

Quality Assessment Algorithm for Vapor–Liquid Equilibrium Data

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A quality assessment algorithm for vapor–liquid equilibrium (VLE) data has been developed. The proposed algorithm combines four widely used tests of VLE consistency based on the requirements of the Gibbs–Duhem equation, with a check of consistency between the VLE binary data and the pure compound vapor pressures. A VLE data-quality criterion is proposed based on the developed algorithm, and it has been implemented in a software application in support of dynamic data evaluation. VLE predictions (NRTL and UNIFAC) were deployed to detect possible anomalies in the data sets. The proposed algorithm can be applied to VLE data sets with at least three state variables reported (pressure, temperature, plus liquid and/or vapor composition) and is applicable to all nonreacting chemical systems at subcritical conditions. Application of the developed algorithms to identification of erroneous published VLE data sets is demonstrated.

Introduction

Vapor–liquid equilibrium (VLE) data are critical for design and operation of separation processes for fluid mixtures. Because of their industrial importance, these data have been intensely measured and reported for more than 100 years by laboratories worldwide. These data require careful reporting and interpretation, due to the complexities of the systems studied (i.e., multiphase, multicomponent systems). In turn, this creates a significant probability for VLE data being reported either erroneously or incompletely, leading to development of low-fidelity models used for chemical process design.

Previously,^{1–3} it was demonstrated that combined expanded uncertainties could be used in the analysis and validation of the thermophysical properties of pure compounds. These uncertainties reflect all sources of the potential errors, including those resulting from impurities in the sample used for the measurements, inherent limitations of the experimental apparatus, as well as propagation of the uncertainties in variables and constraints to those of the measured properties. This approach is certainly applicable to the properties of multicomponent mixtures, including phase equilibrium properties.^{4,5} In addition, data quality analysis and critical data evaluation for vapor–liquid equilibrium must include analysis of their compliance with two principal thermodynamic constraints. One is related to the restrictions following from the Gibbs–Duhem equation, and the other is concerned with the enforcement of the consistencies between the VLE data and pure compound vapor pressures. A number of consistency tests based on the Gibbs–Duhem equation have been developed,^{6–12} providing opportunities for screening VLE data sets on a pass/fail basis. While these tests have proven valuable, their implementation for dynamic data evaluation of VLE has been limited because

there are no existing quantitative criteria providing information on the overall compliance of a particular VLE data set.

This paper summarizes the results of our efforts to establish a data quality criterion for VLE data sets (isobaric and isothermal) that encompasses both compliance with the restrictions of the Gibbs–Duhem equation and enforcement of consistencies between the VLE properties and the pure-compound vapor pressures. The value of such a criterion is demonstrated through a number of cases involving experimental VLE data from the literature. The demonstrated procedures are shown to be valuable in regression analysis of thermodynamic model parameters and detection of anomalies in the published literature.

Quality Assessment Procedure

Consistency Tests for Vapor–Liquid Equilibrium Data. A VLE data set must satisfy the constraint given by the Gibbs–Duhem equation

$$\sum_i x_i d\bar{M}_i - \left(\frac{dM}{dp}\right)_{x,T} dp - \left(\frac{dM}{dT}\right)_{x,p} dT = 0 \quad (1)$$

where M is a molar thermodynamic property; \bar{M}_i is a partial molar property; and T , p , and x are temperature, pressure, and liquid composition, respectively. The summation is over the i components in the chemical system. If the property M is the excess Gibbs energy divided by the product of the gas constant R and T , then

$$M \equiv \frac{G^E}{RT} = \sum_i x_i \ln \gamma_i \quad (2)$$

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$$\sum_i x_i d \ln \gamma_i - \frac{V^E}{RT} dP + \frac{H^E}{RT^2} dT = 0 \quad (3)$$

where γ is an activity coefficient; V^E is the excess volume; and H^E is the excess enthalpy. Equations 1 to 3 are the foundation for the consistency tests described below. The four consistency tests considered in this paper determine the quality of a VLE data set on a pass/fail basis. Although these tests can be useful for rejection of VLE data sets with inconsistencies, it is difficult to decide whether to accept or reject a data set when test results conflict. For such cases, qualitative test results can be very useful for decisions. In this research, we propose quality factors $F_{\text{test},i}$ that can be conveniently evaluated with each test. Each quality factor has values ranging from 0.025 to 0.25, resulting in the sum of the factors having values ranging from 0.1 to 1. The sum of the four quality factors is 1 when all tests are passed.

$$F_{\text{test1,max}} + F_{\text{test2,max}} + F_{\text{test3,max}} + F_{\text{test4,max}} = 1 \quad (4)$$

If one or more consistency tests fail, the sum is less than 1 with a lower limit of 0.1.

Test 1: Herington Test (Area Test). Integration of eq 3 over composition x_1 at constant T or p gives

$$A^* = \int_0^1 \ln \frac{\gamma_1}{\gamma_2} dx + \int_0^1 \varepsilon dx \quad (5)$$

$$\varepsilon = \left(\frac{V^E}{RT} \right) \left(\frac{\partial p}{\partial x_1} \right)_T \quad (T = \text{constant}) \quad (6)$$

$$\varepsilon = - \left(\frac{H^E}{RT^2} \right) \left(\frac{\partial T}{\partial x_1} \right)_p \quad (p = \text{constant}) \quad (7)$$

The integration term containing ε can be neglected for isothermal systems because the absolute value of ε is typically less than $3 \cdot 10^{-5}$, as reported by Kurihara et al.⁹ However, ε for isobaric systems can be large⁹ (as high as $4 \cdot 10^{-2}$) and cannot be neglected. For the evaluation of the integration term containing ε for isobaric systems, variation of the excess enthalpy H^E with temperature and composition is required. Evaluation and integration of H^E causes additional difficulties, due to the degree of availability and reliability of H^E data sets. Herington⁶ provided an empirical estimate of the integration term containing ε for isobaric systems by use of the total boiling range of the mixture. Wisniak¹¹ slightly modified the criteria provided by Herington. Empirical criteria require two values for the test

$$D = 100 \left| \frac{(A - B)}{(A + B)} \right|, \quad J = 150 \left| \frac{\Delta T_{\text{max}}}{T_{\text{min}}} \right| \quad (8)$$

where A is the area above the zero line on the plot of $\ln(\gamma_1/\gamma_2)$ against x_1 , and B is the area below the line. According to Wisniak,¹¹ the test criteria are met for isothermal data sets with $D < 5$, while for isobaric data sets, the condition for passing is $|D - J| < 10$. Kojima and co-workers^{8,9} presented slightly different criteria for the test; for $|A^*| < 0.03$, the test is passed, and otherwise, it is not. These criteria are especially useful when the given mixture is nearly ideal. For such mixtures, values of $|A^*|$ are very small, but D (or $|D - J|$) can remain high. In this

research, we combined the two criteria in our software implementation.

In our approach, if $|A^*| < 0.03$, the test is passed. Otherwise, for an isothermal data set, if $D < 5$, the test is passed, and for an isobaric data set, if $|D - J| < 10$ the test is passed.

For integration of the experimental data, a polynomial equation with order between 2 and 6 is selected automatically based on the correlation coefficient of a fit to the data.

$$y = \sum_{i=1}^{d+1} a_i x^{i-1}, \quad 2 \leq d \leq 6 \quad (9)$$

where d is the order of the polynomial, and a_i are the coefficients of the polynomial.

The Herington test indicates compliance with the Gibbs–Duhem equation over the whole composition range. It has the advantage of simple implementation, and a single plot of $\ln(\gamma_1/\gamma_2)$ against x_1 shows the overall quality of a VLE data set. The quality factor for the Herington test F_{test1} can be calculated by use of the values (D or $|D - J|$) obtained during the test. For isothermal data sets

$$F_{\text{test1}} = 0.25 \frac{5}{D}, \quad 5 \leq D \leq 50 \quad (10)$$

and for isobaric data sets

$$F_{\text{test1}} = 0.25 \frac{10}{|D - J|}, \quad 10 \leq |D - J| \leq 100 \quad (11)$$

Test 2: Van Ness Test. The Van Ness test⁷ is regarded as a modeling capability test.¹² This test shows how a mathematical activity coefficient model can reproduce the experimental data accurately. In the present paper, the five-parameter NRTL model¹³ was used to predict the bubble pressure for a given temperature and liquid composition. The NRTL equation can be represented as follows

$$\ln \gamma_i = \frac{\sum_j \tau_{ji} G_{ji} x_j}{\sum_l G_{li} x_l} + \sum_j \frac{G_{ij} x_j}{\sum_l \tau_{lj} G_{lj} x_l} \left(\tau_{ij} - \frac{\sum_n \tau_{nj} G_{nj} x_n}{\sum_m G_{mj} x_m} \right) \quad (12)$$

$$\tau_{ji} = \exp \left[- \frac{(u_{ji} - u_{ii})}{RT} \right], \quad G_{ji} = \exp[-\alpha_{ji} \tau_{ji}] \quad (13)$$

$$A_{ji} = u_{ji} - u_{ii} \quad (14)$$

For isothermal data sets, binary interaction parameters are considered to be composition-dependent

$$A_{ji} = A_{ji}^A + A_{ji}^B (x_i - x_j) \quad (15)$$

For isobaric data sets, temperature dependence of the parameters is represented as follows

$$A_{ji} = A_{ji}^A + A_{ji}^B / T \quad (16)$$

For a complete T - p - x - y data set, a total of five parameters are determined ($A_{12}^A, A_{12}^B, A_{21}^A, A_{21}^B, \alpha_{12}$). After completion of the fitting process, the following criteria are applied

$$\Delta p = \frac{1}{N} \sum_{i=1}^N \Delta p_i = \frac{1}{N} \sum_{i=1}^N 100 \left| \frac{p_i^{\text{exp}} - p_i^{\text{cal}}}{p_i^{\text{exp}}} \right| \quad (17)$$

$$\Delta y = \frac{1}{N} \sum_{i=1}^N \Delta y_i = \frac{1}{N} \sum_{i=1}^N 100 |y_i^{\text{exp}} - y_i^{\text{cal}}| \quad (18)$$

where N is the number of properties values; the superscript exp indicates experimental data; and the superscript cal indicates values calculated with the NRTL equation. If Δp and Δy are less than 1, the data set passes the test. The quality factor for the Van Ness test is calculated as follows

$$F_{\text{test2}} = 0.25 \frac{2}{\Delta p + \Delta y}, \quad 1 \leq \Delta p \leq 10, \quad 1 \leq \Delta y \leq 10 \quad (19)$$

A more comprehensive modeling test for isobaric data sets can be performed with Barker's method¹⁰ that incorporates experimental excess enthalpy data. Implementation of Barker's method is planned as a future extension of this work.

Test 3: Point Test (Differential Test). The Point test is the test of differential properties of excess Gibbs free energy. The Point test was first introduced by Kojima and co-workers^{8,9}

$$\delta_k^* = \left[\frac{d(G^E/RT)}{dx_1} - \ln\left(\frac{\gamma_1}{\gamma_2}\right) - \varepsilon \right]_k \quad (20)$$

$$\delta = \frac{100 \sum_{k=1}^N \delta_k^*}{N} \quad (21)$$

where δ_k^* represents the deviation for individual experimental points; δ represents an overall deviation in percent; and ε is defined in eqs 6 and 7. As noted earlier for the Herington test, the value of ε cannot be neglected for isobaric data sets. To avoid complexities associated with H^E data sets, the Point test was not applied to isobaric data sets. The values of γ_1 and γ_2 are first calculated from the experimental values of T - p - x - y data. The calculated values of $G^E/RT = x_1 \ln \gamma_1 + x_2 \ln \gamma_2$ are fitted by use of a Padé approximation for the activity coefficient, shown here.

$$\frac{G^E}{RT} = x_1 x_2 \frac{a_0 + \sum_{n=1}^N a_n (x_1 - x_2)^n}{1 + \sum_{m=1}^M b_m (x_1 - x_2)^m} \quad (22)$$

In this research, $M = 1$ and $N = 3$. This expression reduces to the Redlich-Kister expansion when $M = 0$. The quantity δ_k^* (eq 20) is determined with the slope of the fitted Padé approximation and calculated values of $\ln(\gamma_1/\gamma_2)$. The criteria given by Kojima and co-workers^{8,9} are that if $\delta < 5.0$ the VLE data set passes the test; otherwise, it fails.

The quality factor for the Point test can be calculated with the overall percent deviation of the slope

$$F_{\text{test3}} = 0.25 \frac{5}{\delta}, \quad 5 \leq \delta \leq 50 \quad (23)$$

Test 4: Infinite Dilution Test. The Infinite Dilution test is a test for the limiting behavior of $G^E/(x_1 x_2 RT)$ and the activity coefficients γ_1 and γ_2 . The percent deviations in both limits are calculated

$$I_1 = 100 \left| \frac{G^E/(x_1 x_2 RT) - \ln(\gamma_1/\gamma_2)}{\ln(\gamma_1/\gamma_2)} \right|_{x_1=0} \quad (24)$$

$$I_2 = 100 \left| \frac{G^E/(x_1 x_2 RT) - \ln(\gamma_1/\gamma_2)}{\ln(\gamma_1/\gamma_2)} \right|_{x_2=0} \quad (25)$$

The criteria proposed by Kojima and co-workers^{8,9} are used in the present study. If $I_1 < 30$ and $I_2 < 30$, the VLE data set passes the test; otherwise, it fails. For the regression of $G^E/(x_1 x_2 RT)$ and the activity coefficients γ_1 and γ_2 , the Padé approximation (eq 22) is used. The quality factors for the Infinite Dilution test are calculated by use of the relative differences in activity coefficients (eqs 24 and 25) at infinite dilution

$$F_{\text{test4}} = 0.25 \frac{60}{I_1 + I_2}, \quad 30 \leq I_1, I_2 \leq 300 \quad (26)$$

The four consistency tests implemented in the algorithm are based on an assumed excess Gibbs free energy expression. For some systems with complex intermolecular interactions, the assumed Gibbs energy expressions are inadequate for representation of the data, e.g., a highly polar plus nonpolar system, such as (methanol + hexane). In this sense, the proposed algorithm has limitations but remains valuable for identification of data sets with serious errors.

Pure Component Consistency Test. In addition to the requirements related to the Gibbs-Duhem equation described, consistency between the "end-points" of the VLE curve (i.e., mole fraction composition approaching 0 or 1) and the pure component vapor pressures must be enforced.

$$p_{\text{bubble}}(x_1 \rightarrow 1) = p_1^0 \text{ and } p_{\text{bubble}}(x_1 \rightarrow 0) = p_2^0 \quad (27)$$

$$p_{\text{dew}}(y_1 \rightarrow 1) = p_1^0 \text{ and } p_{\text{dew}}(y_1 \rightarrow 0) = p_2^0 \quad (28)$$

where p_{bubble} and p_{dew} are bubble and dew point pressures of the mixture, and p_1^0 and p_2^0 are the pure component vapor pressures, which can be evaluated independently with NIST ThermoData Engine¹⁴ implementing the concept of dynamic data evaluation.^{2,14-17}

$$\Delta p_1^0 = \left| \frac{p_{\text{bubble}}(x_1 \rightarrow 1) - p_1^0}{p_1^0} \right|, \quad \Delta p_2^0 = \left| \frac{p_{\text{bubble}}(x_1 \rightarrow 0) - p_2^0}{p_2^0} \right| \quad (29)$$

Table 1. Comparison of Quality Assessment Results for Five Data Sets Selected from the Literature for Ethanol (1) + Water (2)

set number	ref	data type	N^a	test ^{b,c}				$100\Delta p_1^{0,d}$	$100\Delta p_2^{0,d}$	Q_{VLE}
				1	2	3	4			
1	22	isothermal	19	—	—	—	—	2.20	0.57	0.23
2	23	isobaric	22	+	—	—	—	5.69 ^e	5.69 ^e	0.09
3	24	isothermal	28	—	+	—	—	1.26	1.27	0.36
4	25	isothermal	12	—	—	—	+	0.04	0.06	0.58
5	26	isothermal	9	+	+	+	+	1.22 ^e	0.10 ^e	0.90

^a N is the number of experimental data points in the VLE data set.

^b Test 1 is the Herington test; test 2 is the Van Ness test; test 3 is the Point test; test 4 is the Infinite Dilution test. ^c ‘+’ indicates test passage; ‘—’ indicates test failure. ^d Δp_1^0 and Δp_2^0 are defined in eqs 29 and 30.

^e Vapor pressures of the pure components were not reported, and values were obtained by extrapolation with the NRTL equation.

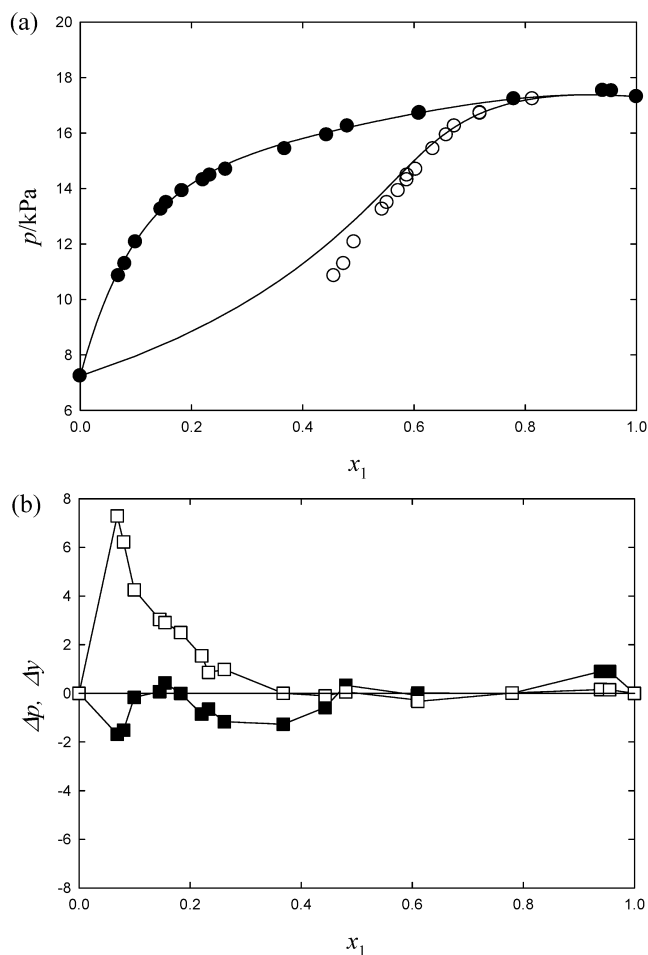


Figure 1. Van Ness test result for the isothermal ethanol (1) + water (2) system at 312.91 K, data from Vrevskii et al.²² (a) Comparison of calculated values with the five-parameter NRTL equation (line) with experimental values: ●, liquid composition; ○, vapor composition. (b) Deviations in pressures and vapor compositions: ■, Δp_i defined in eq 17 (average $\Delta p = 0.56$); □, Δy_i defined in eq 18 (average $\Delta y = 1.62$).

$$\Delta p_1^0 = \left| \frac{p_{\text{dew}}(y_1 \rightarrow 1) - p_1^0}{p_1^0} \right|, \Delta p_2^0 = \left| \frac{p_{\text{dew}}(y_1 \rightarrow 0) - p_2^0}{p_2^0} \right| \quad (30)$$

If the data set type is T - p - x - y , eqs 29 and 30 are equivalent. For T - p - x data, eq 29 is used, and for T - p - y data, eq 30 is used. If no experimental values are reported for the pure components, the values of Δp_1^0 and Δp_2^0 can be

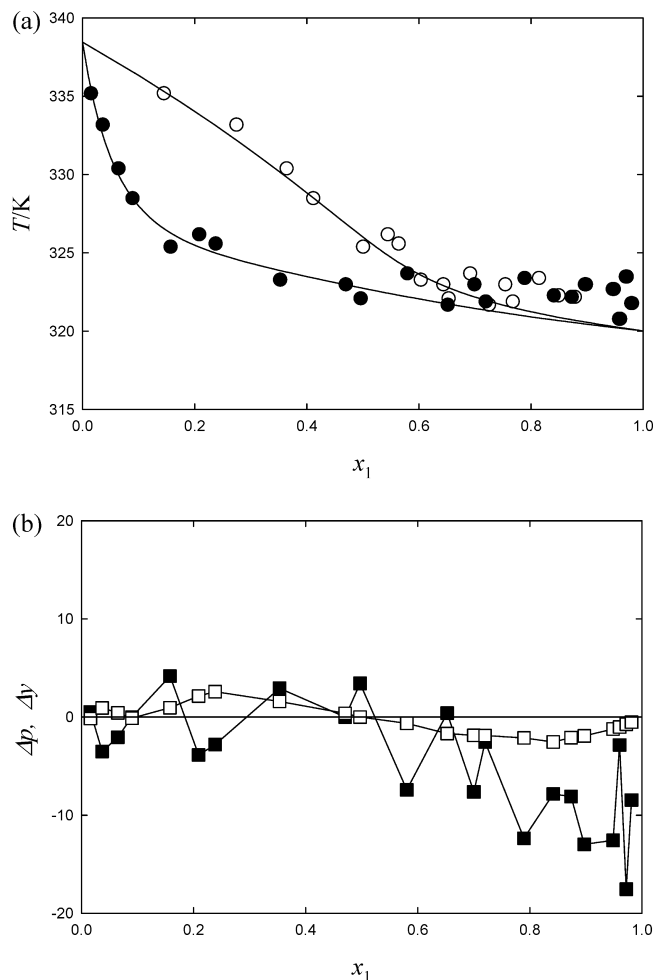


Figure 2. Van Ness test result for the isobaric ethanol (1) + water (2) system at 25.33 kPa, data from Beebe et al.²³ (a) Comparison of values calculated with the five-parameter NRTL equation (line) and experimental values: ●, liquid composition; ○, vapor composition. (b) Deviations in pressures and vapor compositions: ■, Δp_i defined in eq 17 (average $\Delta p = 5.69$); □, Δy_i defined in eq 18 (average $\Delta y = 1.37$).

calculated with extrapolated vapor pressures derived with the three-parameter NRTL model. The vapor pressures and three NRTL parameters (five parameters in total) are fitted to experimental VLE values with the following conditions: (1) the data set is isothermal, (2) the minimum number of experimental values is 8, (3) there is, at least, one experimental value in the composition range $x_1 < 0.2$ to allow estimation of the vapor pressure for component 2, (4) there is a minimum of one value in the composition range from $x_1 > 0.8$ to allow estimation of the vapor pressure for component 1. If the data set is isobaric or any of the four conditions are not met, the values of Δp_1^0 and Δp_2^0 are replaced by the average deviation in bubble or dew pressure calculated with the three-parameter NRTL model fit based on pure component vapor pressures.

Unlike the four consistency tests based on the Gibbs–Duhem equation, this test can be performed for T - p - x or T - p - y data sets. The quality factor associated with the Pure Component Consistency test is defined as

$$F_{\text{pure}} = \frac{2}{100(\Delta p_1^0 + \Delta p_2^0)}, 1 \leq \Delta p_1^0, \Delta p_2^0 \quad (31)$$

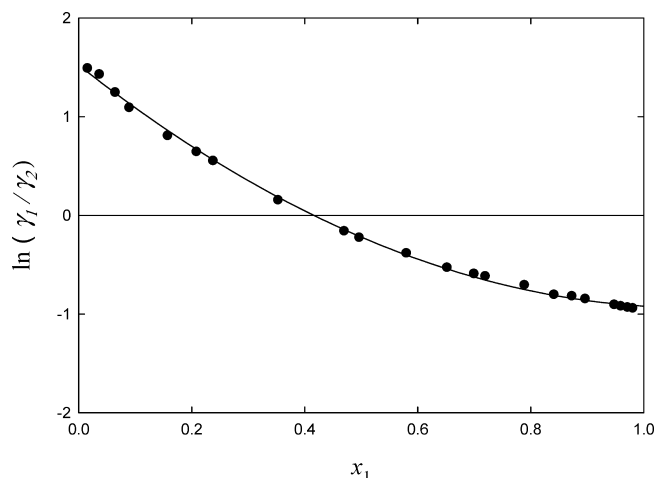


Figure 3. Herington test result for the isobaric ethanol (1) + water (2) system at 25.33 kPa, data from Beebe et al.²³ ●, reduced experimental data. The curve represents a second-order polynomial fit to the experimental data. $D-J$ (defined in eq 8) = 0.65.

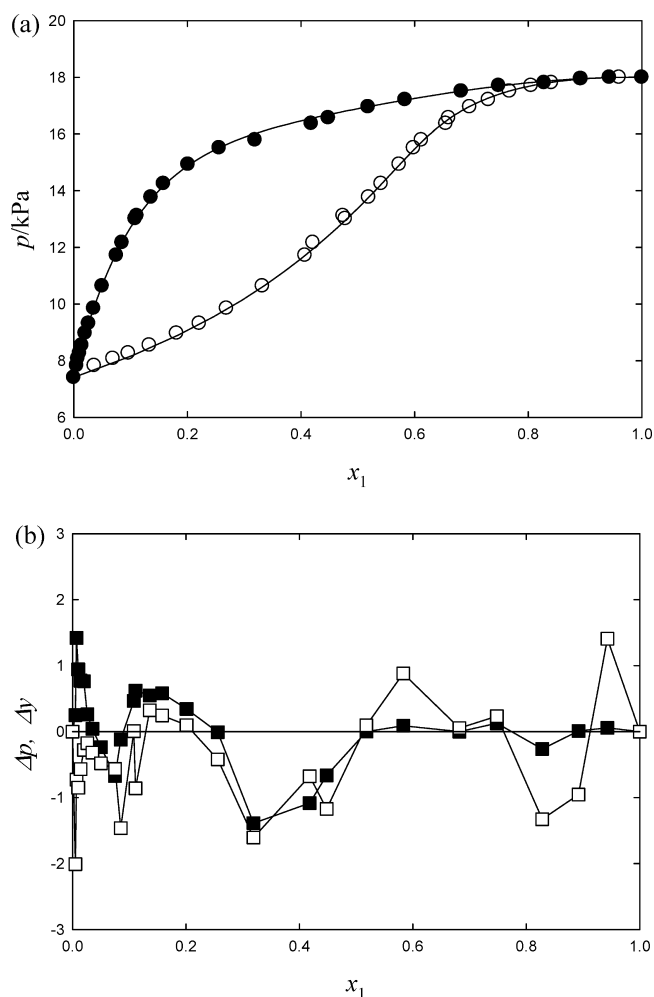


Figure 4. Van Ness test result for the isothermal ethanol (1) + water (2) system at 313 K; data from Vu et al.²⁴ (a) Comparison of calculated values with the five-parameter NRTL equation (line) with experimental values: ●, liquid composition; ○, vapor composition. (b) Deviations in pressure and vapor compositions: ■, Δp_i , defined in eq 17 (average $\Delta p = 0.43$); □, Δy_i , defined in eq 18 (average $\Delta y = 0.67$).

In this study, the values of Δp_1^0 and Δp_2^0 have lower limits of 1. If the vapor pressure agrees within $0.01p^0$ for both components, the factor F_{pure} is 1. If the vapor pressure inconsistency is larger, the factor becomes smaller.

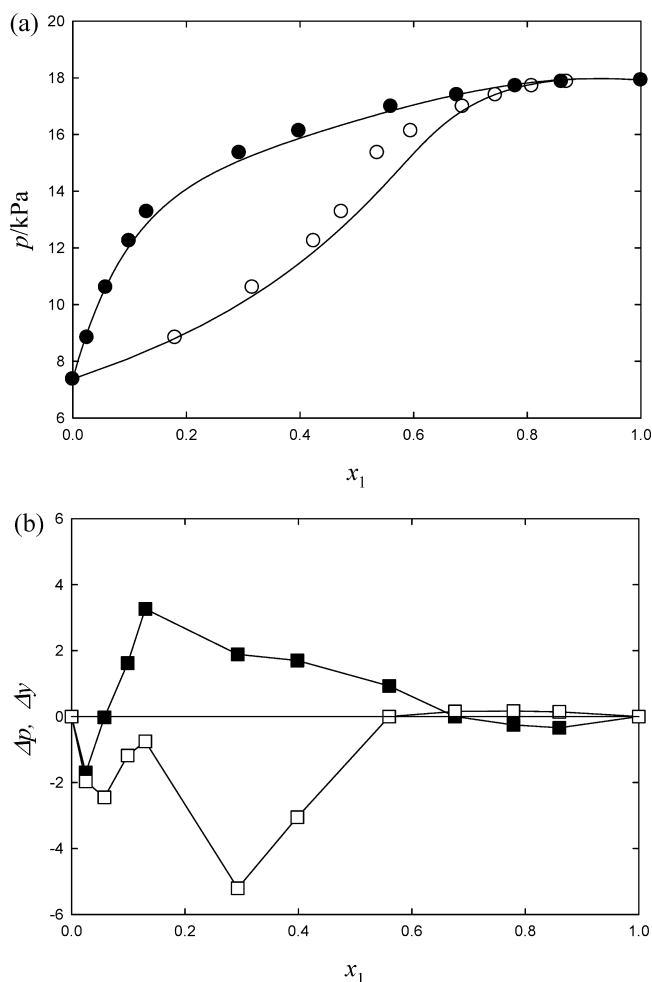


Figure 5. Van Ness test result for the isothermal ethanol (1) + water (2) system at 313.15 K; data from Udovenko et al.²⁵ (a) Comparison of calculated values with the five-parameter NRTL equation (line) with experimental values: ●, liquid composition; ○, vapor composition. (b) Deviations in pressure and vapor compositions: ■, Δp_i , defined in eq 17 (average $\Delta p = 0.98$); □, Δy_i , defined in eq 18 (average $\Delta y = 1.26$).

Overall Quality Factor for a VLE Data Set. Simultaneous use of all five tests provides the opportunity to establish an overall VLE data quality factor, Q_{VLE}

$$Q_{\text{VLE}} = F_{\text{pure}}(F_{\text{test1}} + F_{\text{test2}} + F_{\text{test3}} + F_{\text{test4}}), \quad Q_{\text{VLE}} \leq 1 \quad (32)$$

Q_{VLE} and the F factors were formulated so that if a particular test cannot be performed the F factor for that test is set to $0.5F_{\text{test},\text{max}}$, where $F_{\text{test},\text{max}}$ is the maximum value of F_{test} for test i . $F_{\text{test},\text{max}}$ is 0.25 for tests 1 to 4 and 1.0 for the Pure Component Consistency test. In the hypothetical case where none of the tests can be applied, Q_{VLE} is 0.25.

The overall VLE data quality factor Q_{VLE} can be used in the regression of VLE data together with the evaluated combined uncertainties for the VLE data. The objective function (or adequacy function, A_{VLE}) of minimization can be constructed as follows

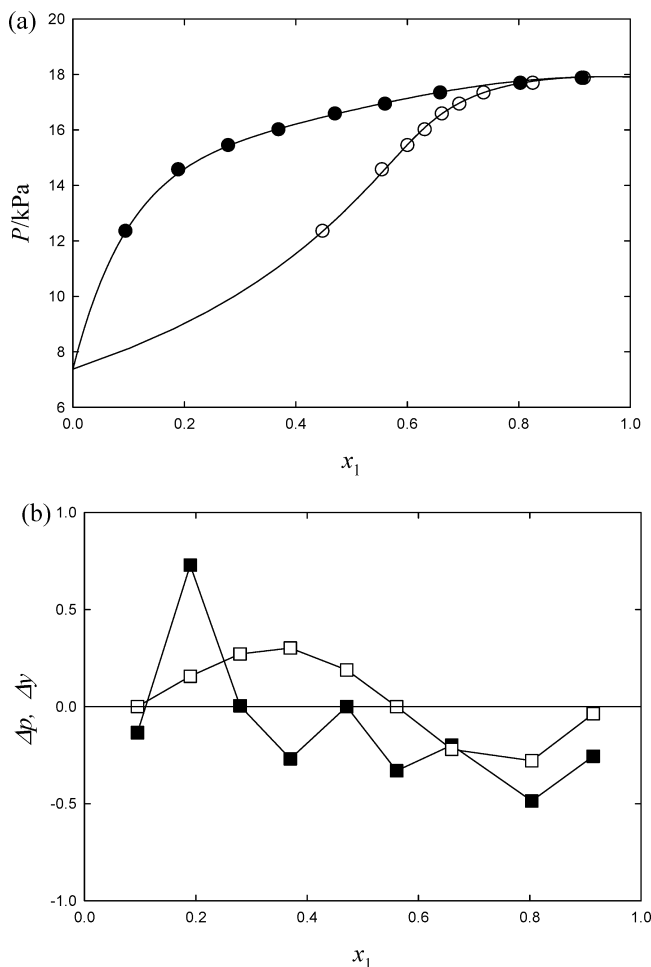


Figure 6. Van Ness test result for the isothermal ethanol (1) + water (2) system at 313.15 K; data from Herraiz et al.²⁶ (a) Comparison of calculated values with the five-parameter NRTL equation (line) with experimental values: ●, liquid composition; ○, vapor composition. (b) Deviations in pressure and vapor compositions: ■, Δp_i , defined in eq 17 (average $\Delta p = 0.27$); □, Δy_i , defined in eq 18 (average $\Delta y = 0.16$).

$$A_{\text{VLE}} = \sum_{\text{set}} Q_{\text{VLE}} \frac{1}{N} \sum_i \left[\frac{(T_i^{\text{cal}} - T_i^{\text{exp}})^2}{(\sigma_i^T)^2} + \frac{(P_i^{\text{cal}} - P_i^{\text{exp}})^2}{(\sigma_i^P)^2} + \frac{(x_i^{\text{cal}} - x_i^{\text{exp}})^2}{(\sigma_i^x)^2} + \frac{(y_i^{\text{cal}} - y_i^{\text{exp}})^2}{(\sigma_i^y)^2} \right] \quad (33)$$

where σ_i^T , σ_i^P , σ_i^x , and σ_i^y are evaluated combined uncertainties in measured variables T , p , x , and y , respectively.

Preparation and Reduction of Data. To perform the described consistency tests, the VLE data sets must satisfy several conditions: (1) pure component properties must be available (critical properties for fugacity calculations and vapor pressures), (2) the data set must be subcritical, (3) the number of experimental values N , excluding the pure-component values, must be large enough to perform an NRTL regression or polynomial fitting (here, $N \geq 5$), (4) the composition span of the data set should be adequately wide (here, at least half of the composition range in mole fraction), and (5) the maximum gap between liquid compositions should be less than 0.8. The consistency tests involve integration or polynomial fitting over the liquid composition range, and a test over a narrow composition range is likely to produce misleading results.

The Pure Component Consistency test requires only three state variables: T – p – x or T – p – y . However, for the four VLE

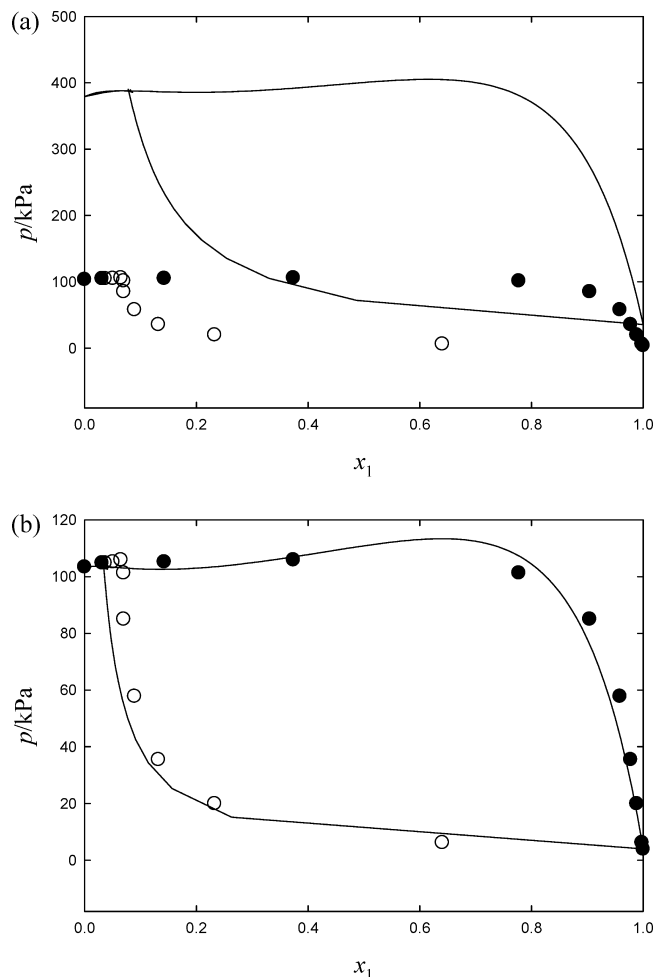


Figure 7. Comparison of UNIFAC predictions and experimental data for the isothermal methanol (1) + butane (2) system, data from Leu et al.²⁷ UNIFAC predictions, line. Experimental values: ●, liquid composition; ○, vapor composition (a) before the correction, $T = 313.15$ K, and (b) after the correction, $T = 273.15$ K.

consistency tests based on the Gibbs–Duhem equation, complete T – p – x – y data are needed for calculation of experimental activity coefficients. The experimental activity coefficients were calculated with the following equation

$$\varphi_i \gamma_i P = x_i \gamma_i^0 P_i^0 \varphi_i^0 \exp \left[\frac{v_i^L (p - p_i^0)}{RT} \right] \quad (34)$$

where φ_i and φ_i^0 are, respectively, the fugacities for component i in the mixture and for the pure component, and v_i^L is the specific volume of the liquid. For the calculation of the vapor phase fugacities, the second virial coefficient correlation of Tsonopoulos^{18,19} was used. The vapor pressure P_i^0 was taken from the same data set, if available, or evaluated with the NIST ThermoData Engine.

Detection of Anomalies in the VLE Data Sets. There are numerous situations that might lead to the appearance of erroneous VLE data sets in the public domain. These include flawed apparatus design, effects of sample impurities, unsatisfactory analytical techniques used to determine equilibrium compositions, unreliable data acquisition systems, errors in data processing and communication during manuscript preparation and publication, erroneous data propagation from the published article to electronic databases and engineering software, etc.

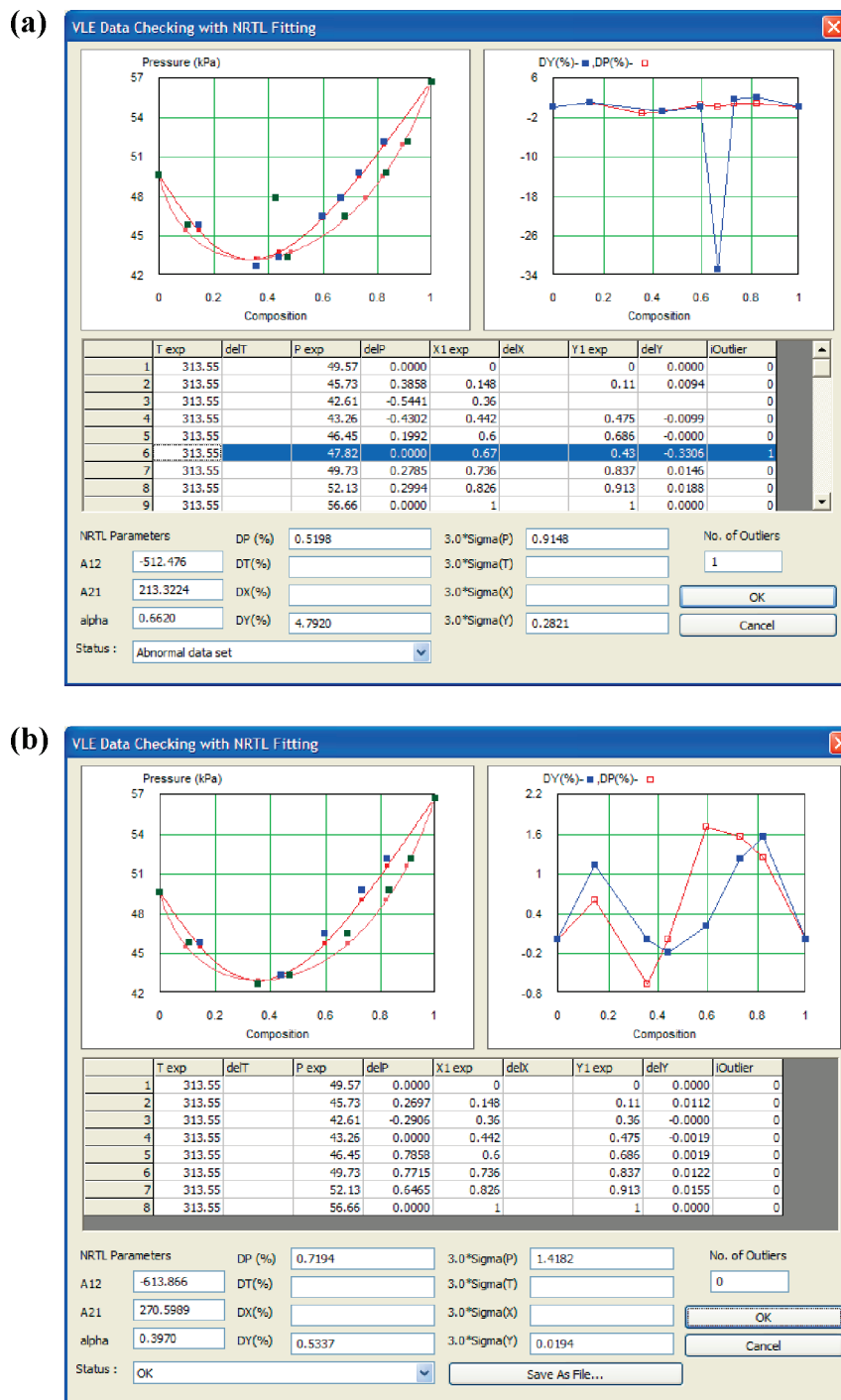


Figure 8. Screen shots from the software developed for detection of anomalies in the reported experimental isothermal T - p - x - y data set for acetone (1) + chloroform (2) at $T = 313.55$ K using NRTL prediction. Data from Beckmann et al.²⁸ (a) before correction and (b) after correction (one erroneous point removed).

Identification of anomalous VLE behavior allows detection of erroneous data and supports the process of its rectification. In this study, approximately 20 000 T - p - x - y , T - p - x , and T - p - y experimental data sets stored in the NIST SOURCE Data Archival System²⁰ (SOURCE) were tested. These data sets are used in the NIST ThermoData Engine.^{2,14-17} The general procedure used was: (1) the quality factor Q_{VLE} is evaluated, as described above; (2) a three-parameter fit of the NRTL equation was performed with the VLE data under test; (3) UNIFAC²¹ estimation is compared with the experimental values if all needed parameters are available; (4) the average percent deviations, average absolute deviations, and the standard deviations

in phase variables (T - p - x - y) are calculated, and (5) large deviations (more than three times the overall standard deviation) are identified.

Criteria for identification of anomalous data sets are: (1) the value of Q_{VLE} is less than or equal to 0.05; (2) the average percent deviation in temperature or pressure is greater than 10; (3) the average absolute deviation in temperature is greater than 5 K; (4) the average absolute deviation in composition is greater than 0.05; and (5) one or more experimental values deviates by more than three times the standard deviation for the variable. Criterion 1 corresponds to data scenarios where the deviations in four consistency tests are more than two times the imposed

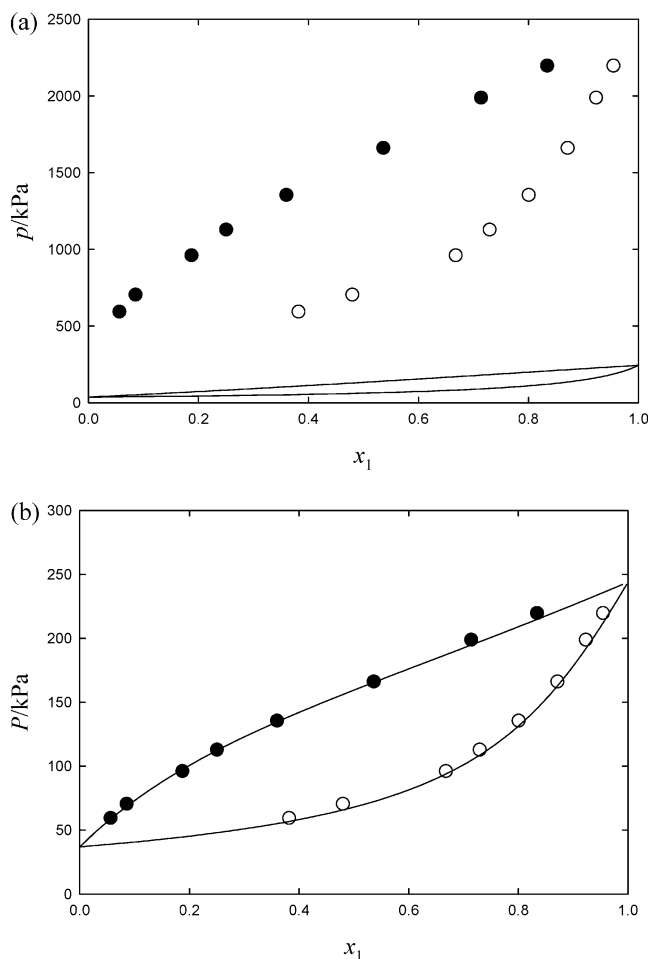


Figure 9. Comparison of NRTL predictions and experimental data for the isothermal chlorodifluoromethane (1) + 1,2-dichlorotetrafluoroethane (2) at $T = 253$ K; data from Kruse et al.²⁹ NRTL predictions, line. Experimental values: ●, liquid composition; ○, vapor (a) before the correction and (b) after the correction (pressure value corrected).

criteria (for example, $D \geq 10$ for test 1, $\Delta p, \Delta y \geq 2$ for test 2, $\delta \geq 10$ for test 3, and $I_1, I_2 \geq 60$ for test 4 or when none of the tests can be applied ($F_{\text{test1}} + F_{\text{test2}} + F_{\text{test3}} + F_{\text{test4}} = 0.5$)) and vapor pressures p differ with pure component data for both components by more than $0.1p$ ($F_{\text{pure}} = 0.1$). Noncompliance with any of the six criteria identifies the data set as anomalous. The described test process was implemented in a computer program for application to a large electronic collection of VLE data sets. Anomalies were flagged by the software for subsequent detailed inspection.

Results and Discussion

Typical Assessment Results. (Ethanol + water) is one of the most frequently measured systems for VLE. SOURCE²⁰ contains 185 VLE data sets for this system published between 1910 and 2010. To show typical evaluation results, five VLE data sets^{22–26} were tested; four isothermal data sets at similar conditions from different sources,^{22,24–26} plus one isobaric data set.²³ The test results, as well as the calculated overall VLE data quality factor Q_{VLE} , are summarized in Table 1 for each data set. None of the five sets were found to be anomalous based on the algorithm.

The selected VLE tests are diverse in nature (isothermal and isobaric) and yield very different outcomes in the consistency tests. Indeed, set 1 passed none of the consistency tests, while

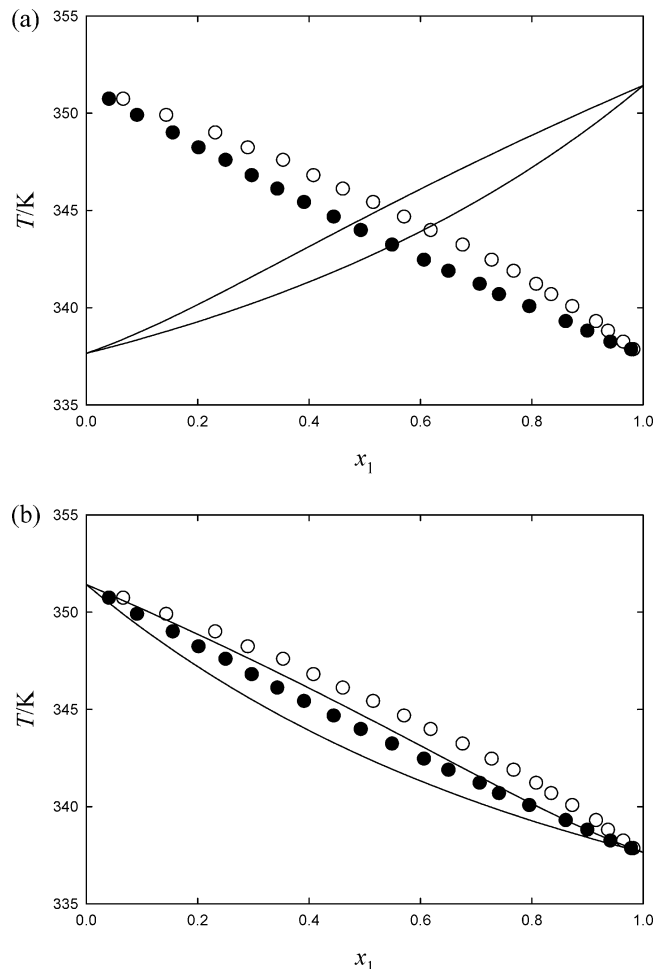


Figure 10. Comparison of UNIFAC predictions and experimental data for the isobaric methanol + ethanol system at $p = 101.32$ kPa, data from Arce et al.³⁰ UNIFAC predictions, line. Experimental values: ●, liquid composition; ○, vapor (a) before the correction, ethanol (1) + methanol (2), and (b) after the correction, methanol (1) + ethanol (2).

sets 2, 3, and 4 passed one and set 5 all tests. While set 1 would be rejected if based on any one of the four tests, its overall performance, as well as its performance on the Pure Component Consistency test, is fair. The calculated value of the overall quality factor is $Q_{\text{VLE}} = 0.23$, where the maximum value is 1. It is likely that the principal reason of this set not passing the consistency tests is poorly measured vapor phase composition (see Figure 1). The fractional deviation in pressure and absolute deviation in composition using the five-parameter NRTL fit were $0.006p$ and 0.016 , respectively.

Even though sets 2, 3, and 4 failed all but one of four consistency tests, the algorithm yielded an overall data quality factor Q_{VLE} that ranged widely from 0.09 for set 2 to 0.58 for set 4. As is evident from Figure 2, the measurement results for set 2 are scattered in T - x space, so that, essentially, any thermodynamic model can successfully fit the data. Nonetheless, this set passed the Herington test (Figure 3). This shows that a judgment of quality based on a single, though well-established, test can be misleading.

Data set 3 has slight deviations in extrapolated vapor pressures ($0.013p$ for each component), and the Van Ness test result shows that a fair correlation can be achieved with the NRTL equation (see Figure 4). However, the other three tests (Herington test, Point test, and Infinite Dilution test) failed, which is indicative of that data set violating the constraints on excess properties

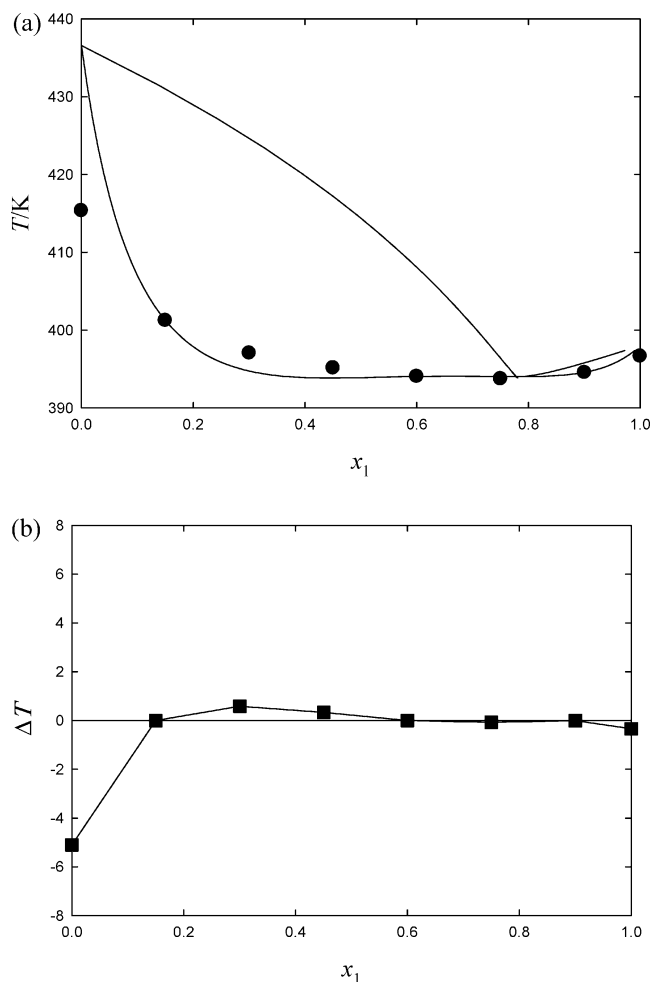


Figure 11. Comparison of NRTL predictions and experimental data for the isobaric 2-methylpyrazine (1) + *N,N*-dimethylacetamide (2) at $p = 94.7$ kPa, data from Prasad et al.³¹ (a) Comparison of calculated values with the NRTL equation (line) with experimental values: ●, liquid composition; ○, vapor composition. (b) Percent deviations in temperatures, average $\Delta T = 7.57$ K.

imposed by the Gibbs–Duhem equation. This behavior cannot be easily detected by a graphical inspection or comparison with a thermodynamic model fit.

For set 4, only the Infinite Dilution test was passed (see Figure 3). The vapor pressure deviations are very small ($0.0004p$ and $0.0006p$), and the value of Q_{VLE} is 0.58. As shown in Figure 5, average absolute errors in vapor composition are quite small (0.012) but still larger than the criterion required to pass the Van Ness test (less than 0.01).

Set 5 passed all consistency tests, and the resulting $Q_{VLE} = 0.9$ is close to the maximum value possible. The errors in vapor composition are very small (0.0016) in this case (see Figure 6). A slight deviation in the vapor pressure lowers the value of Q_{VLE} from the maximum value of 1. For this set, no data were reported at the composition extremes, and extrapolated vapor pressures were used for the vapor pressure difference calculations in eqs 29 and 30.

The quality assessment for the five selected VLE data sets indicates the usefulness of the described data quality assessment algorithm. The normalized values of Q_{VLE} can be used as weighting factors in dynamic evaluation of the phase equilibrium data. Implementation of this approach in the NIST ThermoData Engine software^{15–17} is in progress and will be described in a separate publication. Application of the anomaly detection

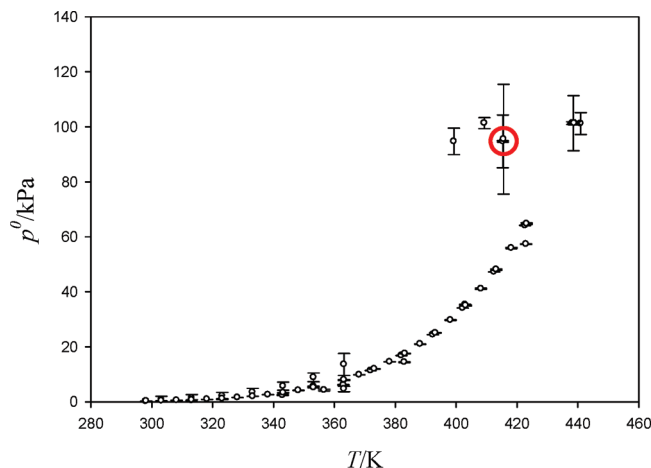


Figure 12. Experimental vapor pressure data reported for *N,N*-dimethylacetamide: ○, experimental data values with uncertainties expressed in error bars. The circled value indicates the vapor pressure reported by Prasad et al.³²

algorithm to the very large collection of VLE data sets stored in SOURCE²⁰ provided an opportunity to demonstrate some typical cases of anomalies in the published literature. Descriptions of these follow.

Problem: Erroneous Information in the Table Heading. This anomalous data set²⁷ contains isothermal T – p – x – y data for (methanol + butane) at $T = 313.15$ K (11 experimental values). As is clear from Figure 7a, comparison with UNIFAC prediction indicates that the original data are reported for an erroneous temperature. The calculated value of $Q_{VLE} = 0.0004$ was exceptionally low. Inspection of the original source revealed that the heading of Table 2²⁷ erroneously stated the temperature to be 40 °C, contrary to the text of the article, which indicated the temperature to be 0 °C. After temperature correction, the calculated Q_{VLE} increased to 0.06, to pass the test, and the UNIFAC prediction was much closer to the measured experimental data (see Figure 7b).

Problem: Typographical Error in a Numerical Value. The identified anomalous data set²⁸ involves isothermal T – p – x – y data for (acetone + chloroform) at $T = 313.55$ K. While $Q_{VLE} = 0.16$, this set is flagged as anomalous because one value ($y_1 = 0.43$) deviates from the prediction ($y_1 = 0.76$) by more than three times the standard deviation ($3\sigma = 0.282$). This erroneous value was reported in the original publication.²⁸ After removal of the erroneous value, the set is no longer identified as anomalous (see Figure 8b), and the value of Q_{VLE} increases to 0.26.

Problem: Erroneous Unit Conversion. This isothermal T – p – x – y data set²⁹ is for (chlorodifluoromethane + 1,2-dichlorotetrafluoroethane) at $T = 253$ K. As shown in Figure 9a, the p – x line deviates widely from the UNIFAC prediction. The calculated Q_{VLE} was 0.001, indicative of an anomalous result, and the average deviation in pressure is $0.904p$. Comparison with the pure component vapor pressures revealed that the pressures were too large by a factor of 10. After correction (see Figure 9b), $Q_{VLE} = 0.2160$ with no indication of anomalous results.

Problem: Reversed Identification of Mixture Components. This anomalous T – p – x – y isobaric data set³⁰ is for (methanol + ethanol) at $p = 101.32$ kPa. The comparison of the originally reported data with the UNIFAC prediction (Figure 10a) indicates that the components of the mixture were misidentified, resulting in $Q_{VLE} = 0.0086$ (all tests failed). After the identities of the components were reversed, UNIFAC prediction became much

closer to the experimental data, as shown in Figure 10b. The recalculated value of Q_{VLE} increased to 0.44.

Problem: Vapor Pressure Discrepancies. This isobaric T - p - x data set³¹ is for (2-methylpyrazine + *N,N*-dimethylacetamide) at $p = 94.7$ kPa. In this example, the deviation in the boiling temperature for *N,N*-dimethylacetamide was more than 20 K, which is very large at this moderate pressure (94.7 kPa). The calculated Q_{VLE} was 0.06, which means that this data set is not detected as anomalous using the first criterion only. However, the average deviation in temperature using the NRTL fit was greater than 5 K, which is a violation of criterion 3 of the algorithm. Therefore this set was flagged as anomalous (see Figure 11a,b). As shown in Figure 12, the measured vapor pressure for *N,N*-dimethylacetamide scattered near $p \sim 100$ kPa. The circled value indicates the boiling temperature reported with the anomalous VLE data set.³¹

Conclusions

1. A VLE data quality factor, Q_{VLE} , was developed. Test results showed its usefulness in determining the relative reliability of reported VLE data sets. This development allows deployment of weighting-based procedures in on-demand critical evaluation of VLE data. Similar procedures could be used for generating UNIFAC-based group parameters.

2. An algorithm for identification of anomalous VLE data sets was established and implemented. Application of this algorithm to an extensive collection of VLE data sets led to elucidation of common causes of erroneously reported VLE data. It is currently planned to use this algorithm as a foundation for further enhancement of the global data validation process for thermophysical and thermochemical property data³² involving major journals in the field.³³

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