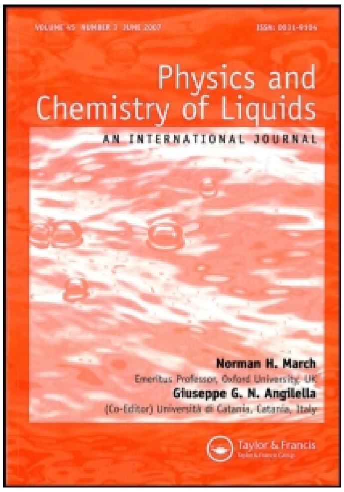
This article was downloaded by:
On: *28 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Physics and Chemistry of Liquids

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646857

An Assessment of Thermodynamic Consistency Tests for Vapor-Liquid Equilibrium Data

Jaime Wisniak[a]; Alexander Apelblat[a]; Hugo Segura[ab]
[a] Department of Chemical Engineering, Ben-Gurion University of the Negev, Beer-Sheva, Israel [b] Department of Chemical Engineering, Universidad de Concepción, Concepción, Chile

To cite this Article Wisniak, Jaime , Apelblat, Alexander and Segura, Hugo(1997) 'An Assessment of Thermodynamic Consistency Tests for Vapor-Liquid Equilibrium Data', Physics and Chemistry of Liquids, 35: 1, 1 — 58
To link to this Article: DOI: 10.1080/00319109708030571
URL: http://dx.doi.org/10.1080/00319109708030571

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Phys. Chem. Liq., 1997, Vol. 35, pp. 1-58
Reprints available directly from the publisher
Photocopying permitted by license only

AN ASSESSMENT OF THERMODYNAMIC CONSISTENCY TESTS FOR VAPOR-LIQUID EQUILIBRIUM DATA

JAIME WISNIAK[1], ALEXANDER APELBLAT and
HUGO SEGURA*

Department of Chemical Engineering, Ben-Gurion
University of the Negev, Beer-Sheva, Israel

(*Received 12 December 1996*)

Consistency tests are techniques that allow, in principle, the assessment of experimental vapor-liquid equilibrium data on the basis of the Gibbs-Duhem equation. Much empiricism and arbitrariness is frequently observed in the analysis and application of consistency tests, a situation that may question their usefulness. Perfect data satisfy exactly the Gibbs-Duhem relation, but acceptable data obey it within a tolerable limits (*consistency criteria*) which does not give a unique answer, regarding the quality of the data, when different consistency procedures are used. As with any approximation, application of consistency tests requires rigour, reasonable assumptions and models, and an examination of the data and results of the test. In this work, a set of guidelines that allow a critical interpretation of consistency analysis is proposed and special attention is given to the point-to-point test which is extensively used today in data evaluation.

Keywords: Thermodynamic consistency; vapor-liquid equilibrium

INTRODUCTION

Consistency tests are techniques which, in principle, allow the analysis and assessment of vapor-liquid equilibrium (VLE) data. Their significance can be defined as follows
if the data satisfy the criteria of well-formulated consistency tests, then they are considered appropriate for design and modeling purposes and

---

[1] To whom correspondence should be addressed.

*Permanent address: Department of Chemical Engineering, Universidad de Concepción, Concepción, Chile.

their reproducibility and matching with any thermodynamical relation is assumed.

Since the first papers of Herington [1, 2, 3] and Redlich and Kister [4] on binary isothermal and isobaric area tests, many papers have been written about consistency. Some of them have proposed new consistency tests, as is the case of the work of McDermott and Ellis [5] for the treatment of multicomponent systems using the area test; the work of Van Ness *et al.* [6] on point-to-point consistency, based on excess models and bubble-point pressure calculations, the papers of Christiansen and Fredenslund [7] and Fredenslund *et al.* [8], the work of Kojima *et al.* [9] For an integrated method of point-to-point, integral and infinite dilution consistency (PAI), the work of Wisniak [10] on the L-W test for the analysis of isobaric consistency of binary and multicomponent systems, and the recent revision of Van Ness [11] where a direct point-to-point test of consistency is analyzed and proposed. Other papers are devoted to the critical analysis of the usefulness of consistency tests, such as the works of Samuels [12], Samuels *et al.* [13], and Van Ness *et al.* [6] on the critical revision of integral consistency, and more recently, the paper of Wisniak [14] where the assumptions of the isobaric integral test of Herington are revised in-depth.

Thus our motivation for writing a new paper on consistency raises a good question that needs a good answer. Presently, the majority of publications regarding VLE data are complemented with a consistency analysis as a standard section of the paper but, surprisingly, in spite of the rigour of the definition given above, few or vague details about this important tool are generally given and no major discussion accompanies the results. We can observe that many points regarding consistency tests are not clear, probably due to the non clear-cut present state of the problem and to the overvaluation of empirical consistency criteria: the assumptions, weakness and the validity range of some *well established* consistency tests are not completely understood and in many cases, the analysis is incomplete or based on partial information. In addition, the information that allows the reproduction of the consistency analysis is not always reported and certainly, for some good reasons, the *user* of the data would wish to test himself the data. Considering that consistency tests constitute a kind of certification of published data this tendency is worrisome, because the usefulness of this thermodynamic tool becomes unclear and, in a way, a misdirecting and routine task whose value is perfectly refutable. As pointed by Van Ness [11], the thermodynamic treatment of binary VLE is a *topic more complex and less widely understood than might be supposed.* We believe that the best opportunity for a consistency analysis occurs when the researcher ends the experimental work and wishes to evaluate seriously the measured data, nobody rather than he (*or she*) knows better the conditions which accomplish the experiment, nor has a better access to the data of the system in question. Hence, we postulate that consistency analysis is a task of experimentalists, who can give an interpretative and quantitative approach to their results and can tell us something objective about the quality of the measurements.

In this work we do not propose a new consistency test because, as pointed by Prausnitz *et al.* [15], a *gram of good data is worth more than a ton of consistency tests.* However, considering the limited present knowledge about the behavior of the liquid phase, it is not so easy to judge *which data are good* but, according to our experience on VLE data treatment, it seems possible to judge *which data are bad, which data needs to be better explained, or which experimental measurements deserve repetition.* In addition, many consistency tests with a common basis (the Gibbs-Duhem equation) require data which usually are not available, or whose acquisition exceeds the capabilities of the experimental equipment or finding them in the literature. *The lack of data not related to the VLE in question, such as accurate virial coefficients and excess enthalpies, is the main limitation of any consistency procedure.* Our objective here is to provide some guidelines that allow one to pass judgement about the quality of the data and to show how revisited consistency tools can be used in the right way, considering their limitations, for the evaluation of experimental data.

THEORY

The Gibbs-Duhem Equation

According to the Gibbs-Duhem equation, any extensive molar thermodynamic property of a given phase, such as the Gibbs and Helmholtz energies, the enthalpy, and molar volume, must satisfy the following differential relation [16]

$$\left(\frac{\partial \tilde{M}}{\partial T}\right)_{P,\underline{z}} dT + \left(\frac{\partial \tilde{M}}{\partial P}\right)_{T,\underline{z}} dP - \sum_{i=1}^{C} z_i \, d\bar{M}_i = 0 \qquad (1)$$

In Eq. (1) $\tilde{M}$ is a generic molar property, "z_i" the molar fraction of component i in the phase under consideration, $\underline{z}$ the pertinent set of compositions, C the number of components, and $\bar{M}_i$ is the partial contribution of component i to $\tilde{M}$. Equation (1), a pure mathematical result due to the fact that extensive properties are homogeneous functions of the first degree in relation to the mass of the system, is one of the most important relations of the thermodynamics of solutions. Provided that a relationship of the form $\tilde{M} = \tilde{M}(T, P, \underline{z})$ exists, Eq. (1) establishes an analytical relation among $(C+2)$ variables (i.e., T, P, $\bar{M}_i$) having $(C+1)$ degrees of freedom. Mathematically Eq. (1) couples the variables of the set (T, P, $\bar{M}_i$); thus, if all the elements of this set are known and have a *perfect* thermodynamical meaning, then Eq. (1) is exactly satisfied yielding the main hypothesis of consistency.

The Gibbs-Duhem equation is a thermodynamic relation in the same sense that the Maxwell relations are. It allows to deduce certain thermodynamical properties when only partial information is available and when equilibrium states are assumed. An excellent illustration of this kind relation can be found in a paper by Kohler *et al.* [17] where partial experimental information on the liquid phase activity coefficients of the system acetic acid + triethylamine system is used for a theoretical calculation of the associative interactions present. Another interesting theoretical application is the displacement theory described by Malesinski [18], where the Gibbs-Duhem equation is used to represent the evolution of phase equilibrium for varying conditions of pressure and temperature.

From a practical point of view, the differential form of Eq. (1) as the basis for a consistency test is unfortunate because, usually, the analytical function $\tilde{M} = \tilde{M}(T, P, \underline{z})$ is not known. Although it can be derived from molecular *ab initio* considerations for few and idealized systems with the aid of statistical mechanics, in most cases, $\tilde{M}$ and its derivatives must be considered as *unknown analytical functions* or *state properties* which can be correlated by means of empirical or semiempirical models, such as equations of state (EOS) and excess models (G^E).

Depending on the nature of $\tilde{M}$, some of its values (*discrete points*) and the derivatives required in Eq. (1) can be obtained from direct or indirect *determination*, within *experimental error*, for various conditions of temperature, pressure and composition. This experimental set of $\tilde{M}$ may be qualified as satisfactory if the following relation is satisfied

$$\left(\frac{\partial \tilde{M}}{\partial T}\right)_{P,z}^{\text{expt}} dT^{\text{expt}} + \left(\frac{\partial \tilde{M}}{\partial P}\right)_{T,z}^{\text{expt}} dP^{\text{expt}} - \sum_{i=1}^{C} z_i^{\text{expt}}\, d\bar{M}_i^{\text{expt}} \approx 0 \qquad (2)$$

Nevertheless, it should be noted that Eq. (2) is insufficient to guarantee the quality of the experimental data. As a simple illustration of this let us assume that the property $\tilde{M}$ has been measured at constant temperature and pressure with noncalibrated instrumentation. Although we can measure $\tilde{M}$ as a function of the composition with high precision in such a way that Eq. (2) is satisfied with $dT^{\text{expt}} = 0$ and $dP^{\text{expt}} = 0$, the obtained value will not correspond to the *assumed* temperature and pressure values. In addition, fluctuations of fixed variables, or *nonequilibrium states*, that escape our control even in highly accurate experiments, can produce cancellation of errors in an unpredictable way. From this point of view, Eq. (2) is more informative when it is not satisfied, or equivalently, it is a *necessary but not a sufficient condition of consistency* when satisfied by experimental data. This role is usually attributed to simplified consistency test versions derived from the Gibbs-Duhem equation; but as mentioned here, the origin of a *necessary but not sufficient condition* is a consequence of the application of Eq. (1) to *experimental data* constrained *to systematic and random errors*. The practical aim of a consistency test, therefore, is the detection of a *significant* systematic error in the measurements. Another alternative is that $\tilde{M}$ be given by a parameter-dependent empirical model; usually, empirical correlations in thermodynamics must satisfy Eq. (1) in order to be considered acceptable. In this sense, Eq. (1) can be considered useful for model testing, although it should be pointed out that the Gibbs-Duhem equation is *unable* to detect some model pitfalls, a good example being the *Michelsen-Kistenmacher pathology* [19] observed in some models of mixing rules for cubic equations of state, such as that of Panagiotopoulos and Reid [20].

Consistency Tests for VLE Data

When considering VLE the excess Gibbs energy, $\tilde{G}^E$, can be evaluated from measurable (T, P, x, y) data using activity coefficient relations. Replacing $\tilde{M}$ *by* $\tilde{G}^E/RT$ in Eq. (1) yields the following well-known relation [16]

$$-\frac{\Delta\tilde{H}}{RT^2}\,dT+\frac{\Delta\tilde{V}}{RT}\,dP-\sum_{i=1}^{C} x_i d\ln\gamma_i = 0 \tag{3}$$

where $\Delta\tilde{H}$ and $\Delta\tilde{V}$ are the molar enthalpy and volume of mixing of the liquid phase and

$$\frac{\tilde{G}^E}{RT}=\sum_{i=1}^{C} x_i \ln\gamma_i \tag{4}$$

Combining Eqs. (3) and (4) yields

$$d\left[\frac{\tilde{G}^E}{RT}\right]-\sum_{i=1}^{C}\ln\gamma_i\,dx_i=\sum_{i=1}^{C}x_i d\ln\gamma_i=-\frac{\Delta\tilde{H}}{RT^2}\,dT+\frac{\Delta\tilde{V}}{RT}dP \tag{5}$$

Application to a binary system gives

$$d\left[\frac{\tilde{G}^E}{RT}\right]-\ln\frac{\gamma_1}{\gamma_2}dx_1=-\frac{\Delta\tilde{H}}{RT^2}dT+\frac{\Delta\tilde{V}}{RT}dP \tag{6}$$

Simultaneous solution of Eqs. (4) and (6) yields

$$\begin{aligned}\ln\gamma_1 &= \frac{\tilde{G}^E}{RT}+x_2\left[\frac{\Delta\tilde{H}}{RT^2}\frac{dT}{dx_1}-\frac{\Delta\tilde{V}}{RT}\frac{dP}{dx_1}+\frac{d}{dx_1}\left(\frac{\tilde{G}^E}{RT}\right)\right]\\ \ln\gamma_2 &= \frac{\tilde{G}^E}{RT}-x_1\left[\frac{\Delta\tilde{H}}{RT^2}\frac{dT}{dx_1}-\frac{\Delta\tilde{V}}{RT}\frac{dP}{dx_1}+\frac{d}{dx_1}\left(\frac{\tilde{G}^E}{RT}\right)\right]\end{aligned} \tag{7}$$

Equations (5), (6) and (7) constitute the basis of all the thermodynamic consistency tests currently used, which are analyzed below.

1. Point-to-Point Test

The point-to-point test, or slope test, corresponds to a direct application of Eq. (3) to experimental binary data in the form

$$\frac{\Delta \tilde{V}}{RT}\frac{dP}{dx_1} - \frac{\Delta \tilde{H}}{RT^2}\frac{dT}{dx_1} - x_1\frac{d\ln\gamma_1}{dx_1} - x_2\frac{d\ln\gamma_2}{dx_1} \approx 0 \tag{8}$$

where the pressure compositional derivative or the temperature compositional derivative are neglected for isobaric or isothermal data respectively. The total derivatives required in Eq. (8) must be determined from experimental $[T, P, \gamma_1, \gamma_2]$ data using a graphical or an equivalent numerical method; experimental volume and heat of mixing data are supposed to be available. Equation (8) constitutes the most rigorous thermodynamic test because no empirical model nor correlation is assumed, an exception being the approximations made in the calculation of activity coefficients. In addition, each experimental point can be analyzed independently from the rest, hence the test can reject particularly bad information from a set of data. In spite of its rigor, Eq. (8) has never found a practical application in consistency analysis because the determination of derivatives from experimental data is cumbersome and inaccurate. Thus inconsistency, or even consistency, can be achieved by experimental data having a systematic error. Nevertheless, application of Eq. (8) to the simple case of constant temperature and pressure

$$x_1\frac{d\ln\gamma_1}{dx_1} + x_2\frac{d\ln\gamma_2}{dx_1} = 0 \tag{9}$$

yields the following important characteristics of the activity coefficient curves:

- the slope of the activity coefficient curve tends to zero as the concentration approaches pure component, this is the basis of the Lewis and Randall reference state, which does not depend on the conditions being isobaric or isothermal because mixing properties tend to zero at infinite dilution.
- in binary systems activity coefficients will yield stationary points at the same composition. If $\ln\gamma_1$ is maximum then $\ln\gamma_2$ must be minimum and conversely. If one of the restrictions of constant

pressure or constant temperature is removed then the extreme values will occur at compositions slightly different one from the other.

These two simple results, schematically shown in Figures 1, are illustrated in many elementary thermodynamic textbooks and constitute a rudimentary test of consistency. Figure 1.a shows the usual behavior of activity coefficients in binary systems with positive deviations from ideality, it can be seen that each activity coefficient curves becomes tangent to the ideal solution line ($\ln\gamma = 0$) at infinite dilution. Figure 1b shows a case where the activity coefficients achieve stationary points with opposite curvature. An incorrect behavior of

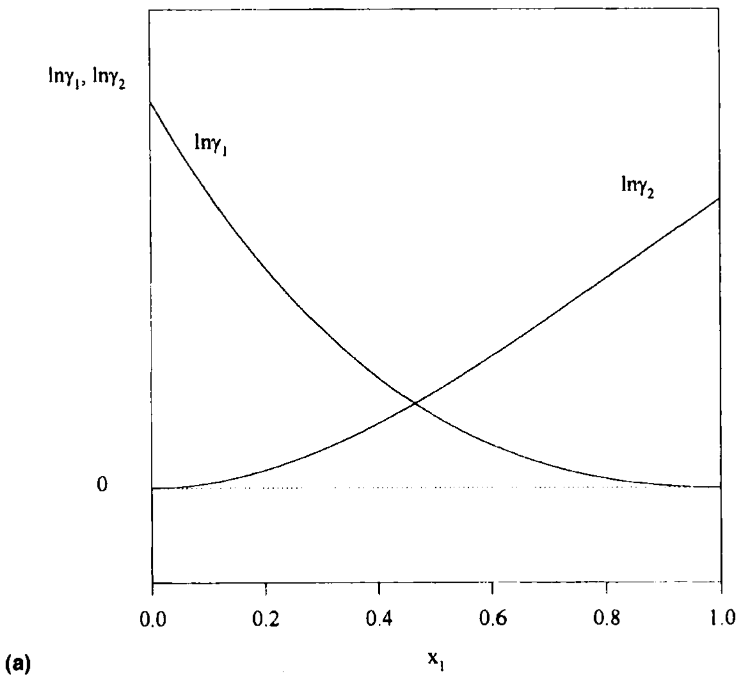


FIGURE 1 [1] Correct and incorrect dependency of activity coefficients on composition

a. correct stationary points of activity coefficients.
b. correct slope of activity coefficients in the concentrated range, tangency to the zero line is observed when $x_1 \rightarrow 1$.
c. incorrect dependence of activity coefficients: γ_2 shows a minimum not reflected in γ_1 and the curve for γ_2 is not tangent to the zero line in $x_1 = 0$.
d. activity coefficients calculated from the data reported by Costa-López *et al.* [34]

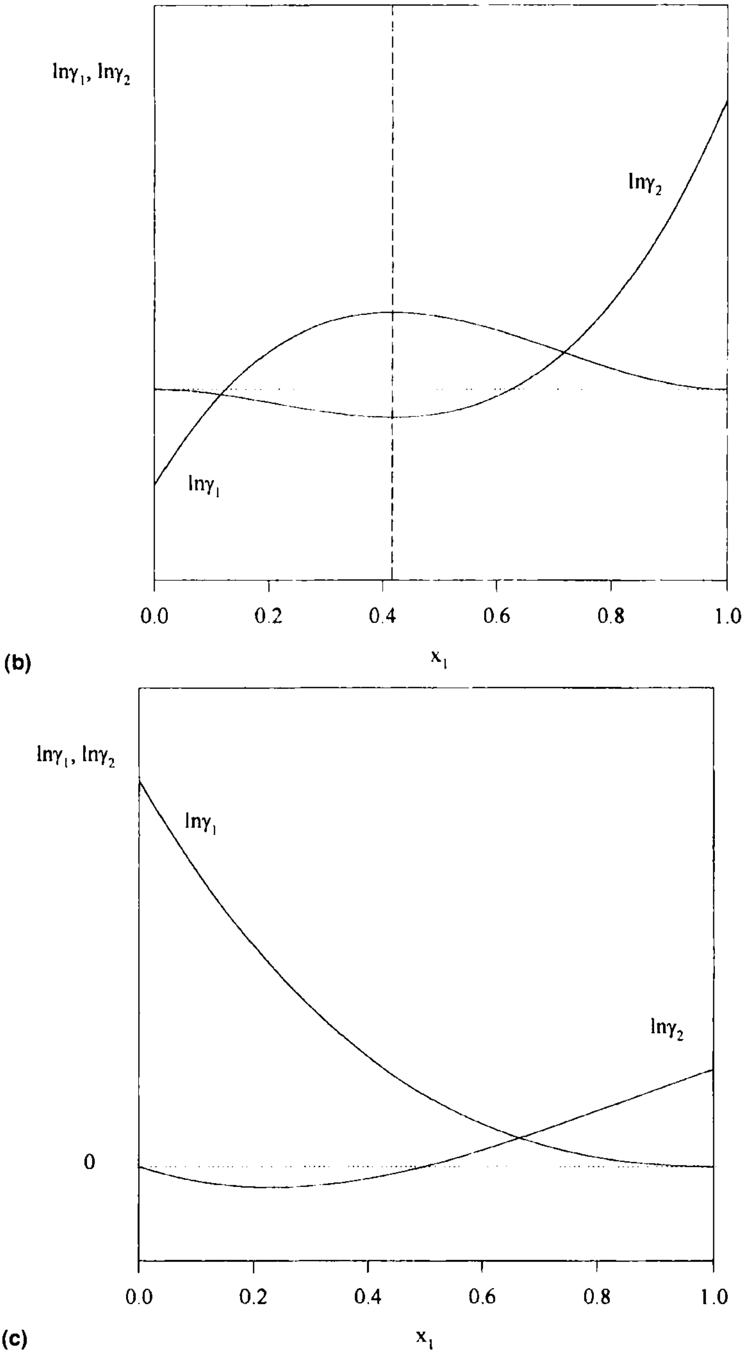


FIGURE 1 (Continued).

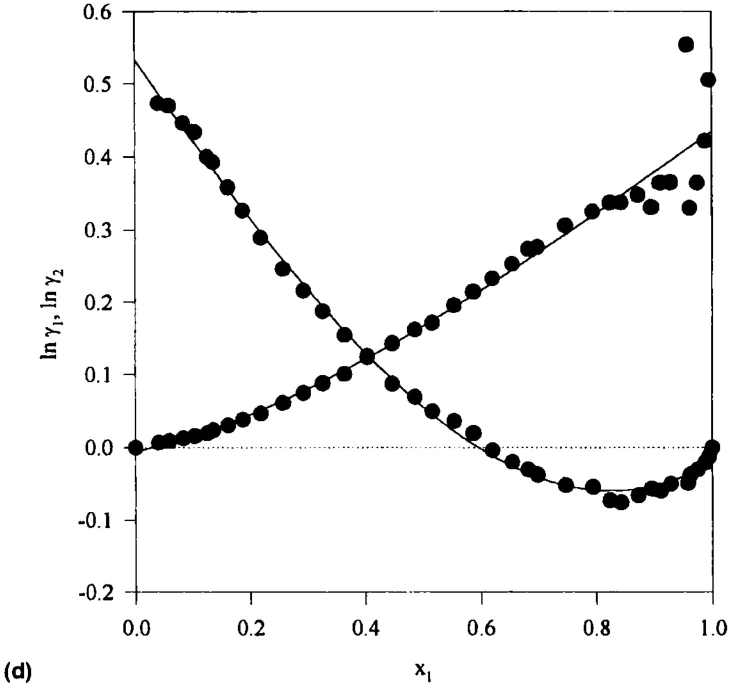


FIGURE 1 (Continued).

activity coefficients is shown in Figure 1.c were $\gamma_2(x_1)$ does not become tangent to the ideal solution line when $x_2 \rightarrow 1$ and the minimum observed in γ_2 is not reflected by a maximum point of γ_1. It should be pointed that some published experimental data, ***qualified as consistent***, do not match these simple rules, as illustrated in Figure 1.d for the system propyl butanoate (1) - 1-propanol (2) at 101.3 kPa [21]. The behavior of $\gamma_1(x_1)$ is incorrect when the mixture is concentrated in propyl butanoate and $\gamma(x_1)$ shows a minimum not clearly reflected in the tendency of $\gamma_2(x_1)$. In spite of these anomalies the experimental results for this system have been declared consistent by the test of Fredenslund *et al.* [8]. Hence, an important point to be learned here is the necessity to ***plot and tabulate*** the activity coefficients as a first ***symptom of the consistency*** of the data. Although the slope test is not easily applicable, it can help in the visual detection of pitfalls and outliers.

2. *Area Tests*

Area tests were independently proposed by Herington [1] and Redlich and Kister [4] for the assessment of VLE data. Basically, this kind of tests constituted the first systematic approach to the consistency problem and continues to be extensively used and popular until today, probably due to their simplicity. General area tests are derived from an integration of the relation of Gibbs-Duhem given by Eq. (6)

$$\int_{x_{1,a}}^{x_{1,b}} \ln\frac{\gamma_1}{\gamma_2}dx_1 = \int_{T_a}^{T_b} \frac{\Delta\tilde{H}}{RT^2}dT - \int_{P_a}^{P_b} \frac{\Delta\tilde{V}}{RT}dP + \frac{\tilde{G}^E}{RT}\bigg|_{x_{1,a}}^{x_{1,b}} \qquad (10.a)$$

Generally, integration is extended to the full composition range, yielding the more familiar relation

$$\int_0^1 \ln\frac{\gamma_1}{\gamma_2}dx_1 = \int_{T_2^{\text{sat}}}^{T_1^{\text{sat}}} \frac{\Delta\tilde{H}}{RT^2}dT - \int_{P_2^{\text{sat}}}^{P_1^{\text{sat}}} \frac{\Delta\tilde{V}}{RT}dP \qquad (10.b)$$

The left-hand side of Eq. (10.b) represents the net area of $\ln[\gamma_1/\gamma_2]$, as a function of the composition (Fig. 2), given by $|S_1 - S_2|$, where *both areas are considered positive*. This integral is easily calculated by smoothing the experimental $\ln[\gamma_1/\gamma_2]$ data with an appropriate correlation. The first term on the right-hand side of Eq. (10.b) corresponds to the contribution of the heat effect, and the integral must be calculated over the complete trajectory of bubble-point temperatures. The second term corresponds to the contribution of the volume of mixing, and the integral must be evaluated over the complete trajectory of bubble-point pressures. A rigorous treatment of VLE data with Eq. (10.b) requires mixing volumes and enthalpies as a function of the composition, temperature and pressure; in practice, these information is rarely available, hence some approximations are needed for the practical application of Eq. (10.b) to isothermal and isobaric systems.

For constant temperature data, Eq. (10.b) yields

$$\int_0^1 \ln\frac{\gamma_1}{\gamma_2}dx_1 = -\int_{P_2^{\text{sat}}}^{P_1^{\text{sat}}} \frac{\Delta\tilde{V}}{RT}dP \approx 0 \qquad (11)$$

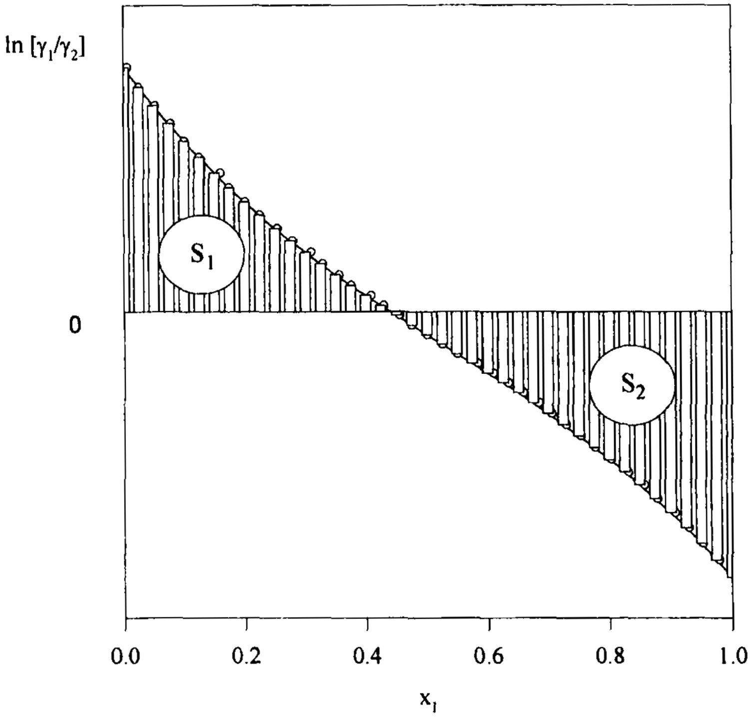


FIGURE 2 Typical plots for area tests.

The second integral in Eq. (11) reflects the influence of the volume of mixing of the liquid phase, it exhibits a weak dependence on pressure and its numerical value is usually negligible when compared to the value of the integral on the left-hand side [22]. The consistency relation is given by the following relation

$$D = \frac{\left|\int_0^1 \ln[\gamma_1/\gamma_2]dx_1\right|}{\int_0^1 \left|\ln[\gamma_1/\gamma_2]\right|dx_1} \times 100 = \frac{\left||S_1| - |S_2|\right|}{|S_1| + |S_2|} \times 100 \qquad (12)$$

where D is an acceptance criterion. On the basis of the scarce experimental information available at his time, Herington [2] proposed that a *system is probably consistent if* $D < 10$; with the improved instrumental and analytical techniques available today it seems appropriate to adopt the more stringent criteria $D \leq 2$ [12], [15].

The isobaric version of the area test is given by

$$\int_0^1 \ln\frac{\gamma_1}{\gamma_2}dx_1 = \int_{T_2^{\text{sat}}}^{T_1^{\text{sat}}} \frac{\Delta\tilde{H}}{RT}dT \tag{13}$$

In this case the right-hand side term cannot be neglected [22]. Proper use of Eq. (13) requires the availability of heats of mixing as a function of composition and temperature. In a few cases this information is available in the DECHEMA Chemistry Data Series [23]. In order to obviate this limitation Herington [3] developed the following approximation for the integral on the right-hand side of Eq. (12)

$$D = \frac{||S_1| - |S_2||}{|S_1| + |S_2|} \times 100 = \frac{|\int_0^1 \ln[\gamma_1/\gamma_2]dx_1|}{\int_0^1 |\ln[\gamma_1/\gamma_2]|dx_1} \times 100 \tag{14.a}$$

$$J = 50 \times \left|\frac{\Delta\tilde{H}_{\text{max}}}{\tilde{G}^E_{\text{max}}}\right| \times \frac{T_{\text{max}} - T_{\text{min}}}{T_{\text{min}}} \tag{14.b}$$

Indexes max and min represent the maximum and the minimum values that can be acquired by the pertinent variable. Maximum and minimum temperatures must consider all the temperature range covered by the system, including azeotropes, if any. From the limited experimental information available in his time, Herington [2] estimated that $|\Delta\tilde{H}_{\text{max}}/\tilde{G}^E_{\text{max}}|$ would never exceed the value 3 so that

$$J \approx 150\frac{T_{\text{max}} - T_{\text{min}}}{T_{\text{min}}} \tag{14.c}$$

According to Herington, an *isobaric system is always consistent if $D < J$ and probably consistent* if

$$|D - J| < 10 \tag{15}$$

For the smoothing of the $\ln[\gamma_1/\gamma_2]$ experimental function, the use of a flexible G^E model, such as the Redlich-Kister expansion, is always tempting. However, it should be pointed out that when the parameters of the G^E model are temperature independent, Eq. (14.a) will always yields a *zero value*, hence the use of G^E models as possible correlation functions of $\ln[\gamma_1/\gamma_2]$ *must be avoided.* The Herington area test is one of the consistency procedures used currently by the DECHEMA Chemistry Data Series [24] for the assessment of VLE data with the recommendations and approximations proposed by Herington [2].

The main advantages of the area test are its simplicity and independence of any kind of empirical model, but the area test is a gross examination when applied to a VLE data set as a whole [11] and many inconsistent systems can satisfy it. This weakness is implicitly stated in the original papers of Herington [2] where a system is not declared as consistent but as *probably consistent* when the acceptance criteria is achieved. The principal limitation of the area test comes from its geometrical origin, because many drastically different $\ln[\gamma_1/\gamma_2]$ experimental curves can have the same, or approximately the same, net area. In addition, the integration procedure required by Eqs. (12) and (14.a) covers the whole concentration range, but activity coefficients at infinite dilution, which generally are not determined experimentally, must be extrapolated inducing important changes in the net area. As pointed out by Van Ness *et al.* [6], the $\ln[\gamma_1/\gamma_2]$ function depends weakly on pressure, hence this important equilibrium variable is not assessed by area tests.

The isobaric consistency test must be used with precautions when heat of mixing data are not available because the test can be extremely *stringent or generous* depending on the system under consideration. For example, a perfectly isobaric and athermic system can be easily rejected by the test due to the approximation expressed by Eq. (14.b) where it is supposed that all systems have a nonnegligible heat of mixing. Wisniak [14] has shown that some basic assumptions made by Herington are wrong: (a) The value of the parameter $|\Delta\tilde{H}_{\max}/\tilde{G}^E_{\max}|$ can go as high as 28, exceeding by far the upper limit of 3 assumed by Herington, (b) The availability of better instrumentation suggests setting the upper limit of D as ≤ 2 and not ≤ 10 as assumed by Herington, so that in the best case Eq. (15) should actually read $|D - J| < 2$. In addition, Wisniak has shown that certain algebraic approximations assumed by Herington are also inappropriate. In other words, the Herington test, although used extensively in the literature can be *unreliable.*

Local tests are a subcategory of integral tests, in this case integration is performed over part of the compositional range; it can proceed, for example, between neighbouring experimental points. In this case Eq. (10.a) becomes

$$\int_{x_{1,a}}^{x_{1,b}} \ln\frac{\gamma_1}{\gamma_2}dx_1 = \int_{T_a}^{T_b} \frac{\Delta\tilde{H}}{RT^2}dT - \int_{P_a}^{P_b} \frac{\Delta\tilde{V}}{RT}dP + \frac{\tilde{G}^E}{RT}\bigg|_{x_{1,a}}^{x_{1,b}} \tag{16}$$

McDermott and Ellis [5] proposed the trapezoidal rule between adjacent points for the integration of Eq. (16). For a binary isothermal system where the contribution of volume of mixing can be neglected Eq. (16) can be written

$$\frac{x_{1,j+1} - x_{1,j}}{2}\left[\ln\frac{\gamma_{1,j+1}}{\gamma_{2,j+1}} - \ln\frac{\gamma_{1,j}}{\gamma_{2,j}}\right] = \frac{\tilde{G}^E(x_{1,j+1})}{RT} - \frac{\tilde{G}^E(x_{1,j})}{RT} \tag{17}$$

In principle, Eq. (17) constitutes another consistency test, reduced to a pair of adjacent experimental compositions, where all the experimental points contribute to the global integration with the same weight. Equation (17) can be used for the detection of outliers and can give more reliability to the area test because, as discussed by Van Ness and Mrazek [25], every system that achieves local consistency achieves integral consistency, but the reverse is not necessarily true. A relation similar to Eq. (17) can be deduced for isobaric systems, but local consistency analysis is not recommended when information regarding heat of mixing is not available.

3. *Consistency Tests Based on VLE Calculations*

The fundamental advantages of consistency tests based on VLE calculations is that they are directly related to measurable properties of the equilibrium, i.e., compositions, temperature and pressure, variables for which the maximal experimental error is controlled or well known. On the other hand, this test allows exploring the possibility of data reduction using well established G^E models. This test will discussed here in more detail due to its extensive use in data evaluation. Considering the relations of the $\gamma - \varnothing$ approach to the VLE problem we have [16]

$$y_i\hat{\varnothing}_iP = x_i\gamma_iP_i^{\text{sat}}\varnothing_i^{\text{sat}}\vartheta_i \tag{18}$$

where ϕ_i is the fugacity coefficient and ϑ_i is the Poynting factor defined as

$$\vartheta_i = \int_{P_i^{\text{sat}}}^{P} \frac{\bar{V}_i}{RT} dP \tag{19}$$

The following relation for the bubble-point pressure [26] can be obtained by combining Eqs. (7) and (18)

$$P = \frac{x_1 P_1^{\text{sat}}}{\Phi_1} \exp \gamma_1 + \frac{x_2 P_2^{\text{sat}}}{\Phi_2} \exp \gamma_2 \tag{20}$$

where Φ is a pressure correction defined as

$$\Phi_i = \frac{\hat{\phi}_i}{\phi_i^{\text{sat}} \vartheta_i} \tag{21}$$

Equation (20) constitutes the main relation for the different versions of consistency test based on bubble-point pressure calculations, called also *residual methods*. The test of Van Ness *et al.* [6] and the point-to-point version of Fredenslund *et al.* [8] for isothermal data, are typical examples of the application of Eq. (20) together with Eq. (7). The method of consistency analysis based on bubble-point pressure calculations was originally suggested by Van Ness *et al.* [6] for the treatment of *isothermal* data, a case in which the excess Gibbs energy does not depend on the heat of mixing because the constant temperature constraint $dT/dx_1 \equiv 0$. From an experimental point of view, this simplification is valid when the VLE data are obtained with a good control of the temperature, an experimental condition which involves *some challenges* when mixtures with unusually large heats of mixing are being measured (for example, methanol + diethylamine). Rarely the excess volume is exactly zero, but its contribution can be reasonable neglected at low pressures. Under these assumptions Eqs. (7) become

$$\begin{aligned} \ln \gamma_1 &\approx \frac{\tilde{G}^E}{RT} + x_2 \frac{d}{dx_1}\left(\frac{\tilde{G}^E}{RT}\right) \\ \ln \gamma_2 &\approx \frac{\tilde{G}^E}{RT} - x_1 \frac{d}{dx_1}\left(\frac{\tilde{G}^E}{RT}\right) \end{aligned} \tag{22}$$

Replacing Eq. (22) in Eq. (20) yields

$$P = \frac{x_1 P_1^{\text{sat}}}{\Phi_1} \exp\left[\frac{\tilde{G}^E}{RT} + x_2 \frac{d}{dx_1}\left(\frac{\tilde{G}^E}{RT}\right)\right] + \frac{x_2 P_2^{\text{sat}}}{\Phi_2} \exp\left[\frac{\tilde{G}^E}{RT} - x_1 \frac{d}{dx_1}\left(\frac{\tilde{G}^E}{RT}\right)\right] \tag{23}$$

In the practice of point-to-point consistency testing by means of Eq. (23), an analytical (*and empirical*) function for the excess Gibbs energy on the composition is postulated, then its parameters are fitted to the experimental bubble-point pressures. Vapor phase compositions can be calculated as follows

$$y_1 = \frac{x_1 P_1^{\text{sat}}}{\Phi_1 P} \exp\left[\frac{\tilde{G}^E}{RT} + x_2 \frac{d}{dx_1}\left(\frac{\tilde{G}^E}{RT}\right)\right] \tag{24}$$

Combination of Eqs. (23) and (24) requires only $T-x$ data for the estimation of bubble-point pressures and vapor phase compositions which can be compared with experimental data. The basic idea of the point-to-point test is to verify if a fit of the pressure produces simultaneously a fit of the vapor phase composition which was not considered in the parametrization of the assumed excess model. Consistency of the data is declared when the mean absolute deviation (MAD) of the calculated composition with respect to the experimental composition in the vapor phase *does not exceed a certain value* (arbitrarily selected as 0.01, as have been suggested by Fredenslund *et al.* [8]) with a *random scattering of the residuals* $\delta y = y_i^{\text{calc}} - y_i^{\text{expt}}$ about the zero line, as suggested by Van Ness *et al.* [6] and Gess *et al.* [27].

The simplicity of this procedure is tempting due to the availability of good computational tools for handling any kind of complex fit. However, these tools induce also one of the most common errors in consistency treatment: *confusion between consistency analysis and a routine curve fitting task.* Computer and curve fitting software "do not know thermodynamics", thus consistency should not be considered as an automatic procedure.

Common misunderstandings regarding point-to-point consistency are the following:

- *rarely a residual analysis is reported.*

The role that residuals play in the point-to-point consistency test *reliability* will be explained later from a mathematical point of view. *the rules of selection of a G^E model are not clear-cut.*

These rules cannot be strictly defined because G^E models are *empirical functions* which not necessarily represent the behavior of the system. Van Ness *et al.* [6] suggested the four-suffix Margules model corresponding to a second degree polynomial on the composition for the function $\tilde{G}^E/[RTx_1x_2]$. This model was selected also by Gess *et al.* [27] Fredenslund *et al.* [8] suggested the use of Legendre polynomials of arbitrary degree for the function $\tilde{G}^E/[RTx_1x_2]$ and pointed that a second- or third-order polynomial will normally give a good fit of the pressure for systems that do not contain carboxylic acids. The suggestions of Fredenslund have been widely adopted and have become almost standard in VLE publications. Nevertheless, the consequences of the critical assumption of a G^E model are usually not verified; the model used for fitting the data is normally *different* from that used for verifying consistency. This is poor practice and should be avoided. In the DECHEMA Chemistry Data Series [24], as an example, the model that yields positive point-to-point consistency is never recommended as the best fit of the data and the corresponding parameters are not listed. The same criticism applies to the data base prepared by the Design Institute for Physical Property Data (DIPPR) of the American Institute of Chemical Engineers [27].

A pertinent reflection here is to which degree consistency can be achieved as a consequence of overcorrelation of data (and therefore *an autocorrelation of experimental error*) or, equivalently, to which degree inconsistency can be achieved as a consequence of undercorrelation of experimental data. To illustrate this point we can consider that, currently, the majority of researchers claim a precision of the order of 0.1% in the measure of the bubble-point pressure of a particular system, hence an error of 1 kPa should be considered a *high experimental error* in an atmospheric range determination, probably very bad if this error is systematic. Figure 3.a shows a fictitious VLE system (constructed as explained in Appendix A) with a constant systematic error of -1.5 kPa in the bubble-point pressure. Figure 3.b shows the pertinent activity coefficients and it is immediately noticed that the simulated systematic error is not detected in this Figure. The consistency of this system is tested with a second order polynomial for the $\tilde{G}^E/[RTx_1x_2]$ function with three adjustable parameters, using the method of Fredenslund *et al.* [8] and Van Ness *et al.* [6] (*both tests are equivalent for second order polynomials*) and assuming that the vapor phase is ideal. From the statistics reported in Table I it is concluded that the data should be considered consistent because the minimization of the bubble-point pressure yields a MAD(y) within the tolerance suggested by Fredenslund *et al.* [MAD(y) < 0.01]. In addition, *looking* at the δy residuals in Figure 3.c, as suggested by Van Ness *et al.* [6], we can conclude the residuals show a random scatter distribution about the zero line, as confirmed also by the small numerical value of the bias of the vapor phase composition (Tab. I). Hence, the system will be declared consistent although the systematic *error was completely absorbed by the procedure used to fit the experimental bubble-point*

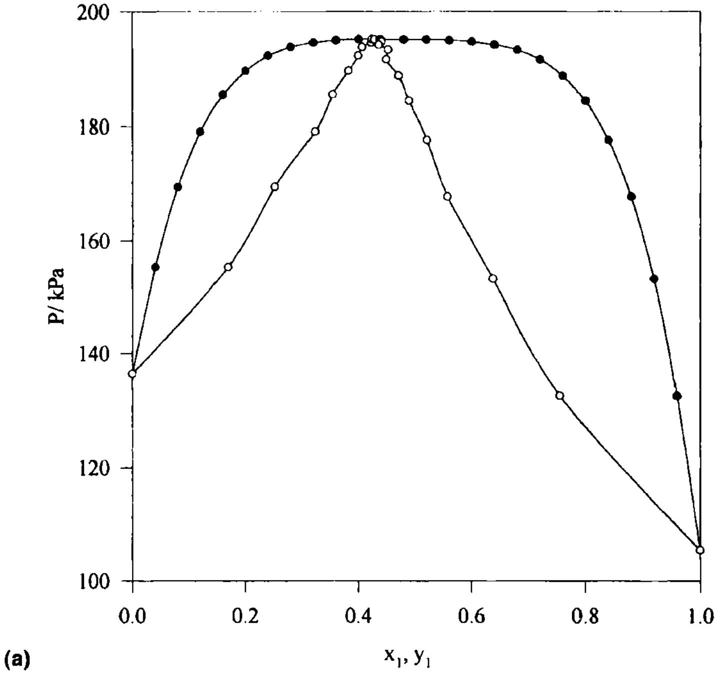


FIGURE 3 Fictitious experimental system: Systematic error in bubble-point pressure. (See data and details in Appendix A)
a. equilibrium diagram.
b. activity coefficients.
c. bubble-point pressure residuals.
d. vapor phase composition residuals.

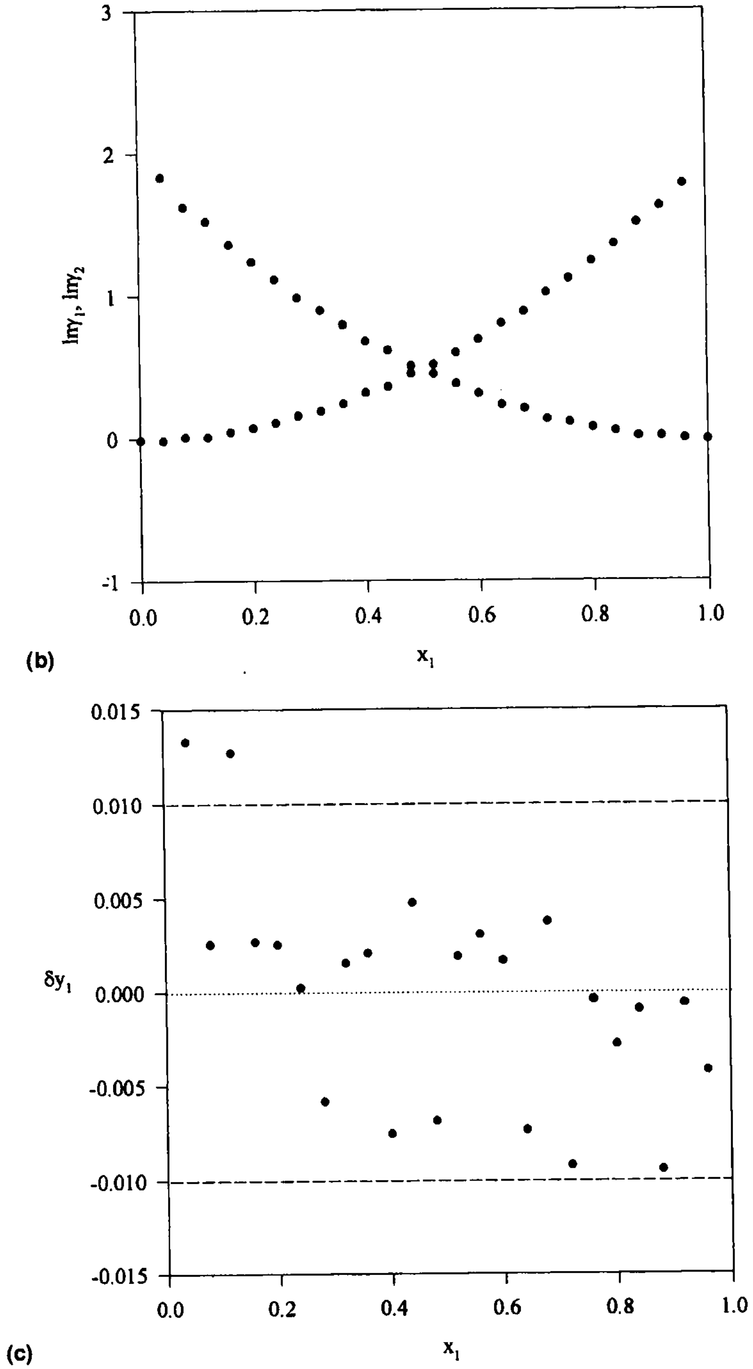


FIGURE 3 (Continued).

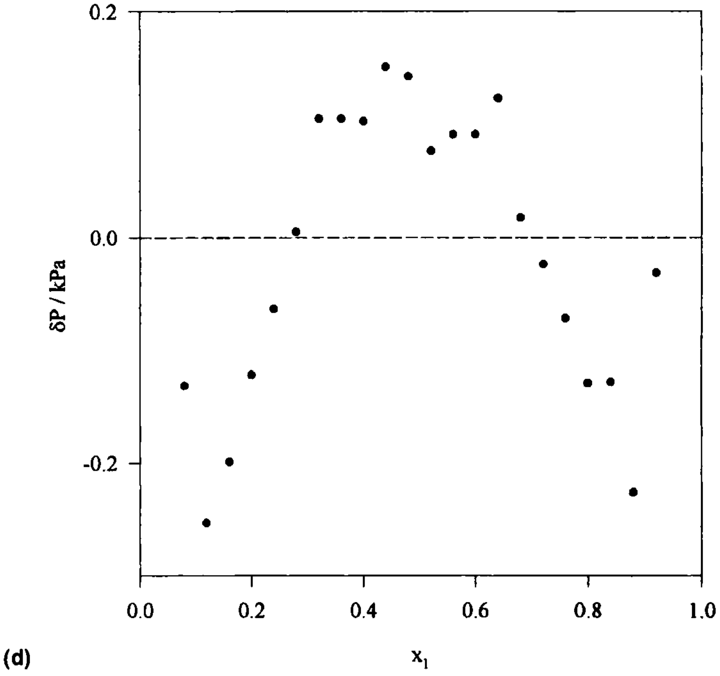


FIGURE 3 (Continued).

TABLE I Statistics for Figures 3 to 5

Pertinent Figure	*BIAS(P)/kPa*	*MAD(P)/kPa*	*BIAS(y)*	*MAD(y)*
Figure 3	−0.4358	0.1331	−0.0024	0.0045
Figure 4	–	–	0.0035	0.0016
Figure 5	−0.0170	0.5350	0.7260	1.1520

BIAS: average of residuals.

$$\mathrm{BIAS}(\theta) = \frac{1}{N_d}\sum_{i=1}^{N_d}(\theta_{\mathrm{calc},i} - \theta_{\mathrm{exp},i}).$$

MAD: mean absolute deviation.

$$\mathrm{MAD}(\theta) = \frac{1}{N_d}\sum_{i=1}^{N_d}|\theta_{\mathrm{calc},i} - \theta_{\mathrm{exp},i}|.$$

pressures, as can be deduced from the magnitude of δP residuals in Figure 3. d. A more detailed look at this Figure reveals a *suspicious and almost sharp functionality* of the δP residuals in x_1. These residuals do not seem to be biased, but nevertheless, if the errors in pressure measurement were random and the selected G^E model perfect, the δP

residuals should be random *and by none means correlationable.* In the example under consideration we can anticipate that the behavior of the δP residuals is due to the systematic error in the bubble-point pressure imposed on the artificial system, because the regular model that generates this fictitious system (see Appendix A) can be derived from a reduction of the four-suffix Margules model, or from a Legendre polynomial. When real systems are taken under consideration the model becomes an *unknown* of the consistency problem, the simultaneous correlation of systematic errors and the behavior of the system is unfortunate because the distribution of residuals can be influenced by the selection of a particular G^E model. Simple statistics like the mean absolute deviation or the bias are not necessarily informative about consistency, but they can inform us about the *goodness of the model to give a simultaneous and incongruent fit of systematic errors and of the behavior of the system.* Figures 4 presents an additional example taken from the DIPPR data base [27] corresponding to the consistency analysis of VLE data for the system octane (1) + methanol (2) reported by Budantseva *et al.* [28]. The pertinent statistics appear in Table I. Gess *et al.* [27] declare the data to be consistent but, as can be seen from Figure 4.b, the vapor phase residuals fail to scatter randomly about the zero line and show some degree of *curvilinear* correlation with the liquid phase composition. In addition, a phase stability study using the four-suffix Margules model suggested by Gess *et al.* shows that the bubble-point pressure fit produces an *immiscibility gap not present in the experimental data* (Fig. 4.c). In this case the consistency analysis is not conclusive, in part due to the inability of the model to give a correct representation of the system stability. Similar mistakes can be detected in the DIPPR book in the consistency analysis of the systems pentane (1) + 1-butanol (2) at 303.15 K [29] and cyclohexane (1) + ethanol (2) at 308.15 K [30]. Thus the common practice of *fitting bubble-point pressures and recovery of partial statistics* such as mean absolute averages and biases, should be avoided; it is *imperative* to study the capability of the selected model to give a full representation of the system under consideration.

We should also mention that inspection of the 104 systems that constitute the data base suggested by DIPPR indicates that in at least 60% of them the residual distribution seems to be nonrandom and would probable fail an statistic test for randomness.

- *Equation (14) requires good vapor pressure estimates for the pure components and models for nonidealities in the vapor phase.*

As pointed by Van Ness *et al.* [6]. and by Van Ness [11], accurate values of the vapor pressures of pure components are fundamental for an adequate application of point-to-point consistency tests and must exhibit compatibility with the VLE data. This compatibility is the best test of purity of the reagents involved in the experiments and of the performance of the equipment in the infinite dilution range. Normal boiling temperatures are usually measured separately and are reported in most published experimental works but, both in isothermal and isobaric determinations, vapor pressures of the pure components are not always measured in the experimental range. In principle, it seems

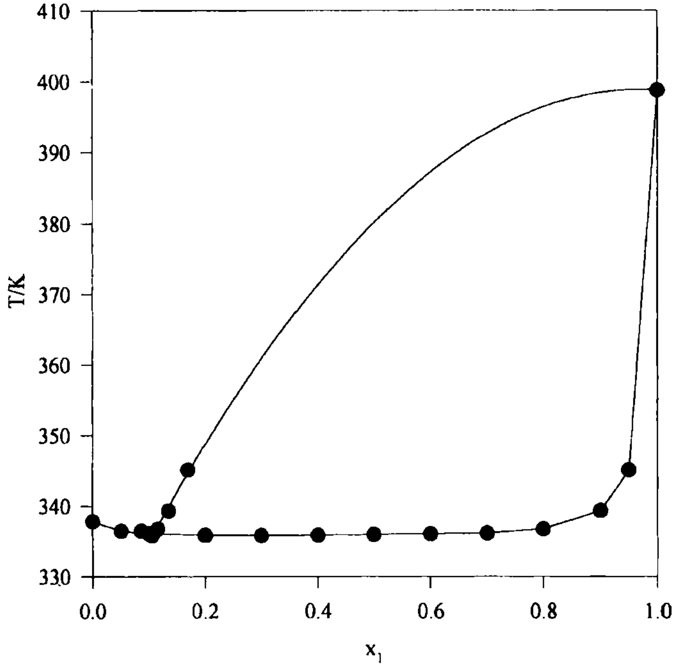


FIGURE 4 Point-to-point consistency analysis of the system octane (1) + methanol (2) using a four-suffix Margules model [27].
a. VLE diagram. (•): experimental data of Budantseva *et al.* [28];(–): smoothing curves.
b. vapor phase composition residuals.
c. Gibbs energy of mixing calculated from the G^E model parameters, after fit of pressure. (....): tangent joining LLE compositions.

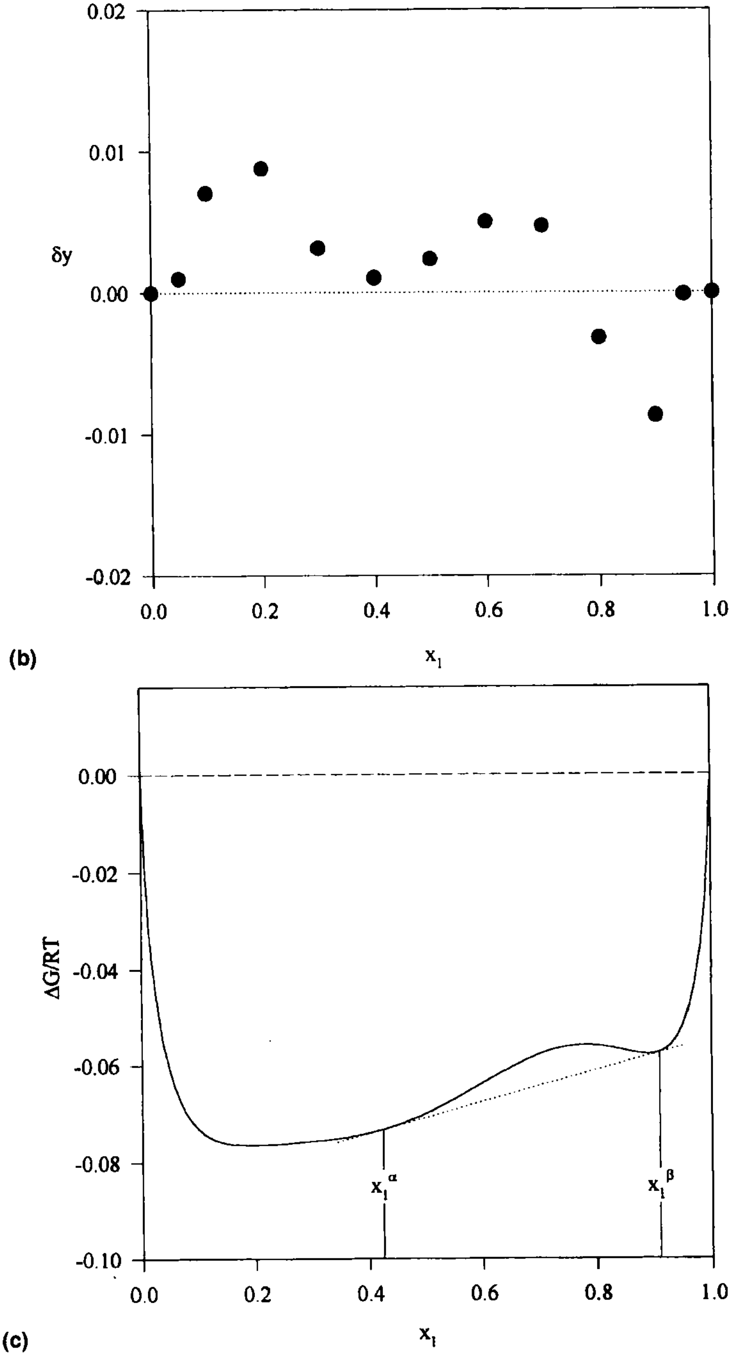


FIGURE 4 (Continued).

desirable to measure the vapor pressure of the pure components in the same equipment used for determining the VLE data. However, in most cases this is not feasible: The boiling point of the more volatile component is usually lower than the boiling points of the solutions, hence fulfillment of the requirement means measuring vapor pressures that may well exceed the pressure limitations of the equipment, particularly if it is made of glass. In addition, Antoine's equation is commonly used for the estimation of vapor pressures, it is of great importance to guarantee that the parameters of the Antoine equation (or other correlation for vapor pressures) cover the complete boiling point range of the system. TRC Thermodynamic Tables [31] are usually utilized as a source for the parameters of Antoine equations, but in this reference the temperature range of the parameters is not always given. The contribution of nonidealities of the vapor phase becomes crucial when fugacity coefficients exhibit strong dependency on the vapor phase composition, as can be deduced from Eq. (12). Fugacity coefficients are usually estimated using correlations for the second virial coefficients such as that of Hayden and O'Connell [32] and Tsonopoulos [31]. Both correlations are a very good predictive tool that can be handled with minimal information to take into account vapor phase nonidealities, but they do not substitute experimental data, when available. The use of inadequate vapor pressures and/or inadequate vapor phase corrections induces *artificial systematic error* in the consistency analysis.

- *Not every binary VLE system is adequate for a standard point-to-point consistency analysis.*

Consistency analysis requires information in the complete composition range, both for liquid and vapor phases, this requirement generates some complications for binary systems whose constituents show large differences in vapor pressures. When components have radically different vapor pressures the vapor phase will be highly concentrated in the more volatile component and its composition will not differ greatly from the value one in a wide range of liquid phase compositions. In such cases point-to-point consistency is easily achieved but due to the properties of the system the point-to-point test is of little value if the pressure is not fitted well. Consider, for example, the data of Costa-López *et al.* [34] for the system methanol

(1) + o-xylene (2) at atmospheric pressure. The normal boiling points of both components differ by about 80 K. The variation of the activity coefficients with composition is shown in Figure 5.a and indicates an abnormal behavior for the activity coefficient of o-xylene in the high temperature range ($x_1 \rightarrow 0$), no sufficient experimental data are reported to demonstrate the existence of a min-max behavior in activity coefficients, although it seems unlikely. On the other hand, the vapor phase composition in the reported data is always greater than 0.8 in methanol, as can be deduced from the VLE diagram in Figure 5.b where the experimental data is compared with the fit obtained by adjusting the bubble-point pressures with a four-suffix Margules model. Table I presents the statistics of the point-to-point consistency analysis, although we cannot replicate the consistency claimed by the authors for the data according to the method of Van Ness *et al.* [6] (considerable differences appear in the vapor phase corrections, using the data and the references indicated by the authors), it is clear that the value of MAD(y) tends to the criterion of consistency. Studying the vapor phase composition residual plot in Figure 5.c we can see that deviations become greater for low vapor phase compositions of methanol; on the other hand, the bubble-point pressure residual plot in the same Figure shows that pressure residuals scatter randomly about the zero line. Hence, we cannot conclude that the model is unable to give an adequate fit of pressure. In this case, the point of lowest composition in methanol (point A in Figs. 5.b and 5.c) seems to be an outlier, although this conclusion cannot be confirmed because few data points are reported in the range of low methanol composition where important variations of the vapor phase composition are expected. The only thing that can be concluded from the present data is inconsistency or experimental errors in the range rich in o-xylene. A reliable application of point-to-point consistency would consider experimental determinations over the whole composition range, particularly in the mid-range compositions where a better analytical accuracy is expected.

Systems with immiscibility gaps are not good candidates for point-to-point consistency analysis because, in general, activity coefficient models cannot give a simultaneous fit of VLE and LLE data [35]. From this point of view, it is important to assure that the fit of pressure with the selected model will give an adequate description of the point where three phases are present (heteroazeotropic point). In addition, the model selected must guarantee the stability of the liquid phase composition in the neighborhood of this particular point so as to avoid the study of consistency with unstable liquid phase compositions. Consistency analysis with systems which show extreme immiscibility may be inadequate but informative because, in this case, there is no mid-range information for the liquid phase.

Point-to-Point Consistency from a Mathematical Point of View

As indicated before, when performing a point-to-point consistency test for isothermal data, a G^E and a vapor phase correction models are

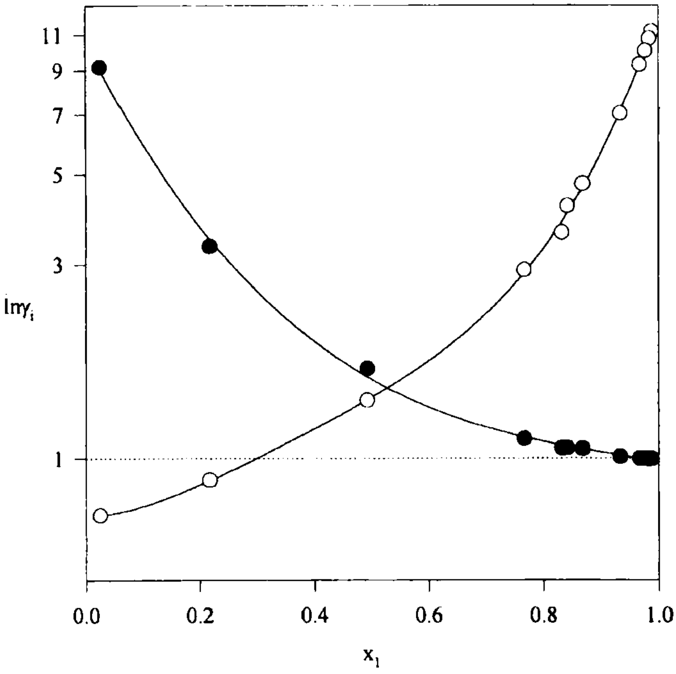


FIGURE 5 Point-to point consistency analysis of the system methanol(1) + o-xylene(2) at 101.325 kPa using a four-suffix Margules model. Data of costa-López *et al.* [34].
a. activity coefficient plot. (•): $\ln\gamma_2$; (o):$\ln\gamma_2$; (—): smooth tendency.
b. VLE diagram, (•, o): experimental data; (—): predicted by a four-suffix Margules model with parameters obtained from a consistency analysis.
c. plot of residuals. (•): pressure residuals; (o): vapor phase composition residuals.

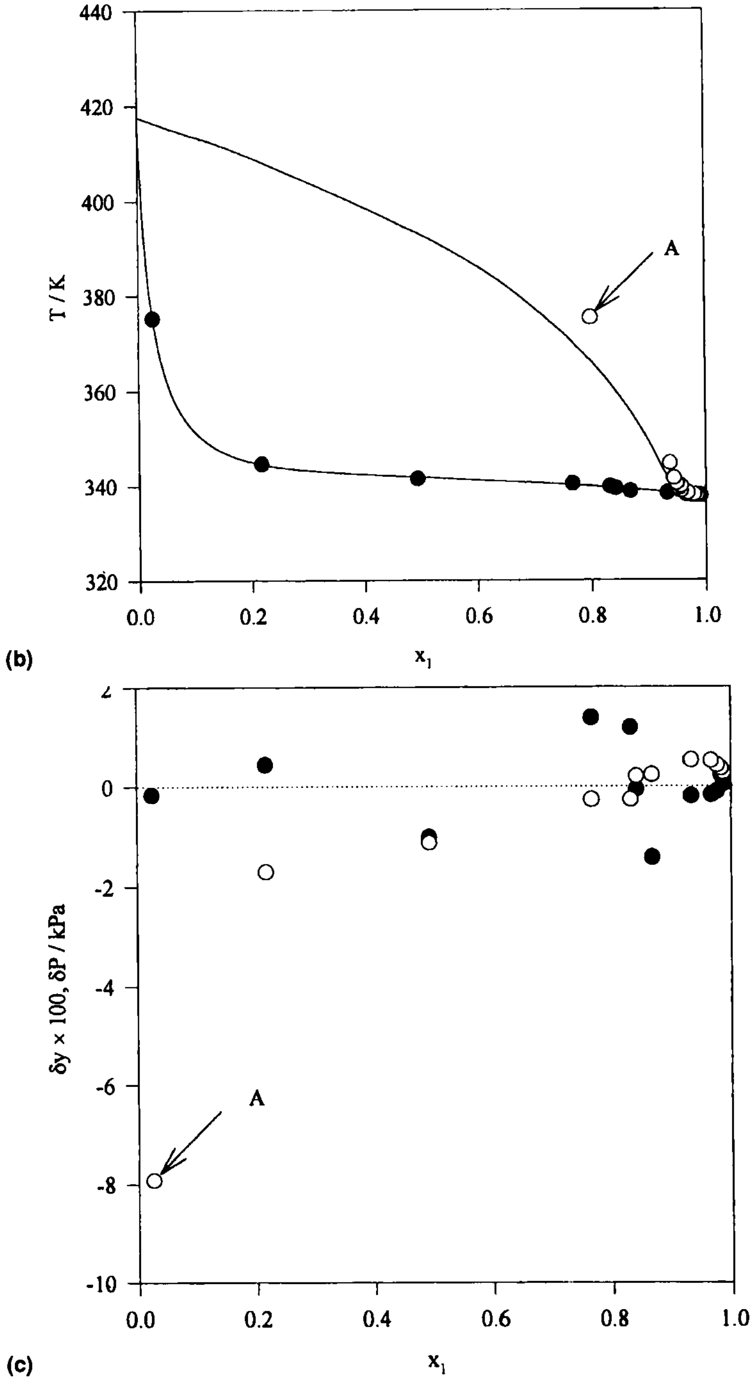


FIGURE 5 (Continued).

first selected and then Eq. (23) is fitted to the experimental bubble-point pressure data. This procedure requires only T-x data, and generates fitted bubble-point pressures and vapor phase compositions, although the latter is no used in the fit. The fit procedure is usually done using a least squares method with the following objective function

$$\Im(\underline{A}) = \frac{1}{N_d}\sum_{i=1}^{N_d}(P_{\text{exp}} - P_{\text{calc}})^2 \tag{25}$$

In Eq. (25) N_d is the number of experimental points and $\underline{A}$ the set of parameters of the selected G^E model. Note that in Eq. (17) the objective function has been selected as the *difference* between the experimental and calculated pressures. Another reasonable objective function could be square of the *percentual error* between predicted and calculated bubble-point pressures, but Eq. (25) is retained because usually the standard deviation instead of *the percentual standard deviation* is reported. It should be remembered that in a nonlinear fit of data the values of the calculated parameters will depend on the objective function selected. From a practical point of view we can postulate that the experimental bubble-point pressure is given by the relation

$$P_{\text{exp},j} = P_{\text{calc},j} - \delta^*_{P,j} \tag{26}$$

$P_{\text{calc},j}$ is obtained from Eq. (23) and the *residual errors* $\delta^*_{P,j} = P_{\text{calc},j} - P_{\text{exp},j}$ take into account the random error present in pressure measurements when and *if the model can be considered perfect*. Equation (26) is not necessarily rigorous because random errors in the liquid phase composition and temperature have not been considered. They can be small but influent, and usually their effect will not be linear, as can be deduced from Eq. (23), this complication is analyzed later. The common (*and reasonable*) assumption is that random errors in experimental measurements are normally distributed with an expected value of zero. The formulation of the minimization problem of the objective function given in Eq. (26) has been discussed by Edgar and Himmelblau [36], and the procedure is briefly discussed in Appendix B for the determination of the parameters of a G^E model.

The optimal parameters are calculated by solving the following relation

$$\sum_{j=1}^{N_P}(P_{\mathrm{exp},j}-P_{\mathrm{calc},j})\frac{\partial P_{\mathrm{calc},j}}{\partial A_k}=-\sum_{j=1}^{N_P}\partial_{P,j}\frac{\partial P_{\mathrm{calc},j}}{\partial A_k}=0 \qquad (27)$$

From Eq. (27) it can be deduced that pressure residuals generated by a specific G^E selection are directly related to the model because the derivatives $\partial P_{\mathrm{calc},j}/\partial A_k$ are obtained analytically from it. The pressure residuals in Eq. (27), $\delta_{P,j}$, should not be confused with those discussed in Eq. (18) because they are generated by *arbitrary* G^E *models* (*not necessarily the perfect model*). From Eq. (27) it is deduced also that different models will generally give different pressure residuals. A bubble-point pressure fit procedure is *an estimation of the residuals of the actual pressure* which are generally not available, but have known (*or reasonably assumed*) characteristics: if they represent random errors they must be distributed normally or *they must scatter randomly* about the zero line with a magnitude within the range of the experimental pressure measurement error. This last condition imposes some constraints on the G^E model selected, to be adequate it must, in particular, reflect the postulated pressure residual characteristics. If this is not the case, consistency analysis *can be inconclusive* even when vapor phase composition residuals scatter randomly about the zero line with small deviations, because bubble-point pressure residuals [Eq. (24)] *are affected by the particular model selected* and, as discussed above (Fig. 3), systematic error (which generates inconsistencies) can be absorbed by the bubble-point pressure fit procedure. Hence, not only vapor phase composition is important, residuals and statistic in pressure must also be considered in the consistency analysis.

Vapor phase residuals are similarly calculated as

$$\delta_{y,j}=y_{\mathrm{calc},j}-y_{\mathrm{exp},j}=\frac{x_{\mathrm{exp},j}\gamma_{1,j}P_1^{\mathrm{sat}}}{P\Phi_1}-y_{\mathrm{exp},j} \qquad (28)$$

where the activity coefficients and the pressure are calculated from an adequate G^E model. Again, the vapor phase composition residuals that appear in Eq. (28) are not available but must represent a *modeled* random error for consistent information, *i.e.*, they must scatter randomly about the zero line. Vapor phase residuals depend not only on the selected model but also on the calculated bubble-point pressure [Eq. (28)]. The model dependence of residuals is regrettable and constitutes the fundamental weakness of any point-to-point model based test because there is no simple way in which model fit inability and moderate systematic error can be *distinguished* from a residual plot when an arbitrary G^E model is used.

As mentioned before, although in residual analysis the values of T and x_1 are considered fixed and exact values, experience show that they can fluctuate randomly in a limited range (generally, publications report the standard deviations of T and x_1). These fluctuations will induce a nonlinear random error propagation in the bubble-point pressure and in the vapor phase composition calculated by means of phase equilibrium relations, these errors must be considered in addition to the pertinent errors involved in the measurements. Fluctuations in pressure and vapor phase compositions about the equilibrium state are given by

$$\delta P = \left(\frac{\partial P}{\partial x_1}\right)_T \delta x_1 + \left(\frac{\partial P}{\partial T}\right)_{x_1} \delta T$$

$$\delta y_1 = \left(\frac{\partial y_1}{\partial x_1}\right)_T \delta x_1 + \left(\frac{\partial y_1}{\partial T}\right)_{x_1} \delta T \qquad (29)$$

The pertinent partial derivatives required in Eq. (29) are given by [18]

$$\left(\frac{\partial P}{\partial x_1}\right)_T = -\frac{(y_2 - x_2)\,(\partial^2 \tilde{G}^L/\partial x_1^2)_{T,P}}{y_1 \Delta \bar{V}_1 + y_2 \Delta \bar{V}_2} \qquad (30.a)$$

$$\left(\frac{\partial P}{\partial T}\right)_{x_1} = \frac{y_1 \Delta \bar{H}_1 + y_2 \Delta \bar{H}_2}{T(y_1 \Delta \bar{V}_1 + y_2 \Delta \bar{V}_2)} \qquad (30.b)$$

$$\left(\frac{\partial y_1}{\partial x_1}\right)_T = \frac{(x_1 \Delta \bar{V}_1 + x_2 \Delta \bar{V}_2)\,(\partial^2 \tilde{G}^L/\partial x_1^2)_{T,P}}{(y_1 \Delta \bar{V}_1 + y_2 \Delta \bar{V}_2)\,(\partial^2 \tilde{G}^V/\partial y_1^2)_{T,P}} \qquad (30.c)$$

$$\left(\frac{\partial y_1}{\partial T}\right)_T = -\frac{(x_1 \Delta \bar{H}_1 + x_2 \Delta \bar{H}_2)}{(y_2 - x_2)(\partial^2 \tilde{G}^V/\partial y_1^2)_{T,P}} \qquad (30.d)$$

where $\Delta\bar{H}_i$ is the partial heat of vaporization for component $i(\Delta\bar{H}_i = \bar{H}_i^V - \bar{H}_i^L)$, $\Delta\bar{V}_i$ is the partial volume of vaporization $(\Delta\bar{V}_i = \bar{V}_i^V - \bar{V}_i^L)$, and $\tilde{G}^L$, $\tilde{G}^V$ are the molar Gibbs energy for the vapor and liquid phase respectively. Certainly, Eqs. (30) contain information which is not always available, but reasonable approximations can be done in order to estimate the fluctuations in Eq. (26), for example, the vapor phase can be considered ideal, liquid volumes can be neglected in comparison to the vapor phase volume, and partial vaporization enthalpies can be reasonably approximated by pure component vaporization enthalpies. In addition, molar Gibbs energies can be estimated from liquid phase excess properties and assuming ideal gas behavior for the vapor phase. Considering all the random errors to be independent a combination of Eqs. (29) and (30) yields the following estimates for the vapor composition and pressure standard deviations:

$$\sigma_P^2 = \left(\frac{(y_2 - x_2)\,(\partial^2\tilde{G}^L/\partial x_1^2)_{T,P}}{y_1\Delta\bar{V}_1 + y_2\Delta\bar{V}_2}\right)^2 \delta_{x_1}^{*2} + \left(\frac{y_1\Delta\bar{H}_1 + y_2\Delta\bar{H}_2}{T(y_1\Delta\bar{V}_1 + y_2\Delta\bar{V}_2)}\right)^2 \delta_T^{*2} + \delta_P^{*2} \tag{31.a}$$

$$\sigma_{y_1}^2 = \left(\frac{(x_1\Delta\bar{V}_1 + x_2\Delta\bar{V}_2)\,(\partial^2\tilde{G}^L/\partial x_1^2)_{T,P}}{(y_1\Delta\bar{V}_1 + y_2\Delta\bar{V}_2)\,(\partial^2\tilde{G}^V/\partial y_1^2)_{T,P}}\right)^2 \delta_{x_1}^{*2} + \left(\frac{(x_1\Delta\bar{H}_1 + x_2\Delta\bar{H}_2)}{T(y_2 - x_2)(\partial^2\tilde{G}^V/\partial y_1^2)_{T,P}}\right)^2 \delta_T^{*2} + \delta_y^{*2} \tag{31.b}$$

The significance of Eqs. (31) is their relation with the consistency criteria. In the test of Fredenslund *et al.* [8] it is proposed that the data are consistent if the mean absolute deviation of the vapor phase composition is less or equal than 0.01 but, as pointed by Fredenslund, this selection is arbitrary and corresponds approximately to the sum of liquid and vapor phase composition errors. Equations (31) indicate that in addition to the measurement errors of the vapor phase composition and bubble-point pressure, deviations depend also on the physical properties of the system, on the equilibrium temperature, and on the liquid phase composition (*in the best of the cases these last* *variables are constrained to random error*). This is expectable because, in general, systems are not chemically comparable and experimental conditions differ according to the equipment, the particularities of the system and the temperature range. Obviously Eqs. (31) offer a more theoretical insight for establishing the limits of confidence of the pressure and the vapor phase composition. Equations (31) suggest also that when performing a consistency test the pressure should not be assigned the same statistical weight for every experimental point. Hence, estimation of the parameters for systems which show poor consistency should be done using the maximum likelihood principle *instead* of the Barker equation [37].

Improving the Reliability of Point-to-Point Consistency Tests

In order to give more reliability to the point-to-point consistency test, the following steps are suggested:

- The vapor pressure correlations and the model for vapor phase corrections must be carefully selected. Physical considerations like association should be justified. A routine procedure should include *the calculation and plotting of activity coefficients* because, as explained above, the functionality of activity coefficients is constrained in the infinite dilution range and a smooth behavior of them is a good symptom of consistency. The same physical considerations as for the vapor phase must be used in all the consistency analysis.
- The G^E model selection *is an unknown* factor in the point-to-point consistency procedure but, for theoretical reasons, activity coefficients are well-behaved functions of the composition. It is reasonable to consider that in isothermal systems the activity coefficients can be expanded in a Taylor series of the composition at low pressures or, equivalently, they can be represented by composition polynomials with a degree *determined* by the appropriate fit of the data. Orthogonal polynomials, instead of the Redlich-Kister expansion, are a good selection due to the mathematical property that their coefficients are relatively independent when smoothing discrete data. Legendre orthogonal polynomials are used in the test of Fredenslund *et al.* [8] to fit the bubble-point pressure, another alternative is the use of Chebyshev orthogonal polynomials, as

suggested by Tomiska [38] for representing excess properties. In order to determine the number of polynomial terms used to fit the bubble-point pressure it is suggested to perform a serial fit procedure, starting with a low order polynomial (second or third order). If for a certain polynomial degree consistency is not achieved then selection of higher order degree polynomials is justified *only* when the previous coefficients do not change significantly (with errors in the bubble-point pressure of the order of the error of the Antoine correlation used in the study, and decreasing errors in vapor phase composition). Overcorrelation of bubble-point pressures can be avoided considering the minimum error that can be expected in pressure, which can be estimated from Eq. (31.b).

- Once the empirical consistency criteria is satisfied, the reliability of the model must be tested because the parameters of the model can be biased by systematic errors, even when the objective function and the average of residuals yield small values. Some possible alternatives are the following:

(a) average deviations of the calculated vapor phase compositions are weak statistical tools as *criteria of consistency*. Probably the most important statistic is the maximum absolute deviation because this value will indicate either an outlier an unappropriate model. Surprisingly, statistical studies regarding pressure appear only in a very small number of publications, in spite of the fact that both pressure and vapor phase statistics are relevant for model testing and consistency.

(b) experimental activity coefficients should be smoothed by the *same* model that gives consistency to the data, specifically in mid-range concentrations. Low concentration ranges will show, in general, some degree of discrepancy because they are numerically sensitive to small errors in composition. This is a good opportunity for detecting model wriggle, specifically when polynomials are used.

(c) the parameters of the model should be calculated using the bubble-point pressure version of equilibrium calculations. A very good test is to assess statistically the tendency of other VLE calculations using the consistency parameters, specially informative is the dew-point pressure calculation (using *experimental* vapor phase compositions) because it measures the compatibility of the model parameters for giving liquid phase compositions. Assuming that the data are consistent, a model can be considered adequate when different versions of equilibrium calculations give errors of similar order. This should be *standard practice* not only in consistency testing but also when calculating the parameters of the model.

(d) an stability study using the parameters of the model is highly suggested, specially for systems that show large positive deviations from ideality.

Point-to-point consistency reliability can be largely increased when pressure and vapor phase residuals are analyzed. Interpretation of residuals is not clear-cut, particularly when they show small deviations, because they reflect some bias of the model and even nonlinear perturbations of temperature and liquid phase composition errors. However, it should be clear that when the model is perfect, no systematic error and no random error is committed in the determination of T x_1 residuals, they must scatter randomly about the zero line without any tendency. If the model is properly tested the bias of its residuals should be minimized. Equations (31) give an estimate of the standard deviation that should be expected on pressure and on vapor phase compositions if the experiment is carried out free of systematic error, obviously the use of Eq. (31.b) is limited to non azeotropic ranges. The use of such equations is suggested for the study of biased residuals and for establishing a criteria of acceptance in the procedure of minimization of bubble-point pressures.

To illustrate these concepts, let us analyze the data for the system ethanol (1) + octane (2) system at 343.15 K reported by Hiaki *et al.* [39]. Vapor phase calculations have been made using the method of Hayden and O'Connell [32], liquid volumes have been calculated from the correlation of Spencer and Danner [40], and vapor pressure correlations have been taken from Hiaki *et al.* Figure 6.a shows the activity coefficients as a function of concentration, it is seen that the data have a smooth tendency and the appropriate tangent behavior when approaching the concentrated end. The plot of the G^E/RTx_1x_2 function magnifies the errors in the low concentration range, but in this case the tendency of the activity coefficient curves and the G^E/RTx_1x_2 curve is clear. From this analysis we conclude that vapor pressures and vapor phase corrections are reasonably good. For the analysis of the consistency of the data Legendre polynomials of various degrees have been considered. Figure 6.b shows how the values of the coefficients change between sequential fits and from we can is deduce that no substantial changes occur for ascending polynomial degrees. Table II presents the pertinent statistics for the fit, it can be seen that a reduction in pressure deviations implies a simultaneous reduction of vapor phase composition deviations, which exhibit a permanent positive bias. A third-order degree Legendre polynomial is equivalent to the four-suffix Margules equation, in the case under consideration this is not the best alternative from a fit point of view, although empirical consistency criteria is achieved for three or more terms. Figure 6.c shows the interpolation of activity coefficients for a fit using Legendre polynomials of three and five parameters, it is seen that with five parameters the fit is improved slightly. In general, the interpolation can be qualified as good, but it is clear also that the activity coefficients of methanol are better represented than the activity coefficients of octane. Table III shows the statistics for different VLE calculations when different models are used, the Wilson equation [41] is used as a comparative reference because it has a different functional character. From Table III it is concluded that a good fit of bubble-point pressures is not compatible with dew-point pressures and that the *model seems not to be the origin of the problem*, because three different models give the same response. The discrepancies observed for different VLE calculations present an interesting thermodynamic problem because the parameters of an activity coefficient model have many predictive uses in process simulation. For example, the design of continuous distillation columns is usually based on bubble-point pressures and flash calculations, the design of a total condenser requires dew-point pressure calculations, etc. All these calculations

TABLE II Statistics for successive applications of the point-to-point test. Ethanol (1)+octane (2) system at 343.15 K. Data of Hiaki *et al.* [39]

Statistic	*Number of Legendre polynomial terms*				
	1	*2*	*3*	*4*	*5*
MAD(P)/kPa	2.321	2.369	0.329	0.214	0.096
MAD(y)×100	1.295	1.230	0.557	0.548	0.404
BIAS(y)×100	−0.464	−0.407	−0.457	−0.324	−0.351

BIAS: average of residuals.
MAD: mean absolute deviation.

TABLE III Statistics for different versions of VLE calculations. Ethanol (1) + octane (2) system at 343.15 K. Data of Hiaki *et al.* [39]

Statistic	*LP5*		*LP3*		*WILSON*	
	BUBLP	*DEWP*	*BUBLP*	*DEWP*	*BUBLP*	*DEWP*
MPDP(%)	0.123	1.176	0.459	1.490	0.256	1.193
MAD(y)×100	0.404	–	0.557	–	0.397	–
MAD(x)×100	–	3.838	–	3.179	–	3.845

BIAS : average of residuals.
MAD : mean absolute deviation.
MPDP : mean percentual deviation in pressure.

$$\mathrm{MPDP} = \frac{100}{N_d} \times \sum_{i=1}^{N_d} \frac{|P_{\mathrm{calc},i} - P_{\mathrm{exp},i}|}{P_{\mathrm{exp},i}}.$$

LP3 : Legendre polynomial, three parameters.
LP5 : Legendre polynomial, five parameters.
N_d : number of data points.

usually give errors of different magnitude when the data is parametrized according to a particular objective function, hence a good practice in data treatment is to give statistics for different VLE calculations. An stability analysis shows that no immiscibility gap appears when the data are fit using Legendre polynomials of three to five coefficients. In summary, there is a good basis to claim that the data are reasonably represented by a five-parameter Legendre polynomial. Pressure and vapor phase composition residuals for different Legendre polynomials are shown in Figures 6.d and 6.e. Let us first to examine Figure 6.d, where a three-parameter Legendre polynomial is used; pressure residuals do scatter about the zero line, but not randomly showing a sinusoidal and correlationable tendency. The random scatter of the pressure residuals is important because vapor pressure residuals depend on them. In addition to a systematic error, there are many causes for which pressure residuals do not scatter randomly, one easy to identify is the use of poor vapor pressure data but, it is more difficult to judge the behavior of residuals in terms of subcorrelation of data when they can be biased by the model. This is the reason why to use several models, in the case under consideration the data have been fitted using polynomials of different order. As shown in Figure 6.d, the behavior of vapor phase composition residuals could be biased by a subcorrelation of pressure, but this question has no definite answer. From our previous calculations, however, we have a good basis for establishing that a three-parameter Legendre polynomial is not the best selection for the data. Figure 6.e shows the residuals for the fit with a five-parameter Legendre polynomial, in this case the pressure residuals are scattered randomly about the zero line, but vapor-phase composition residuals are not.

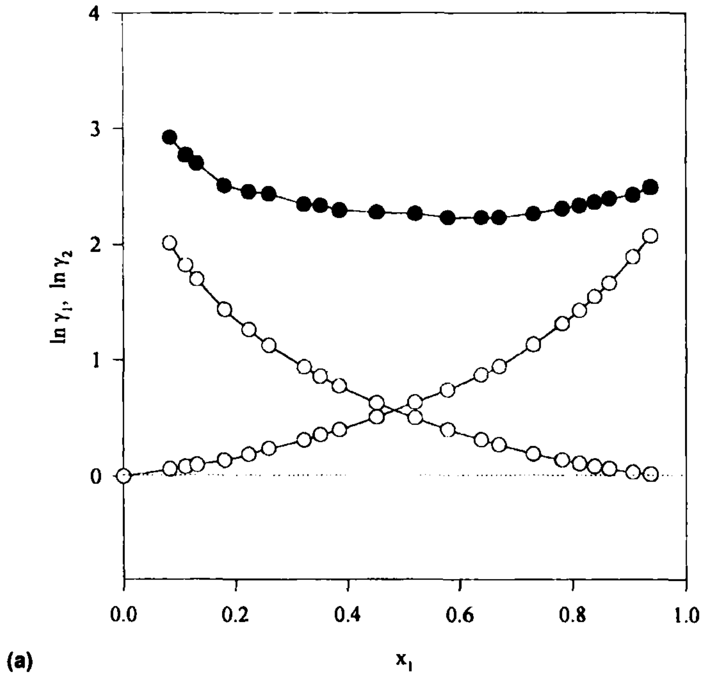


FIGURE 6 Consistency analysis of the system ethanol (1) + octane(2) at 343.15 K. Data of Hiaki *et al.* [39].

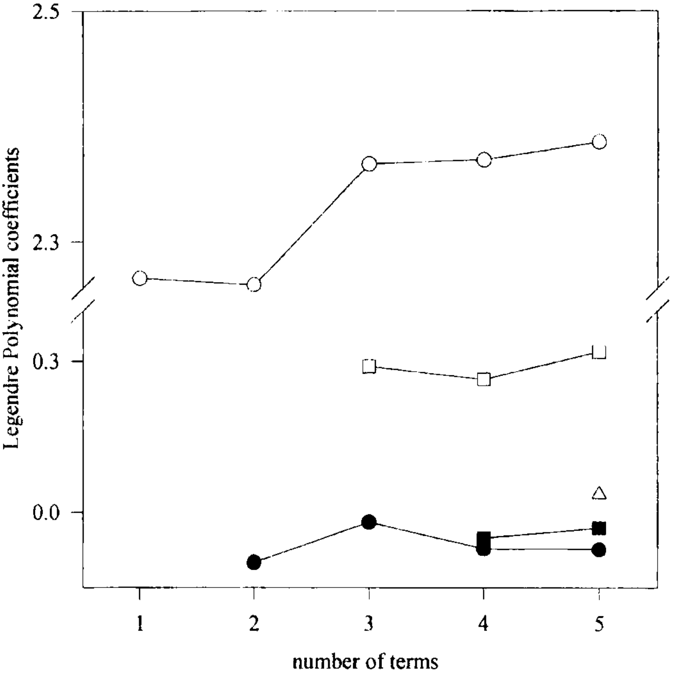
a.activity coefficient plot. (○): ln γ_1, ln γ_2; (•)G^E/RTx_1x_2;(—): smoothed curves.

b. Legendre polynomial coefficients for sequential fits of bubble-point pressure (○)A_1;(•)A_2 : (□): A_3; (■): A_4 (△): A_5.

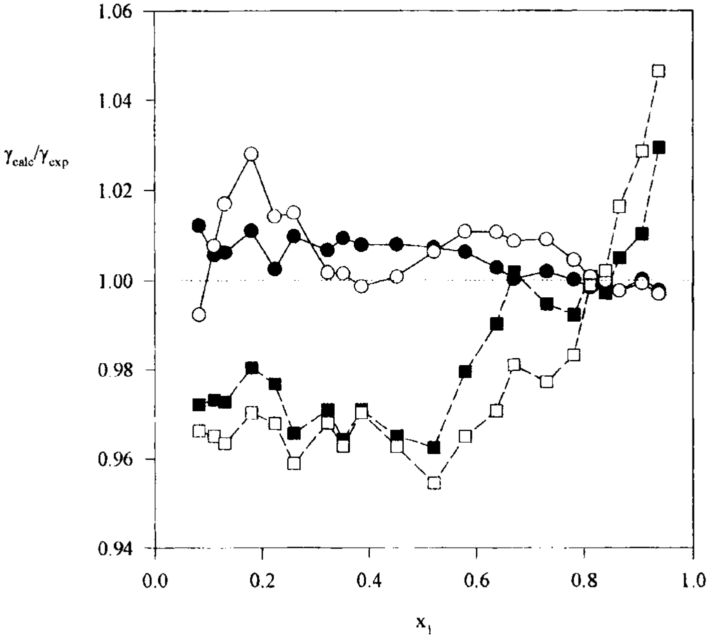
c. interpolation of experimental activity coefficients. (○) : $\gamma_1^{\mathrm{calc}}/\gamma_1^{\mathrm{exp}}$ for a three-parameter Legendre polynomial; (•) $\gamma_1^{\mathrm{calc}}/\gamma_1^{\mathrm{exp}}$ for a five-parameter Legendre polynomial; (□): $\gamma_1^{\mathrm{calc}}/\gamma_1^{\mathrm{exp}}$ for a three-parameter Legendre polynomial; (■): $\gamma_1^{\mathrm{calc}}/\gamma_1^{\mathrm{exp}}$ for a three-parameter Legendre polynomial.

d. pressure vapor composition phase composition for a three-parameter Legendre polynomial. (○) :$y \times 100$; (•) : $\delta P/kPa$..

e. pressure and vapor composition phase composition for a three-parameter Legendre polynomial (○) :$y \times 100$; (•) : $\delta P/kPa$; (...): pressure confidence limit/kPa; (–): vapor phase composition confidence limit.



(b)



(c)

FIGURE 6 (Continued).

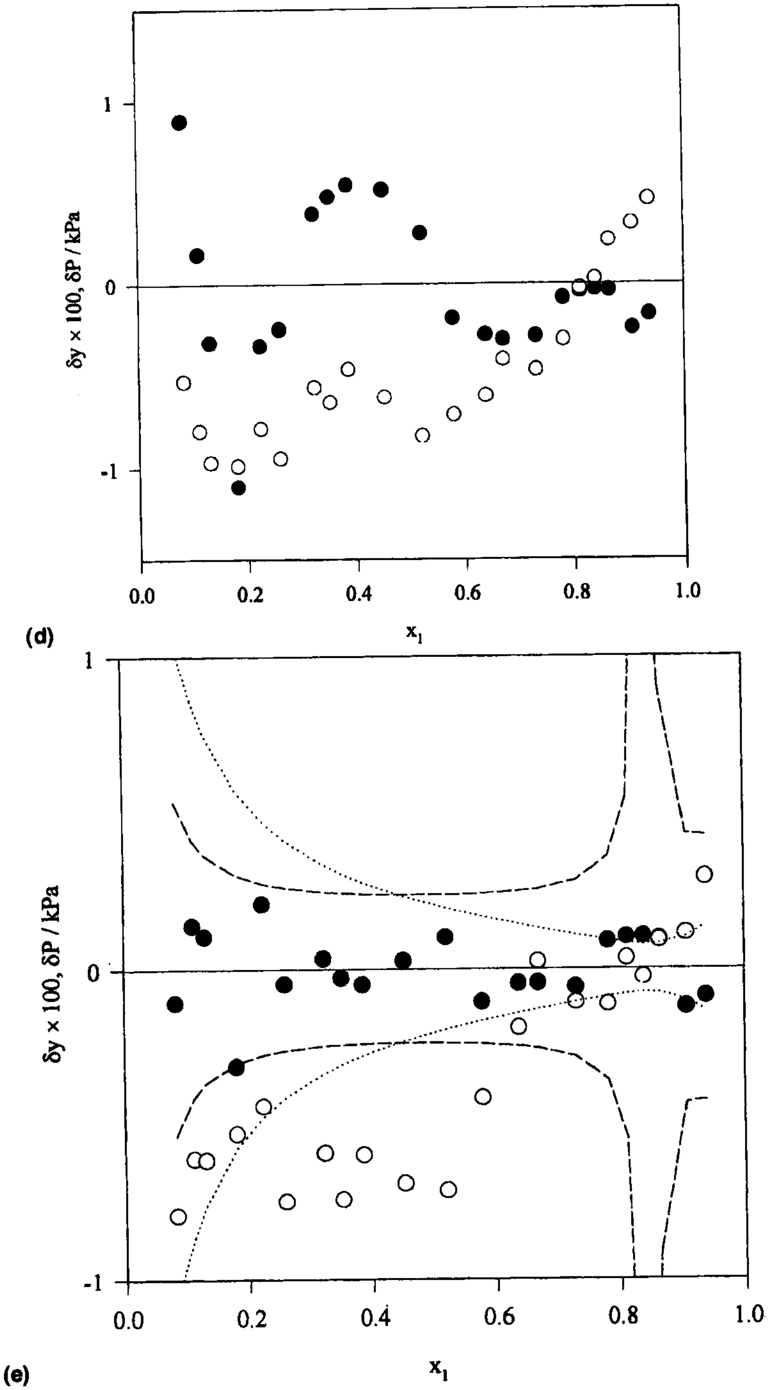


FIGURE 6 (continued).

Figure 6.e shows also the confidence lines calculated from Eqs. (31) assuming ideal gas behavior, partial volumes equal to the ideal gas volume, partial enthalpies equal to pure compound vaporization enthalpies, and approximating $(\partial^2\tilde{G}^L/\partial x_1^2)_{T,P}$ by $(x_1x_2)^{-1}$ (the maximum value in the case under consideration, because the system shows positive deviation). Experimental errors in the liquid phase composition, temperature and pressure where taken equal to the measurement accuracies reported by Hiaki *et al.* [39]. From Figure 6.e it is concluded that the population of pressure residuals is reasonably contained within the pressure confidence interval, but vapor phase composition residuals are contained in the composition confidence interval only for high concentrations of methanol, the excessive deviation of composition residuals at low concentration cannot explained *only* by random errors. The experimental data for the system ethanol (1) + octane (2) reported by Hiaki [39] is one of the best that can be found in the literature, and satisfies the consistency for most of the common tests, but here we present reasonably evidence of systematic error that will induce problems with the correlation of the system.

Consistency of Isobaric Systems

For isobaric systems combination of Eq. (7) and (23) yields

$$P = \frac{x_1P_1^{\mathrm{sat}}}{\Phi_1}\exp\left(\frac{\tilde{G}^E}{RT} + x_2\left[\frac{d}{dx_1}\left(\frac{\tilde{G}^E}{RT}\right) + \frac{\Delta\tilde{H}}{RT^2}\frac{dT}{dx_1}\right]\right) + \frac{x_2P_2^{\mathrm{sat}}}{\Phi_2}\exp\left(\frac{\tilde{G}^E}{RT} - x_1\left[\frac{d}{dx_1}\left(\frac{\tilde{G}^E}{RT}\right) + \frac{\Delta\tilde{H}}{RT^2}\frac{dT}{dx_1}\right]\right) \quad (32)$$

VLE data obtained under isobaric conditions find direct application in conventional distillation and constitute an economical and time saving experimental alternative. Consistency analysis of isobaric systems involve the availability of enthalpies of mixing, which seldom are determined at various temperature levels; in addition, this property exhibits complex and non easily predictable functionalities on liquid phase compositions. According to Eq. (3), a consistency analysis is not possible without enthalpies of mixing, but it is also reasonable to assume that a practical experimental VLE planning cannot be constrained to the requirements of a consistency test. Thus the VLE reduction of isobaric systems, when no enthalpy of mixing is available, is a *theoretical problem instead of an experimental problem* and does not have an easy solution. Group contribution methods, such as modified UNIFAC [24], [42], [43] permit adequate prediction of enthalpies of mixing for a limited number of components. As a result, the point-to-point consistency test of isobaric systems, where the enthalpic term is neglected, is an inaccurate analysis of VLE information. Fredenslund *et al.* [8] have suggested the use of temperature-independent Legendre polynomials for the representation of G^E, the inadequacy of this suggestion can be easily demonstrated with respect to the integral test. From Eq. (13) we have

$$\int_0^1 \ln\frac{\gamma_1}{\gamma_2}dx_1 = \int_{T_2^{\mathrm{sat}}}^{T_1^{\mathrm{sat}}} \frac{\Delta\tilde{H}}{RT^2}dT \neq 0 \tag{33}$$

When a point-to-point consistency test is carried with a G^E model whose parameters do not depend on temperature, *the left-hand side of Eq. (33) will always be zero.* Hence, it can be concluded that a consistency approach based on a particular temperature-independent model will not give an adequate representation of individual activity coefficients when the right-hand side term of Eq. (33) cannot be neglected. From this point of view, it is important to verify the hypothesis that excess enthalpies can be neglected. When no data regarding enthalpies of mixing are available and the VLE data meet the consistency criteria, it is recommended to compare the ratio of the activity coefficient ratio, calculated with different models, with the experimental activity coefficient ratios. Consistency cannot be declared when important differences are appreciated among the results, the only thing that can be said is that the data are reasonably interpolated by temperature-independent models. Consider, for example, the VLE data of Ninov *et al.* [44] for the system diethylamine (1) + chloroform (2) at atmospheric pressure. The pertinent data appear in Figure 7.a. According to Ninov *et al.* the data are consistent because they can be fit with the NRTL [45] and the Wilson [41] models, using temperature-independent parameters. Repetition of the calculations does not yield the consistency claimed by the authors, probably due to the fact that they have used the following simplification of the $\gamma - \phi$ equations for the calculation of activity coefficients

$$\gamma_i = \frac{y_i \hat{\phi}_i P}{x_i P_i^{\text{sat}}} \tag{34}$$

Equation (34) appears in the reduction analysis of some published VLE data, *its use is inadequate and should be avoided in consistency analysis* because the calculated activity coefficients do not tend to unity at infinite dilution. Following the procedure suggested by Fredenslund *et al.* [8], the MAD(y) is calculated to be 0.016 for a three-parameter Legendre polynomial (the use of more parameters induces polynomial wriggle and increasing vapor phase deviations for the data under consideration) and average absolute deviations higher than 0.01 for

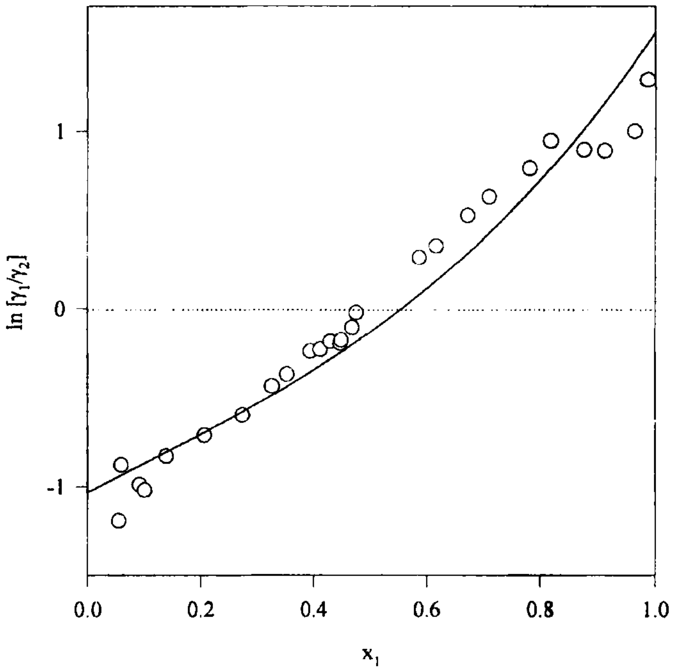


FIGURE 7 Graphical comparison between experimental ln $[\gamma_1/\gamma_2]$ and those obtained from isobaric consistency.

a. analysis of the data of Ninov *et al.* [44]. (o): experimental points; (—): obtained from temperature-independent Legendre polynomials.

b. analysis of the data of Hiaki *et al.* [46]. (o): experimental points; (—): obtained from temperature-independent Legendre polynomials.

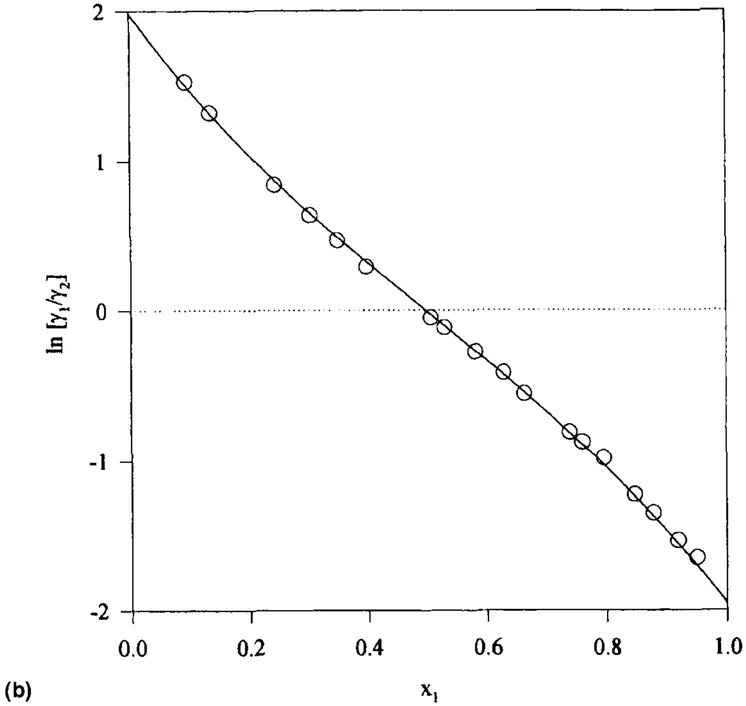


FIGURE 7 (Continued).

the NRTL and the Wilson equations. Considering only the mid-range compositions, from Figure 7a it is concluded that ln[γ_1/γ_2] is not represented well by a G^E model with temperature-independent parameters. In addition, it is not clear if the lack of fit is due inconsistency of the data, to a nonnegligible heat of mixing (usually observed in amine solutions), or by both effects. In contrast to this, Figure 7b presents an analysis of the data of Hiaki *et al.* [46] for the system propanol (1) + octane (2) system at atmospheric pressure, where an excellent prediction of the ln[γ_1/γ_2] function is observed using the same G^E model used in the consistency procedure (a three-parameter Legendre polynomial with temperature-independent parameters). These data satisfy clearly the consistency criteria [MAD(y)] = 0.006], although vapor phase composition residuals fail to scatter randomly about the zero line, and may be qualified hence as consistent.

Although it is tempting to add temperature-dependent parameters to a G^E model in isobaric consistency analysis, it is not recommended to do so unless excess enthalpy data are available. This results from the fact that rarely excess enthalpies can be predicted using only VLE data and empirical temperature dependence for G^E models [8].

4. Direct (or Differential) Consistency Tests

In a recent communication Van Ness [11] proposed a direct test of thermodynamic consistency. As its predecessor [6], this new test is point-to-point, model based and residuals play in it a central role. No VLE calculation is needed because the test proceeds directly with activity coefficients and Gibbs excess energy functions. The main ideas are briefly discussed below.

For experimental data the following thermodynamical relation can be written

$$\frac{dg^E_{\mathrm{exp}}}{dx_1} = \ln\left(\frac{\gamma_1}{\gamma_2}\right)_{\mathrm{exp}} + x_1\frac{d\ln\gamma_{1,\mathrm{exp}}}{dx_1} + x_2\frac{d\ln\gamma_{2,\mathrm{exp}}}{dx_1} - \frac{\Delta\tilde{H}}{RT^2}\frac{dT_{\mathrm{exp}}}{dx_1} + \frac{\Delta\tilde{V}}{RT^2}\frac{dP_{\mathrm{exp}}}{dx_1} \tag{35}$$

where $g^E = \tilde{G}^E/RT$. The Gibbs-Duhem equation is recognized in the four last terms of the right-hand-side of Eq. (35), but due to the fact of errors in experimental data, the sum of these terms does not add to zero. When applied to perfect data, or to a G^E model whose parameters are fitted to experimental data, Eq. (35) becomes

$$\frac{dg^E}{dx_1} = \ln\left(\frac{\gamma_1}{\gamma_2}\right) \tag{36}$$

Subtracting Eq. (35) from (36) yields

$$\frac{d(\delta g^E)}{dx_1} = \delta\ln\left(\frac{\gamma_1}{\gamma_2}\right) - x_1\frac{d\ln\gamma_{1,\mathrm{exp}}}{dx_1} - x_2\frac{d\ln\gamma_{2,\mathrm{exp}}}{dx_1} + \frac{\Delta\tilde{H}}{RT^2}\frac{dT_{\mathrm{exp}}}{dx_1} - \frac{\Delta\tilde{V}}{RT^2}\frac{dP_{\mathrm{exp}}}{dx_1} \tag{37}$$

where δg^E is the excess Gibbs energy residual and $\delta \ln(\gamma_1/\gamma_2)$ is the activity coefficient ratio residual. For calculating the former residuals, the use of an activity coefficient model is proposed, whose parameters $\underline{A}$ are calculated by means of minimization of

$$\Im(\underline{A}) = \sum_{i}^{N_d} [\delta g^E]^2 \tag{38}$$

so as to make the residuals δg^E *scatter about the zero line*. According to Van Ness the minimum value of Eq. (38) yields effectively

$$\frac{d(\delta g^E)}{dx_1} = \frac{d(g^E_{\text{model}} - g^E_{\text{exp}})}{dx_1} = 0 \tag{39}$$

hence Eq. (39) becomes

$$\delta \ln\left(\frac{\gamma_1}{\gamma_2}\right) = x_1 \frac{d\ln\gamma_{1,\text{exp}}}{dx_1} + x_2 \frac{d\ln\gamma_{2,\text{exp}}}{dx_1} - \frac{\Delta H}{RT^2}\frac{dT_{\text{exp}}}{dx_1} + \frac{\Delta \tilde{V}}{RT^2}\frac{dP_{\text{exp}}}{dx_1} \tag{40}$$

The right-hand side of Eq. (40) does not depend on a model but only on experimental data, and, on the other hand, it *represents the rigorous slope test* based on the Gibbs-Duhem equation. Van Ness pointed out that by selecting a particular activity coefficient model and minimizing Eq. (40), consistency can be analyzed revising the activity coefficient ratio residuals. In addition, from Eq. (37) Van Ness deduced the following relation for an alternative area test

$$\int_0^1 \delta \ln(\gamma_1/\gamma_2)dx_1 = -\int_0^1 \left[\ln(\gamma_{1,\text{exp}}/\gamma_{2,\text{exp}}) + \frac{\Delta \tilde{H}}{RT^2}\frac{dT_{\text{exp}}}{dx_1} - \frac{\Delta \tilde{V}}{RT^2}\frac{dP_{\text{exp}}}{dx_1}\right]dx_1 \tag{41}$$

The right-hand-side of Eq. (41) represents the classical integral area test. Instead of it, Van Ness suggests calculating the integral in the left-hand side after the residuals $\delta \ln(\gamma_1/\gamma_2)$ have been minimized.

The proposed test is particularly attractive due to its relation with the slope test given by Eq. (40). Furthermore, the regression of g^E for direct consistency, or $\ln[\gamma_1/\gamma_2]$ for the alternative area test, yields linear fit procedures when the liquid phase is described by polynomials. Hence the application of the test to experimental data is particularly simple, especially when compared with iterative bubble-point pressure method. However, there are some precautions that should be taken into account in its use; maybe the most important is related with Eq. (36). Suppose that an analytical G^E model, say the Wilson equation, is used for generating perfect data, then these data are fitted using other G^E model; although it is possible to obtain a very good representation of the original data, it is not possible, in principle, to obtain the exact value of the compositional derivative pertinent to the original data over the whole concentration range. Hence, there is no mathematical reason for which Eq. (39) must have a zero value, unless perfect data and the pertinent model which represent it is being analyzed. Following this reasoning, there is a residual term that has not been considered in Eq. (40) and, thus regrettably, it *is model biased.* When treating experimental and discrete VLE data an interpretation of Eq. (39) becomes cumbersome and the extent of its effects on the residuals that appear in Eq. (40) are not clear, but the former equation depend on the selected model.

The structure of Eq. (41) is interesting because, as pointed by Van Ness, the right-hand side integral depends only on experimental data, thus the left-hand side integral is independent of the model. This conclusion follows from the fact that Eq. (41) is a thermodynamic identity. The fit of the $\ln[\gamma_1/\gamma_2]$ function by means of G^E polynomial models, which allow the calculation of $\delta\ln[\gamma_1/\gamma_2]$ residuals, is a simple linear fit which include intercept (this follows from the fact that $\ln[\gamma_1/\gamma_2]$ is not zero in the low concentration range, with the exception of ideal systems). In this case, when the ordinary unweighted least square technique is used and the fit is properly done, the bias of $\delta\ln[\gamma_1/\gamma_2]$ residuals is zero [47] yielding always scatter distribution of points about the zero line, *independently of the quality of the data.* Hence, the measure of inconsistency using the left hand side of Eq. (41) depends on its numerical integration as a function of the composition. This integration is model biased because two different linear interpolation functions will generally give a different wriggle in the neighborhood of the interpolated points. There are no advantages in replacing the right-hand side integral of Eq. (41) with an integral of residuals because the former can be easily smoothed previous to numerical integration (*in spite of the bias introduced by the smoothing* model).

Kojima *et al.* [9] proposed a point-to-point test based directly in Eq. (6). For this test the discrepancy

$$\delta = \frac{d}{dx_1}\left(\frac{\tilde{G}^E}{RT}\right) - \ln\frac{\gamma_1}{\gamma_2} + \frac{\Delta\tilde{H}}{RT^2}\frac{dT}{dx_1} - \frac{\Delta\tilde{V}}{RT}\frac{dP}{dx_1} \tag{42}$$

observed in experimental data is evaluated. The functions $\tilde{G}^E/RT$ and $\ln[\gamma_1/\gamma_2]$ are independently fitted to experimental data using, in both cases, the Redlich-Kister expansion with three to four coefficients. The bubble-point pressure and temperature are reduced to pressure and temperature of mixing as follows

$$\begin{aligned} \Delta T &= T - x_1 T_1^{\text{sat}} - x_2 T_2^{\text{sat}} \\ \Delta P &= P - x_1 P_1^{\text{sat}} - x_2 P_2^{\text{sat}} \end{aligned} \tag{43}$$

and then properly smoothed for the estimation of the dP/dx_1 and dT/dx_1 derivatives required by the isothermal and isobaric cases, respectively. The integration of Eq. (43) over the complete concentration range yields the area test and at infinite dilution we have

$$\begin{aligned} I_1^* &= \frac{\left[\dfrac{\tilde{G}^E}{RTx_1x_2} - \ln\dfrac{\gamma_1}{\gamma_2}\right]_{x_1=0}}{\ln[\gamma_1/\gamma_2]_{x_1=0}} \\ I_2^* &= \frac{\left[\dfrac{\tilde{G}^E}{RTx_1x_2} - \ln\dfrac{\gamma_2}{\gamma_1}\right]_{x_1=1}}{\ln[\gamma_2/\gamma_1]_{x_1=1}} \end{aligned} \tag{44}$$

The limiting values given in Eqs. (44) allow the measure of consistency at infinite dilution. The simplicity of the suggested procedure is remarkable because no iterative calculation is needed, the only requirements are activity coefficients carefully calculated from experimental data and enthalpy and volume of mixing data (for isobaric and isothermal systems respectively). The weaknesses of this test are similar to those discussed for the test of Van Ness [11], although the $[\tilde{G}^E/RT]$ function can be well fitted to experimental data, the derivative $d/dx_1[\tilde{G}^E/RT]$ required for Eq. (42) is model biased. In particular, at constant temperature, due to the weak contribution of pressure to the excess Gibbs energy, the following approximation is acceptable

$$\left[\frac{d}{dx_1}\left(\frac{\tilde{G}^E}{RT}\right)\right]_T \approx \ln\frac{\gamma_1}{\gamma_2} \tag{45}$$

When the functions $\tilde{G}^E/RT$ and $\ln[\gamma_1/\gamma_2]$ are independently fitted to experimental data using the same excess model, Eq. (45) is rarely satisfied and different values for the parameters of the model are usually observed, because $\tilde{G}^E/RT$ and $\ln[\gamma_1/\gamma_2]$ constitute different objective functions for regressing the parameters. This result can be attributed not only to the inconsistency of the data but also to the fitting capabilities of the model, hence we can expect that the test to be model biased. Fortunately, Kojima *et al.* [9] selected a variable Redlich-Kister expansion, thus the problem of bias due to the model can be reduced.

The integral version of the test of Kojima *et al.* is

$$\int_0^1 \delta dx_1 = \int_0^1 \ln\frac{\gamma_1}{\gamma_2}dx_1 + \int_0^1\left[\frac{\Delta\tilde{V}}{RT}\frac{dP}{dx_1} - \frac{\Delta\tilde{H}}{RT^2}\frac{dT}{dx_1}\right]dx_1 \tag{46}$$

Especial attention should be given to the second term of the right-hand side of Eq. (46). When the ratio between the activity coefficients is represented by a Redlich-Kister expansion with temperature- (or pressure) independent parameters, then this term is always zero, independently of the quality of the data, reaching wrong results about consistency.

The L-W Test of Consistency [10]

Recently Wisniak [10] proposed the L-W test of consistency described briefly below. Activity coefficients are calculated from

$$\gamma_k = \frac{y_k P \Phi_k}{x_k P_k^{\text{sat}}} \tag{47}$$

Considering Eq. (47) and the Clapeyron relation yields

$$\ln\gamma_k = \ln\frac{y_k}{x_k} + \ln\Phi_k + \frac{\Delta\tilde{H}_k^V}{R}\left(\frac{1}{T_k^0} - \frac{1}{T}\right) \tag{48}$$

where and T_k^0 and $\Delta\tilde{H}_k^V$ are the boiling point and vaporization enthalpy of the pure component at the operating pressure Rearrangement of Eq. (48) gives

$$\begin{aligned} L_i &= \sum_k^C x_k T_k^0 \Delta\tilde{S}_k^0/\Delta\tilde{S} - T \\ &= \tilde{G}^E/\Delta\tilde{S} - RT\omega/\Delta\tilde{S} - RT\sum_k^C x_k \ln\Phi_k/\Delta\tilde{S} = W_i \end{aligned} \tag{49}$$

In Eq. (49) C is the number of components, $\Delta\tilde{S}^0$ is the entropy of vaporization ($\Delta S^0 = \Delta\tilde{H}^0/T^0$) and

$$\Delta\tilde{S} = \sum_k^C x_k \Delta\tilde{S}_k^0 \tag{50.a}$$

$$\omega = \sum_i^C x_i \ln\frac{y_i}{x_i} \tag{50.b}$$

The function ω is also known as the weighted volatility function discussed by Malesisnki [18]. Equation (49) defines a relation of point-to-point consistency for each experimental point. In addition, integration of Eq. (49) over the whole compositional range gives

$$L = \int_0^1 L_i dx_i = \int_0^1 W_i dx_i = W \tag{60}$$

which represents an integral consistency test. According to Wisniak the set of data is considered consistent if the parameter D, defined as

$$D = 100 \times \frac{|L - W|}{|L + W|} \tag{61}$$

is less than 3 for the case when experimental data on heats of vaporization are available, or less than 5 if the latter has to be estimated by empirical correlations. The main advantages of the L-W test are that no information about heat and/or volume of mixing for the liquid phase is needed, it is a simultaneous point-to-point and area test, and may used *for systems containing any number of components*. The L-W test has not been deduced from the Gibbs-Duhem relation [Eq. (8)], hence a set of data declared consistent by this test will not necessarily satisfy the Gibbs-Duhem equation. Wisniak's test is suitable for testing the information that is used for calculating of activity coefficients of isobaric systems, particularly, the experimental temperature and the vapor pressure correlations. In order to do so it is essential to have reliable information about enthalpies of vaporization of the pure components. When the components differ widely in boiling temperatures it is recommended to modify Eq. (48) to take into account the variation of enthalpies of vaporization with temperature. Anyhow, the L-W test must always be used with a second test derived from the Gibbs-Duhem equation for a more reliable qualification of data.

Conclusions and Recommendations

Different tests for thermodynamic consistency have been analyzed and found to be insufficient for the purpose. The main conclusion is that there is no one test that can give a definite answer to the question accept/reject the data. In addition, because of their inherent weakness, improper application of the consistency tests available today can yield unreliable results. The most advisable policy is to check the quality of the data using several of the available tests simultaneously and in the proper manner. The group of tests used must include the one of Fredenslund *et al.* [8] accompanied by a detailed residual analysis of bubble-point pressures and vapor liquid compositions.

Experimental systems can be classified in one of the following categories

a. inconsistent data that do not satisfy the consistency criteria.
b. inconsistent data that satisfy the consistency criteria.
c. consistent data that do not satisfy the consistency criteria.
d. consistent data that satisfy the consistency criteria.

Cases a. and d. are self-apparent, they should be rejected or accepted by the majority of well-applied consistency tests. Cases b. and

c. require a more elaborated treatment. Assuming that good estimates for the vapor pressures and an adequate model for the vapor phase are available, the following methodology is suggested:

I. Activity Coefficients Plot

Plots of the variation of the activity coefficients with concentration should be routinely drawn and inspected for unusual behavior. If the data show abnormal tendencies, i.e., the curves do not tend tangentially to $\gamma_i = 1$ with increasing concentration, and/or the activity coefficient curves show unexplained stationary points the data should be revised without performing a consistency test.

II. Area Test

The area test should be considered to fulfilled only when $D < 2$. Isothermal data should be revised when this criteria is not achieved, area tests for isothermal systems are well founded and may give problems only for systems which deviate slightly from the ideality. Area tests should be used for isobaric systems only when the appropriate heat of mixing data are available; the Herington test should not be used for this purpose.

III. Tests Based in VLE Calculations

These group of tests are sensitive to the selected model and to the experimental VLE data errors. A necessary but not sufficient condition of consistency is achieved when the empirical criteria of consistency is met, i.e., the deviation of vapor phase residuals is smaller than 0.01 and the model gives an adequate representation of the data. These necessary conditions establish that the data can be fitted with a G^E function for practical purposes such as process simulation, giving a reliable quantitative description of phase equilibrium. The G^E function selected must fulfill the following requirements:

(1) It must satisfy the Gibbs-Duhem equation, experimental data which do not have this mathematical property cannot be modeled.
(2) It will give a representation of bubble-point pressures within the expected random errors and will predict phase stability of the

system for every composition. Pressure residuals must scatter randomly about the zero line as a symptom of adequate fit.

(3) Activity coefficients should be reasonably represented by the G^E model and other expressions of phase equilibrium, such as dew point and bubble-point temperatures, should also be reproduced well with the parameters of the model. If such model does not exist, the data deserve revision.

This refined consistency procedure, however, does not give all the necessary tools for declaring absolute inconsistency, because there is always the possibility that the data cannot be represented by the model. Attention should be paid to the fact that the Barker equation is not the best selection for the estimation of parameters, because it gives a good fit only of bubble-point pressures only when it is assumed that the measurements of temperature and the liquid phase composition have no errors [37]. In this work we have demonstrated that small and random errors in T and x will produce considerable nonlinear propagation of errors when equilibrium is considered. Data are valuable even when they demonstrate model insufficiency, their analysis requires then a model-free treatment of the Gibbs-Duhem equation. One possible solution for this situation is to use one experimental activity coefficient to obtain the second activity coefficient by a numerical integration of the Gibbs-Duhem equation. If the second activity coefficient thus obtained matches the experimental activity coefficient the data should not then be rejected. Other more appropriated free-model techniques are discussed by Mixon *et al.* [48] and by Sayegh and Vera [49].

Sufficient conditions of consistency are achieved when it is possible to demonstrate that the error present in the experimental data is fundamentally random error, in this case vapor phase residuals would have to scatter about the zero line with no predictable tendency. The proof of this point is cumbersome because residuals are model biased, hence a random scatter is a symptom of the situation in which both the model and the data are correct. A random scatter of vapor phase residuals about a clear tendency does not necessarily means inconsistency, it can well be due a symptom of lack of fit or model wriggle. From this point of view, it is necessary that bubble-point pressure residuals have the characteristic of random scatter distribution with an adequate model before testing vapor phase residuals. When sufficient conditions are met, both the model and the data are recommendable; if not, the maximum likelihood principle [50] is strongly suggested for the parametrization of the data.

Isobaric data in general require information about heats of mixing. The bubble-point pressure test can be considered rigorous when the experimental ratio $\ln[\gamma_1/\gamma_2]$ is adequately fitted; if not, the test has only a qualitative value.

The use of multiple consistency tests is always to be recommended because contradictory consistency results can inform one about an incorrect application of a particular test, but it should be pointed that only the bubble-point pressure test can give a diagnosis of parametrization of the data.

IV. Databases

(a) The consistency results which appear in the DECHEMA Chemistry Data Series (+consistent, -not consistent) should be considered only as recommendations (they are based on the Herington test and the Fredenslund criteria).

(b) The method recommended in the DIPPR database [27] of checking consistency with one G^E model (the four-suffix Margules equation) and fitting the data another G^E model is not recommended.

In summary, in the present state of art of consistency tests only two answers are possible:

Reject the data.
Do not reject the data.

References

[1] Herington, E. F. G. (1947). *Nature*, **160**, 610.
[2] Herington, E. F. G. (1951). *J. Inst. Petrol.*, **37**, 457.
[3] Herington, E. F. G. (1968). *J. Appl. Chem.*, **18**, 285.
[4] Redlich, O. and Kister, A. T. (1948). *Ind. Eng. Chem.*, **40**, 345.
[5] McDermott, C. and Ellis, S. R. M. (1965). *Chem. Eng. Sci.*, **20**, 293.
[6] Van Ness, H. C., Byer, S. M. and Gibbs, R. E. (1973). *AIChE J.*, **19**, 238.
[7] Christiansen, L. J. and Fredenslund, Aa. (1975). *AIChE J.*, **21**, 49.
[8] Fredenslund, Aa., Gmehling, J. and Rasmussen, P. (1977). "*Vapor-Liquid Equilibria Using UNIFAC. A Group Contribution Method*", Elsevier, Amsterdam.
[9] Kojima, K., Moon, H. and Ochi, K. (1990). *Fluid Phase Equilibria*, **56**, 269.
[10] Wisniak, J. (1993). *Ind. Eng. Chem. Res.*, **32**, 1531.
[11] Van Ness, H. C. (1995). *J. Chem. Thermodynamics*, **27**, 113.
[12] Samuels, M. R. (1972). *Ind. Eng. Chem. Fundam*, **11**, 422.
[13] Samuels, M. R., Ulrichson, D. L. and Stevenson, F. D. (1972). *AIChE J.*, **18**, 1004.

[14] Wisniak, J. (1994). *Ind. Eng. Chem. Res.*, **33**, 177.

[15] Prausnitz, J., Lichtenthaler, R. and Gomes de Azevedo, E. (1986). "*Molecular Thermodynamics of Fluid-Phase Equilibria*", *Prentice-Hall*, New Jersey.

[16] Van Ness, H. C. and Abbott, M. M. (1982). "*Classical Thermodynamics of Nonelectrolyte Solutions With Applications to Phase Equilibria*", *McGraw-Hill*, New York.

[17] Kohler, F., Liebermann, E., Miksh, G. and Kainz, C. (1972). *J. Phys. Chem.*, **76**, 2764.

[18] Malesinski, W. (1965). "*Azeotropy and Other Theoretical Problems of Vapour-Liquid Equilibrium*", *Interscience Publishers*, Warsaw.

[19] Michelsen, M. L. and Kistenmacher, H. (1990). *Fluid Phase Equilibria*, **58**, 229.

[20] Panagiotopoulos, A. and Reid, R. C. (1986). *ACS Symp. Ser.*, **300**, 571.

[21] Ortega, J. and Galván, S. (1995). *J. Chem. Eng. Data*, **40**, 699.

[22] Tassios, D. P. (1993). "*Applied Chemical Engineering Thermodynamics*", *Springer Verlag*, Berlin.

[23] Gmehling, J., Christensen, C., Holderbaum, Th., Rasmussen, P. and Weidlich, U. (1984). "*Heats of Mixing Data Collection. DECHEMA Chemistry Data Series*", Vol III, Parts 1 to 4. *DECHEMA*, Frankfurt.

[24] Gmehling, J., Onken, U., Arlt, W., Grenzheuser, P., Kolbe, B., Rarey, J. and Weidlich, U. (1977). "*Vapor-Liquid Equilibrium Data Collection. DECHEMA Chemistry Data Series*", Vol I parts 1 to 18. *DECHEMA*, Frankfurt.

[25] Van Ness, H. C. and Mrazek, R. V. (1959). *AIChE J.*, **5**, 220.

[26] Barker, J. A. (1953). *Austral. J. Chem.*, **6**, 207.

[27] Gess, M., Danner, R. and Nagvekar, M. (1991). "*Thermodynamic Analysis of Vapor-Liquid Equilibria: Recommended Models and a Selected Data Base*", *DIPPR*, AIChE, New York.

[28] Budantseva, L. S., Lesteva, T. M. and Nemtsor, M. S. (1975). *Zh. Fiz. Khim.*, **49**, 260.

[29] Scatchard, G. and Satkiewicz, F. G. (1964). *J. Am. Chem. Soc.*, **86**, 130.

[30] Ronc, M. and Ratcliff, G. R. (1976). *Can J. Chem. Eng.*, **54**, 326.

[31] "*TRC Thermodynamic Tables Hydrocarbons*", *Thermodynamics Research Center, The Texas A and M University System*, College Station, TX, 1994.

[32] Hayden, J. and O'Connell, J. (1975). *Ind. Eng. Chem. Process Des. Dev.*, **14**, 209.

[33] Tsonopoulos, C. (1974). *AIChE J.*, **20**, 263.

[34] Costa-Lòpez, R., Garvín, A. and España, F. (1995). *J. Chem. Eng. Data*, **40**, 1067.

[35] Walas, S. (1985). "*Phase Equilibria in Chemical Engineering*", *Butterworth*, Boston.

[36] Edgar, T. F. and Himmelblau, D. M. (1988). "*Optimization of Chemical Processes*", *McGraw-Hill*, New York.

[37] Prausnitz, J., Anderson, T., Grens, E., Eckert, C., Hsieh, R. and O'Connell, J. (1980). "*Computer Calculations for Multicomponent Vapor Liquid and Liquid-Liquid Equilibria*", *Prentice-Hall*, New Jersey.

[38] Tomiska, J. (1984). *CALPHAD*, **4**, 283.

[39] Hiaki, T., Takahashi, K., Tsuji, T., Hongo, M. and Kojima, K. (1995). *J. Chem. Eng. Data*, **40**, 271.

[40] Spencer, C. F. and Danner, R. P. (1973). *J. Chem. Eng. Data*, **18**, 230.

[41] Wilson, G. M. (1964). *J. Am. Chem. Soc.*, **86**, 127.

[42] Larsen, B., Rasmussen, P. and Fredenslund, Aa. (1987). *Ind. Eng. Chem. Res.*, **26**, 2274.

[43] Gmehling, J., Li, J. and Schiller, M. A. (1993). *Ind. Eng. Chem. Res.*, **32**, 178.

[44] Ninov, J., Stefanova, T. and Petrov, P. (1995). *J. Chem. Eng. Data.*, **40**, 199.

[45] Renon, H. and Prausnitz, J. M. (1968). *AIChE J.*, **14**, 135.

[46] Hiaki, T., Takahashi, K., Tsuji, T., Hongo, M. and Kojima, K. (1995). *J. Chem. Eng. Data*, **40**, 274.

[47] Koerts, J. and Abrahamse, A. P. J. (1971). "*On the Theory and Application of the General Linear Model*", *Rotterdam University Press*, Netherlands.

[48] Mixon, F. O., Gumowski, B. and Carpenter, B. H. (1965). *Ind. Eng. Chem. Fundam.*, **4**, 455.

[49] Sayegh, S. G. and Vera, J. H. (1980). *Chem. Eng. Sci.*, **35**, 2247.

[50] Anderson, T. F., Abrams, D. S. and Grens, E. A. (1978). *AIChE J.*, **24**, 20.

APPENDIX A

Data for a fictitious experimental system
A regular solution model is assumed

$$\frac{\tilde{G}^E}{RT} = A\, x_1 x_2 \tag{A.1}$$

where $A = 1.95$, $P_1^{\text{sat}} = 105.0\,\text{kPa}$, $P_2^{\text{sat}} = 136.5\,\text{kPa}$. The following random perturbations have been considered

σ_x	σ_y	σ_A	$\sigma_P(kPa)$
±0.008	±0.001	±0.010	±0.000

The perturbation in the A term takes into account an imperfect control of temperature and a systematic error of -1.5 kPa in the measure of pressure. *Fictitious* data are given in Table A.1.

$P(kPa)$	x_1	y_1	$P(kPa)$	x_1	y_1
155.28	0.0400	0.1690	195.11	0.5200	0.4382
169.44	0.0800	0.2521	194.98	0.5600	0.4407
179.08	0.1200	0.3230	194.74	0.6000	0.4415
185.50	0.1600	0.3540	194.19	0.6400	0.4360
189.68	0.2000	0.3820	193.32	0.6800	0.4529
192.30	0.2400	0.3992	191.64	0.7200	0.4489
193.82	0.2800	0.4066	188.84	0.7600	0.4712
194.58	0.3200	0.4231	184.41	0.8000	0.4888
194.99	0.3600	0.4297	177.61	0.8400	0.5205
195.15	0.4000	0.4238	167.72	0.8800	0.5573
195.12	0.4400	0.4384	153.19	0.9200	0.6377
195.10	0.4800	0.4283	132.55	0.9600	0.7561

APPENDIX B

Some elements of non-linear least squares procedures used in this work.

The non-linear least square fit problem is given by the iterative solution of the following matrix formula equation

$$\underline{\underline{L}}^{(h)}\Delta\underline{A}^{(h)} = \underline{M}^{(h)} \tag{B.1}$$

In Eq. (B.1) h is an iterative index which indicates that all the matrixes are evaluated with the parameters achieved in an iteration h, $\underline{\underline{L}}$ is a matrix of dimension $N_p \times N_p$, where N_p is the number of parameters of an activity coefficient model. The matrix elements of $\underline{\underline{L}}$ are calculated as follows

$$l_{i,k} = \sum_{j=1}^{N_d} \frac{\partial P_{\mathrm{calc},j}}{\partial A_i} \frac{\partial P_{\mathrm{calc},j}}{\partial A_k} \qquad \begin{array}{l} i = 1,\ N_p \\ k = 1, N_p \end{array} \tag{B.2}$$

where N_d is the number of experimental points, A_i designates the parameters of the model and $\Delta\underline{A}$ is a column vector of dimension $N_P \times 1$ defined, for sequential iterations, as follows.

$$\Delta\underline{A} = \begin{bmatrix} A_1^{(h+1)} - A_1^{(h)} \\ A_2^{(h+1)} - A_2^{(h)} \\ \vdots \\ A_{N_p}^{(h+1)} - A_{N_d}^{(h)} \end{bmatrix} \tag{B.3}$$

$\underline{M}$ is a column vector of dimension $N_p \times 1$ defined as follows

$$\underline{M} = \begin{bmatrix} \displaystyle\sum_{j=1}^{N_p} (P_{\mathrm{expt,j}} - P_{\mathrm{calc},j}) \frac{\partial P_{\mathrm{calc},j}}{\partial A_1} \\ \displaystyle\sum_{j=1}^{N_p} (P_{\mathrm{expt,j}} - P_{\mathrm{calc},j}) \frac{\partial P_{\mathrm{calc},j}}{\partial A_2} \\ \vdots \\ \displaystyle\sum_{j=1}^{N_p} (P_{\mathrm{expt,j}} - P_{\mathrm{calc},j}) \frac{\partial P_{\mathrm{calc},j}}{\partial A_{N_p}} \end{bmatrix} \tag{B.4}$$

Given a G^E, initial estimates of the $\underline{A}$ parameters, and the experimental data, each derivative $\partial P_{\mathrm{calc}}/\partial A$ is taken analytically from Eq. (23). Then the elements of the $\underline{\underline{L}}$ and $\underline{M}$ matrixes can be evaluated from Eqs. (B.2) and (B.4). From Eq. (B.3), new parameter estimates for sequential iterations are generated using

$$\underline{A}^{(h+1)} = \underline{A}^{(h)} + \Delta\underline{A}^{(h)} \tag{B.5}$$

When the iterative procedure converges $\Delta\underline{A}^{(h)}$ will tend to the null vector particularly, the norm of $\Delta\underline{A}^{(h)}$ can be used as a convergence criteria. For the solution each element of the column vector in Eq. (B.4) must be zero for the optimal parameters, in the sense of the objective function in Eq. (25).