



IMPROVING SOME THERMODYNAMIC CONSISTENCY TESTS FOR VLE DATA EVALUATION

A. Marcilla*, M.M. Olaya and J.A. Reyes-Labarta

Department of Chemical Engineering, University of Alicante, Apdo. 99, Alicante (Spain)

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INTRODUCTION

Accurate VLE data are demanded for separation process design. VLE data are usually measured under isobaric or isothermal conditions and require the equilibrium vapor (y) or liquid (x) compositions as well as the temperature (T) or pressure (P) of the system, respectively. Only when a full set of measurements P-x, y or T-x, y is available it is possible to check whether they satisfy certain thermodynamic relationships (thermodynamic consistency tests or TC tests). In these cases, the VLE experimental data are declared consistent, but not necessarily correct. Conversely, if the experimental VLE data do not obey these conditions then they will be inconsistent. The fundamental Gibbs-Duhem (GD) equation is the most widely referenced condition for consistency of the experimental data. This equation can be handled in a number of ways, leading to a variety of consistency tests: area or integral test [1], point-to-point tests[2], L-W test[3], infinite dilution test[4] and differential test[5]. However, existing TC tests possess many drawbacks, some of which have already been discussed in the literature[6], and others are partially the subject of the present paper.

A recent example of the application of TC tests is the NIST Thermodata Engine (TDE) software package. TDE 6.0 includes the **ALGORITHM proposed by Kang et al. (2010)** [7] to assess the quality of the experimental VLE data for binary and ternary mixtures (two types of checking by means of 5 tests):

1. Compliance of the Gibbs-Duhem equation (4 tests)
2. Consistency between the VLE data and pure compound vapor pressures (1 test).

Overall quality factor

$$Q_{ELV} = (F_{test 1} + F_{test 2} + F_{test 3} + F_{test 4}) \cdot F_{pure}$$

$$Q_{ELV} \leq 1$$

This ALGORITHM to "qualify" the VLE experimental data quality is a VERY VALUABLE INITIATIVE

GOAL

To suggest some ideas to improve some thermodynamic consistency tests that are included in this algorithm

TEST 1 (NIST): AREA TEST [1]

$$\int_0^1 \ln \frac{\gamma_1}{\gamma_2} dx_1 - \int_{T_2}^{T_1} \frac{H^E}{RT^2} dT + \int_{P_2}^{P_1} \frac{v^E}{RT} dP = \int_0^1 \ln \frac{\gamma_1}{\gamma_2} dx_1 + \varepsilon = 0$$

At constant P: The Herington approximation is used and the error produced is attributed to the "poor" quality of the VLE experimental data.

$$\int_0^1 \ln \frac{\gamma_1}{\gamma_2} dx_1 - \int_{T_2}^{T_1} \frac{H^E}{RT^2} dT = J$$

Herington approximation (1951)

$$J = 150 \frac{T_{max} - T_{min}}{T_{min}} \quad |D - J| < 10$$

Wisniak [8] showed that it contained errors due to the very limited experimental information available to Herington at that time. **We present in the following example (Fig. 1) a different approach to invalidate the Herington approximation:** a set of VLE data theoretically calculated using NRTL are obviously stated as "totally (D-J=0) CONSISTENT", but when the Herington approximation is used in the area test, the result is that these same data are now thermodynamically INCONSISTENT!

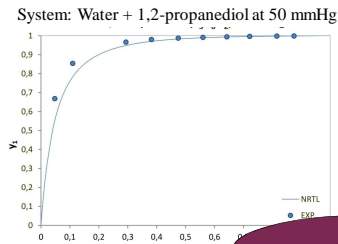


Figure 1.

TEST Result	
VLE cal (NRTL)	Rigorous → CONSISTENT Herington → INCONSISTENT
VLE exp	Herington → INCONSISTENT

THE EXPERIMENTAL DATA COULD BE WRONGLY CALIFIED AS INCONSISTENT DUE TO THE HERINGTON APPROXIMATION

ALTERNATIVE: for isobaric conditions term ε can be evaluated by means of a model for the excess Gibbs energy (G^E), capable to fit the experimental VLE data, using the following relation:

$$\frac{\partial(G^E/RT)}{\partial T} = -\frac{H^E}{RT^2}$$

The obtained results in the VLE data evaluation using tests 1 and 3 will be more realistic that those obtained using the Herington approximation.

IDEA: Because classical models can produce a inadequate fitting for many systems, more flexible models should be used: some improved equations have already been published [9] and new ones should be developed in the near future.

Illustrating the necessity of more flexible models for phase equilibria correlation

NRTL shows GAPS for homogeneous G^E curves. (with $\alpha_{ij}=0.2$)

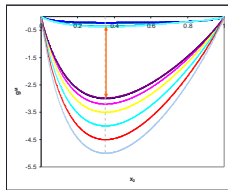


Figure 3.

These GAPS, where solutions for homogeneous binary behaviour are not found, are the reason of the poor correlations of VLE and LLE data for many systems

ALTERNATIVE: Possible modification for NRTL model [9]

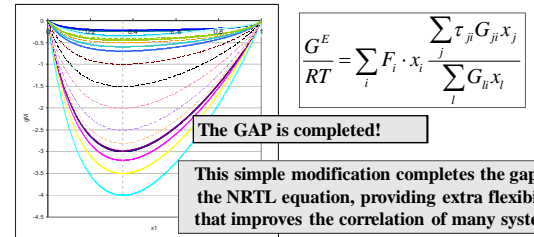


Figure 4.

The GAP is completed!

This simple modification completes the gaps in the NRTL equation, providing extra flexibility that improves the correlation of many systems.

PURE COMPONENT CONSISTENCY TEST (NIST): Consistency between the "end-points" of the VLE curve and the pure component vapor pressures, which are evaluated independently, is checked through deviation parameters that are included in the quality factor associated with the Pure Component Consistency test (F_{pure}).

IDEA: Deviations between vapor pressure measurements for the pure components and "end-points" of the VLE data set only should be used to penalize VLE data sets when total certainty about the precision of the vapor pressure measurements exists. In this respect, we would like to emphasize the importance of the **purity of the substances** used in these measurements. It is accepted that 99% of purity is enough to perform vapour pressures determinations (ASTM E1719-05). Depending on the vapour pressure differences among the impurities and the chemical compound, this purity value may be too low. A one percent content of a strange substance can considerably modify the vapour pressure of the pure compound, and the effect could be very significant even for lower quantities of highly non-ideal impurities. For example, 1% of water in 1-butanol decreases 4 degrees the bubble temperature of 1-butanol at 760 mmHg. This value can be even much higher: 1% of ethanol in toluene reduces the normal boiling temperature 7 degrees. In addition, impurities may be different depending on the source of the chemicals.

CONCLUSIONS

- 1) Consistency tests should be applied with the required degree of rigor to prevent erroneously invalidate correctly obtained VLE data or validate erroneous data.
- 2) Some ideas or alternative calculations are presented in this work to improve the results obtained with different TC tests that are included in the NIST algorithm.
- 3) The analysis of different VLE behaviors reveals that the origin of the problem for different VLE data sets qualified as "inconsistent" is different in each case. Consequently, an algorithm may be conceived that provides information of the specific problem of such data.

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