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Thermodynamic consistency testing of PTx-data via the Gibbs-Helmholtz equation 2.: Methodology and limitations

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ABSTRACT

Measurement of mixture vapor-pressure data, Px or Tx (PTx) data, is a fast, efficient, and often more accurate method to determine low-pressure binary vapor–liquid equilibrium (VLE) data compared with measurement of PTxy data in re-circulating equilibrium stills. PTx data are the minimum necessary to specify VLE according to the phase rule so that Gibbs–Duhem slope and area thermodynamic consistency tests are not possible. However, G^E/RT data derived from PTx data measured at several temperatures can be compared to measured H^E data with the Gibbs–Helmholtz (GH) equation, $G^E/RT = H^E/RT - S^E/R$. This comparison can be used as a thermodynamic consistency test for PTx data. Previous work (Fluid Phase Equilibria, 14 (1983) 383–392) showed that random errors in pressure measurement large enough to give GH inconsistency usually are not large enough to cause unacceptable errors in the vapor compositions calculated by Barker's method. This present work demonstrates that using a Redlich–Kister G^E expansion at each temperature rather than using a Local Composition G^E model, e.g., NRTL, fitted to all of the Px data over the entire temperature range is an effective methodology for GH testing; this methodology is demonstrated by analysis of high-precision ethanol + water Px data. In addition, the special GH testing problems presented by nearly-ideal systems are illustrated by analysis of recent high-precision ethanol + n-propanol Px data. Other limitations of and recommendations for Gibbs–Helmholtz testing of VLE data are discussed.

1. Introduction

The objective of thermodynamic consistency testing is to show the likely absence of systematic errors. The practical uses are: 1) to referee between different data sets on the same system; 2) to justify confidence in the chemical process equipment designed from the data; and 3) to ensure data of the highest quality for experimental reference standards, for development of process engineering estimation methods and correlations, and for testing and extension of theory.

The consistency testing described here is limited to low pressure – 2nd virial equation region – vapor-liquid equilibrium (VLE) data, the "gamma-phi" region (see Refs. [1,2] for recent discussions of consistency testing of high-pressure VLE data). Here the 2nd virial equation region is identified with the vapor-phase densities $<\frac{1}{2}\rho_c$ as discussed by Prausnitz et al. [3,4] who also suggest the rough rule, $P < (T/2)\{(\Sigma\, y_i P_{ci})/(\Sigma\, y_i T_{ci})\}$ for the low-pressure VLE region [4].

Low-pressure binary PTxy (pressure-temperature-liquid mole fraction-vapor mole fraction) VLE data are redundant according to the phase rule. Hence, differential and integral thermodynamic consistency tests can be constructed from the Gibbs-Duhem equation. To summarize Gibbs–Duhem testing briefly, Equation (1) describes thermodynamic equilibrium between vapor and liquid phases at T and P,

$$\phi_i y_i P = x_i \gamma_i P_i^o \phi_i^o \exp\left[\left(P - P_i^o\right)V_i/(RT)\right] \quad i = 1,2 \tag{1}$$

where ϕ is the vapor-phase fugacity coefficient, γ is the liquid-phase activity coefficient (reference state: pure liquid at system T and P), P_i^0 is the pure-component vapor pressure, and V_i is the pure-component saturated-liquid molar volume.

If PTxy data are measured, experimental liquid-phase activity coefficients can be computed by rearranging Equation (1) to give,

$$\gamma_i = \phi_i y_i P / \left\{x_i P_i^o \phi_i^o \exp\left[\left(P - P_i^o\right)V_i/(RT)\right]\right\} \quad i = 1,2 \tag{2}$$

Because activity coefficients are partial molar quantities, these measured activity coefficients (and therefore the measured PTxy

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data) can be tested for thermodynamic consistency (necessary but not sufficient) using the Gibbs-Duhem equation [5,6] as a differential slope test,

$$x_1\, d\ln\gamma_1/dx_1 = x_2\, d\ln\gamma_2/dx_2 \tag{3}$$

and also as an integrated area test,

$$\int_0^1 \ln(\gamma_1/\gamma_2)dx_1 \tag{4}$$

Equation (4) is given in the constant T, constant P form but laboratory data are measured isobarically or isothermally which requires a correction dependent on either excess volume, V^E, (constant T data) or excess enthalpy, H^E, (constant P) data [6,7].

Gibbs-Duhem equation testing has a long history and extensive literature that has been discussed by Van Ness and others [6–8].

In contrast, Px or Tx (PTx), total vapor-pressure data, are the minimum necessary to specify VLE so that Gibbs–Duhem tests are not possible. However, G^E data derived from PTx data measured at several temperatures can be compared to calorimetric H^E data with the Gibbs–Helmholtz (GH) equation,

$$-RT^2\left[\partial\left(G^E\middle/RT\right)\middle/\partial T\right]_{P,\{x\}} = H^E \tag{5}$$

The Gibbs-Helmholtz equation can also be written in the form,

$$G^E\big/RT = H^E\big/RT - S^E\big/R \tag{6}$$

so that a plot of G^E/RT vs. $1/T$ will yield H^E/R as the slope. This is the form that will be shown in our figures. This comparison, H^E derived from the G^E/RT slope vs. measured H^E, can be used as a thermodynamic consistency test for PTx data measured at different temperatures.

An earlier work [9] showed several examples of data sets which passed or failed the Gibbs–Helmholtz test and analyzed the likely reasons for the results. In addition, the effect of the magnitude of random errors in pressure was demonstrated by analysis of simulated data. It was found (because errors are magnified in taking the derivative of G^E data) that errors small enough to still allow the data to be used to calculate accurately vapor compositions needed for design of chemical process units could still be large enough to cause Gibbs–Helmholtz consistency testing failure. However, this stringent condition is appropriate for databank testing to find recommended reference data of the highest quality. The recommended quality condition [9] was that derived equimolar H^E data within a band of ±30% of measured equimolar H^E reference data be considered thermodynamically consistent.

Published uses of GH consistency testing [10–22] include tests of new PTx VLE datasets as well as literature data tests that identified outliers from consistent data. Recent publications describe the use of the GH test as part of a databank quality assessment procedure [23] and rigorous application of GH testing to systems that have both chemical and phase equilibria, particularly amine + water gas-treating systems and reactor design [24,25].

This paper presents: 1) methodological details on the application of GH testing particularly to high-quality data, 2) discussion of the limitations of GH testing, especially when used to analyze nearly ideal systems (equimolar $G^E \approx <30$ J/mol), and 3) recommendations for effective GH testing.

2. Methodology

The key question in the measurement of low-pressure binary VLE data is: ***should y, the vapor-phase mole fraction, be measured?*** H. C. Van Ness in his Rossini lecture [6] shows that vapor-phase sampling and analysis are usually difficult and uncertain. Uncertainties in the derived VLE data are similar whether or not vapor-phase compositions are measured because the vapor-phase compositions are redundant. Vapor-phase composition data usually add little to a study other than to allow Gibbs–Duhem testing. If inaccurate vapor-compositions are used to calculate VLE, the uncertainty of VLE derived from PTxy data can be larger than VLE derived from PTx data.

Van Ness states isobaric PTxy experiments are a leftover from the earlier “unsophisticated” days of VLE measurement when it was thought that measurements at the isobaric conditions of the actual distillation column were the most efficacious way to obtain VLE data for the design and optimization of chemical processing units. PTxy experiments are also more time-consuming and hence more expensive because of the required sampling and chemical analysis.

The only situations where PTxy experiments are advantageous are: 1) measurement of high-pressure VLE, 2) measurement of dilute solution (Henry's law) experiments [26], or 3) measurements on a specifically defined multicomponent mixture.

A faster, more efficient, and often more accurate method to determine low-pressure binary VLE is to measure the vapor pressure, P, of samples of known composition, x, the liquid-phase mole fraction at several temperatures (PTx). Values of G^E and y, the vapor-phase mole fraction, are then computed by a nonlinear least-squares fit to the experimental mixture vapor pressures coupled with a bubble-point calculation during each iteration (Barker's method [27–29]). A typical ebulliometric PTx experiment (described below) can produce 12–14 VLE data points/day compared to 2–4 VLE data points/day produced by a PTxy equilibrium still experiment; the measurement cost/data point for an ebulliometric PTx experiment can therefore be 1/6 to 1/3 the cost of using a PTxy equilibrium still.

These mixture vapor-pressure data can be measured either in static Px experiments at several temperatures [30–32] or ebulliometric Tx experiments at several pressures [17,33]. In a test, vapor pressures measured on acetone + methyl acetate mixtures by both static Px measurements and dynamic Tx measurements agreed within the combined experimental errors [34,35].

The dynamic Tx experiments have the advantage of not requiring the difficult step of degassing of the mixture as is necessary in isothermal Px experiments. A standardized test method, ASTM E-1719 [36], is available for Tx mixture vapor-pressure measurements (one of the test systems in the ASTM E-1719 round robin was equimolar ethanol + n-propanol). In an ebulliometric experiment, Px data at several temperatures can be derived from the measured Tx data by fitting the vapor-pressure data of each mixture to a vapor-pressure equation and then computing isothermal Px data at several temperatures over the temperature range covered by the isobaric experiments [33,37].

If only PTx data are measured, the only possible thermodynamic consistency test is Gibbs–Helmholtz testing. How should the GH consistency test be carried out? The recommended methodology will be illustrated here by analyzing high-precision reference data for ethanol + water measured in two different laboratories: Pemberton & Mash of NPL [31] and Kolbe & Gmehling of the University of Dortmund [32].

A key decision in GH testing is the choice of G^E model used in the Barker's method analysis. The preferred G^E models for process-design engineering are the Local-Composition models [38], most commonly, the Wilson equation [39], the NRTL equation [40], and