\frac{g_{\text{gas}}^n(T,P,y)}{RT} &= y_1 \cdot \ln y_1 + y_2 \cdot \ln y_2,
\end{align*}
$$

(28)

The corresponding curves can be seen in Figure 10 (page 52). At this temperature, the system is solely in a gaseous state. A double tangent characterizing a non-stable LLE is still present. It will disappear when the upper critical solution temperature is reached.

**Application 2**

In this section, it was decided to study the solid-liquid phase diagram of the binary system water(1) + ethylene glycol(2). Condensed phases are seldom sensitive to pressure effects explaining why activity coefficients in the liquid and solid phases are considered as pressure-independent. Consequently, not only the liquidus and the solidus branches of the phase diagram but also the $g^n$ curves are pressure-independent (from now on, pressure will thus not be mentioned further). For simplicity, it was here assumed that the liquid water + ethylene glycol phase was ideal ($\gamma_{\text{liq}}^1 = \gamma_{\text{liq}}^2 = 1$) and that total immiscibility occurred in the solid phase. In Figure 11 (page 53), the SLE behavior of the simple eutectic system water(1) + ethylene glycol (2) is shown. Solid phases $S_1$ and $S_2$, respectively, contain pure water and pure ethylene glycol. The phase diagram was built with the following data:

$$
\begin{align*}
T_{m,1} &= 273.15 \text{ K} \\
T_{m,2} &= 255.75 \text{ K} \\
\Delta h_{m,1}(T_{m,1}) &= 6009 \text{ J} \cdot \text{mol}^{-1} \\
\Delta h_{m,2}(T_{m,2}) &= 11600 \text{ J} \cdot \text{mol}^{-1}
\end{align*}
$$

(29)

The mathematical equation of each liquidus branch is:

$$
T = \frac{\Delta h_{m,1}(T_{m,1}) \cdot x_1}{\Delta h_{m,1}(T_{m,1}) - R \cdot T_{m,1} \cdot \ln x_1},
$$

(30)

By varying $x_1$ between zero and one, the phase diagram shown in Figure 11 can be built. The two liquidus branches intersect at an eutectic point (E in Figure 11) where 3 phases (2 solid phases and one liquid phase) are simultaneously in equilibrium. The coordinates of this point were found to be:

$$
\begin{align*}
T_E &= 223 \text{ K} \\
x_1^E &= 0.55
\end{align*}
$$

(31)

Below $T_E$, the stable state is a solid-solid equilibrium and the non-stable liquidus branches are materialized by dashed lines in Figure 11. At this step, it was decided to plot the Gibbs energy change on mixing of the considered system at seven different temperatures: $T_1 = 210 \text{ K}$, $T_2 = 220 \text{ K}$, $T_3 = T_E$, $T_4 = 230 \text{ K}$, $T_5 = T_{m,2}$, $T_6 = T_{m,1}$, and $T_7 = 280 \text{ K}$. Three different aggregation states are involved in the phase diagram shown in Figure 11: liquid, pure solid $S_1$, and 

![Figure 9. Butan-2-one(1) + water(2) system at $T_7 = 373.14 \text{ K} = T_{b,2}$. Dashed double tangent: non-stable equilibrium. (+) starting and ending points of a double tangent. (*) particular double tangent of null length.](image-url)
pure solid $S_2$. Consequently, three $g^m$ curves need to be plotted at each temperature. Since each solid phase is assumed to be pure, the $g^m_{S_1}$ and $g^m_{S_2}$ curves reduce each to a single point. They indeed only have a physical meaning for $z_1 = 1$ and $z_1 = 0$, respectively. From a mathematical point of view, it is not possible to define the tangent to a curve made up of a single point and the double-tangent construction needs to be slightly revisited. When the $g^m_{solid}$ curve reduces to a single point, a solid-liquid equilibrium involving a pure solid phase is characterized by a segment that is both tangent to the $g^m_{liquid}$ curve and that passes through the point representing the solid phase. Mathematically, such a segment is not a double tangent to the $g^m$ curve but contains the same information (it links two phases in equilibrium). Similarly, a solid-solid equilibrium between two pure solid phases is characterized by a segment joining the two points characterizing the two pure solid phases. Once again and strictly speaking, such a segment cannot be called a double tangent but it has exactly the same meaning. For the sake of simplicity, any segment joining two phases in equilibrium on a $g^m$ plot will be subsequently called a double tangent, even if the equilibrium involves a pure solid phase.

• For $T = T_1$, or $T_2$, or $T_3$, or $T_4$, the two pure components are solid so that according to Eq. (16):

$$
\frac{g^m_{liquid}(T,x)}{RT} = x_1 \left[ \ln x_1 + \frac{\Delta h_{m,1}(T,x_1)}{RT} \left(1 - \frac{T}{T_{m,1}}\right) \right] + x_2 \left[ \ln x_2 + \frac{\Delta h_{m,2}(T,x_2)}{RT} \left(1 - \frac{T}{T_{m,2}}\right) \right] + \Delta g^m_0
$$

(32)

The corresponding curves can be seen in Figure 12 (page 54). At temperature $T_1$, it is possible to draw three double tangents noted $DT_1$, $DT_2$, and $DT_3$ (see Figure 12a). $DT_1$ and $DT_2$ characterize non-stable SLE; they indeed respectively lie above the $g^m$ curve defined as

$$
g^m(T,z) = \min \{g^m_{liquid}(T,z), g^m_{S_1}(T), g^m_{S_2}(T)\}
$$

(32a)

for $z_1 = 1$ and 0. On the other hand, $DT_3$ highlights a stable solid-solid equilibrium as expected at this temperature from Figure 11. At temperature $T_2$ (see Figure 12b) the situation is similar except that the $g^m_{liquid}$ curve increased in size, making the 3 double tangents get closer to each other. They merge at $T_3$ (see Figure 12c) and give birth to a unique triple tangent that characterizes the 3-phase (eutectic) temperature.

By again increasing the temperature (see Figure 12d), the $g^m_{liquid}$ curve, which continues growing up, now twice crosses $DT_3$ which thus becomes non-stable. In return $DT_1$ and $DT_2$ become stable and characterize the two SLE visible in Figure 11 on each side of the eutectic point.

• For $T_4 = T_{m,2}$ pure component 2 is in SLE but component 1 is still solid. Eq. (15) or (16) can thus indifferently be used for
component 2 whereas Eq. (16) must be applied to component 1. We thus obtain:

\[
\begin{align*}
\frac{g_{\text{liquid}}^m(T,x)}{RT} &= x_1 \left[ \ln x_1 + \frac{\Delta h_{m,1}(T_{m,1})}{RT} \left( 1 - \frac{T}{T_{m,1}} \right) \right] + x_2 \left[ \ln x_2 + \frac{\Delta h_{m,2}(T_{m,2})}{RT} \left( 1 - \frac{T}{T_{m,2}} \right) \right] \\
&= x_1 \left[ \ln x_1 + \frac{\Delta h_{m,1}(T_{m,1})}{RT} \left( 1 - \frac{T}{T_{m,1}} \right) \right] + x_2 \ln x_2 \\
&= x_1 \left[ \ln x_1 + \frac{\Delta h_{m,1}(T_{m,1})}{RT} \left( 1 - \frac{T}{T_{m,1}} \right) \right] + x_2 \ln x_2 \quad \text{Eq. (16)}
\end{align*}
\]

(33)

\[
\begin{align*}
\frac{g_{S_1}^m(T)}{RT} &= 0 \\
\frac{g_{S_2}^m(T)}{RT} &= \frac{\Delta h_{m,2}(T_{m,2})}{RT} \left( 1 - \frac{T}{T_{m,2}} \right) \\
&= 0 \\
&= \frac{\Delta h_{m,2}(T_{m,2})}{RT} \left( 1 - \frac{T}{T_{m,2}} \right) \quad \text{Eq. (15)}
\end{align*}
\]

Between \( T_4 \) and \( T_5 \), the \( g_{\text{liquid}}^m \) curve continues its growth and the abscissa of its minimum moves on the left (towards small mole fractions). Consequently, the length of the DT, double tangent diminishes rapidly. Such a DT, which characterizes the stable \( S_1\text{LE} \), disappears at \( T_5 = T_{m,2} \). Its length becomes zero (see the symbol * in Figure 13, page 55) and the \( g_{\text{liquid}}^m \) and the \( g_{S_2}^m \) curves are superimposed for \( z_1 = 0 \). As a consequence, DT — which characterizes the \( S_1\text{LE} \) — is the unique DT to remain stable at this temperature.

- For \( T_6 = T_{m,1} \) pure component 1 is in SLE but component 2 is liquid. Eq. (15) or (16) can thus indifferently be used for component 1 whereas Eq. (15) must be applied to component 2. We thus obtain:

\[
\begin{align*}
\frac{g_{\text{liquid}}^m(T,x)}{RT} &= x_1 \left[ \ln x_1 + \frac{\Delta h_{m,1}(T_{m,1})}{RT} \left( 1 - \frac{T}{T_{m,1}} \right) \right] + x_2 \ln x_2 = x_1 \ln x_1 + x_2 \ln x_2 \\
&= x_1 \left[ \ln x_1 + \frac{\Delta h_{m,1}(T_{m,1})}{RT} \left( 1 - \frac{T}{T_{m,1}} \right) \right] + x_2 \ln x_2 \\
&= x_1 \left[ \ln x_1 + \frac{\Delta h_{m,1}(T_{m,1})}{RT} \left( 1 - \frac{T}{T_{m,1}} \right) \right] + x_2 \ln x_2 \quad \text{Eq. (15)}
\end{align*}
\]

(34)

\[
\begin{align*}
\frac{g_{S_1}^m(T)}{RT} &= 0 \\
\frac{g_{S_2}^m(T)}{RT} &= \frac{\Delta h_{m,2}(T_{m,2})}{RT} \left( 1 - \frac{T}{T_{m,2}} \right) \\
&= 0.35 \text{ at } T_{m,1}
\end{align*}
\]

Figure 11. Solid-liquid and solid-solid equilibria of the water(1) + ethylene glycol(2) system.
From $T_5$ to $T_6$, the $g_{\text{liquid}}^m$ curve continues to grow up so that the length of the $DT_2$ double tangent diminishes: it vanishes at $T_6 = T_{m,1}$ (see the symbol * in Figure 14) and the $g_{\text{liquid}}^m$ and $g_{S_1}^m$ curves are superimposed for $z_1 = 1$. As a consequence, at this temperature pure component 1 is in SLE. The $DT_3$ double tangent that stands above the $g_{\text{liquid}}^m$ curve still characterizes a non-stable SSE.

• For $T_7 = 280$ K, the two pure components are liquid so that according to Eq. (15):

$$\frac{g_{\text{liquid}}^m (T, x)}{RT} = x_1 \ln x_1 + x_2 \ln x_2$$
$$\frac{g_{S_2}^m (T)}{RT} = -\frac{\Delta h_{n,1} (T_{m,1})}{RT} \left( 1 - \frac{T}{T_{n,1}} \right) = 0.065 \text{ at } T_7$$
$$\frac{g_{S_1}^m (T)}{RT} = -\frac{\Delta h_{n,1} (T_{m,2})}{RT} \left( 1 - \frac{T}{T_{m,2}} \right) = 0.47 \text{ at } T_7$$

The corresponding curves can be seen in Figure 15 (page 56). At this temperature, as expected from Figure 11, the system is
Figure 12. (facing page) Coupling of stability analysis and Gibbs double-tangent construction of coexisting phases. Example of the water(1) + ethylene glycol(2) system. Full-line double (or triple) tangents: stable equilibria. Dashed double tangents: non-stable equilibria. (+) starting and ending point of a double (or triple) tangent. (a) \( T_1 = 210 \) K, (b) \( T_2 = 220 \) K, (c) \( T_3 = T_{m,2} = 223 \) K, (d) \( T_4 = 230 \) K.

Figure 13. Water(1) + ethylene glycol(2) system at \( T_3 = T_{m,2} \). Full-line double tangent: stable solid-liquid equilibrium. Dashed double tangent: non-stable SSE. (+) starting and ending point of a double tangent. (\( \ast \)) particular stable double tangent of null length.

Figure 14. Water(1) + ethylene glycol(2) system at \( T_6 = T_{m,1} \). Dashed double tangent: non-stable SSE. (+) starting and ending point of a double tangent. (\( \ast \)) particular stable double tangent of null length.

homogeneous and totally liquid: the \( g^m_{\text{liquid}} \) curve is concave upward and is merged with min \( \{ g^m_{\text{liquid}} (T,z), g^m_{S_1} (T), g^m_{S_2} (T) \} \). A double tangent characterizing a non-stable SSE is still present.

CONCLUSION

In this paper, the double-tangent construction of coexisting phases has been applied to any type of phase equilibrium (VLE, LLE, VLLE, SLE, SSE, SSLE) through two binary systems modeled with the gamma-phi approach. The mathematical expressions of \( g^m \) to be used are simple enough to be easily implemented by students in tools such as Excel or Matlab. Such a graphical technique is very useful to build any type of isothermal or isobaric phase diagrams including the most complex ones (with homogeneous azeotrope, with 3-phase lines...). The coupling of the double-tangent construction and of the stability analysis makes it possible for the students to well understand that the equality of chemical potentials for each component in all phases is only a necessary but not a sufficient condition to reach a thermodynamically stable equilibrium.

Although well-described in the literature\(^{[5,6]}\), such a construction cannot be performed with an equation of state during class exercises. The equations to handle are indeed complex and need good mathematical skills.

This technique was also applied with the gamma-phi approach by Marcilla’s research group in two very interesting papers.\(^{[8,9]}\) The pure-component reference state they selected in Eq. (2) was, however, the pure liquid. This choice is obviously adequate but may, in our opinion, introduce confusion in students who find it hard to understand the difference between
Moreover, at a given T and P, the pure liquid is not always stable and by experience, the students do not like working with hypothetical states.

In return, to our knowledge, this paper is the first one in which such a technique is used taking as reference the stable pure component at the considered T and P. Such a choice is extremely convenient since:

1) It never creates hypothetical states.

2) It does not lead to the definition of a new thermodynamic function. The students only need to know the correct definition of the molar Gibbs energy change on mixing. Indeed, in such a case:

\[ \Delta g_{\text{stable}}(T, P, z) = g(T, P, z) - \sum_{i=1}^{z} z_i \cdot g_{\text{pure}}^i(T, P) = g^m(T, P, z) \]  

\[ (37) \]

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11. Jaubert, J.N., and R. Privat, “Possible existence of a negative (positive) homogeneous azeotrope when the binary mixture exhibits positive (negative) deviations from ideal solution behavior (that is when \( g^E \) is positive (negative)),” *Ind. Eng. Chem. Res.*, **45**, 8217 (2006)