



THERMODYNAMIC CONSISTENCY TEST FOR THE VAPOUR- LIQUID EQUILIBRIUM (VLE) DATA: A REVIEW

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ARTICLE INFO

Article History:

Received 15th November, 2017

Received in revised form 6th December, 2017

Accepted 19th January, 2018

Published online 28th February, 2018

Key words:

VLE -Vapour-liquid equilibrium, Thermodynamic consistency, Gibbs Duhem equation,

ABSTRACT

Vapour-Liquid equilibrium (VLE) data plays very important role in the field of mass transfer operations like distillation column design. Distillation column is one of important unit operation and equipment used for separation of pure component from the binary mixture or multicomponent mixture. Vapour liquid equilibrium of binary mixture can be used to derive information about molecular interaction between the components of the mixtures. Vapour liquid equilibrium data provide information for calculation of thermodynamic properties and optimization of thermodynamic cycles. The equilibrium vapour composition is related to the liquid composition, this is called vapour-liquid equilibrium. Thermodynamic consistency test for vapour liquid equilibrium data have been developed, providing that at constant temperature and pressure, activity coefficients determined using accurate VLE data must satisfy Gibbs-Duhem (GD) equation. There are few test available to check thermodynamic consistency of VLE data. These are 1) Area test 2) Point to point test 3) Van Ness test 4) An infinite dilution test 5) Differential test etc. In this review paper while comparative study of the various thermodynamic consistency test and it is find that Area test is widely used for the consistency.

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INTRODUCTION

Vapour liquid equilibrium data plays very important role in the field of design of distillation column which is widely used chemical process equipment. Vapour liquid equilibrium of binary mixture can be used to derive information about molecular interaction between the components of the mixtures^[2]. Vapour liquid equilibrium data provide information for calculation of thermodynamic properties and optimization of thermodynamic cycles. Comparative study about the capability of several models to describe the experimental behaviour is present in literature. The importance of vapour liquid equilibrium data is in the process design in order to separate given mixture by distillation. Nevertheless, a unique method for predicting the vapour liquid equilibrium has not yet been established and on the other hand significant number of vapour liquid equilibrium data available in literature.

When two component are mixed together and allow to hold parameter like temperature after certain time the mixture will attain new equilibrium state, it will have different set of liquid and vapour concentration at new total pressure in a closed vessel. The equilibrium vapour composition is related to the liquid composition, this is called vapour-liquid equilibrium. Thermodynamic consistency test for vapour liquid equilibrium data have been developed, proving that at constant temperature and pressure, activity coefficients determined using accurate VLE data must satisfy Gibbs-Duhem (GD) equation^[1].

There are few test available to check thermodynamic consistency of VLE data. These are 1). Area test 2). Point to point test 3). Van Ness test 4). An infinite dilution test 5). Differential test etc.^[3] Using data regression the binary VLE data can be represented by combination of an activity coefficient equation and its binary parameters or infinite dilution activity coefficient. Analytically activity coefficient equations satisfy the Gibbs-Duhem equation; therefore the errors determined by the activity coefficient equations and the VLE data cannot be measured of thermodynamic consistency because the activity coefficient equations shows remarkable experimental error and still satisfy GD equation to avoid this problem thermodynamic consistency use the vapour phase composition data and vapour phase non-ideality. Vapour liquid equilibrium data for high pressure and low pressure is essential for chemical process and unit operation involving higher pressure. For high pressure VLE data is highly dependent on bubble pressure calculation.

Thermodynamic consistency test is used to verify reliability of experimental data which is vital for more accuracy. The study of thermodynamic consistency for binary system at low pressure is based on equal area criterion. Equal area test based on circulation of the Redlich and Kister's methods for isothermal VLE data at low pressure. The most complex problem in chemical engineering is of measurement, modelling and computation of multicomponent phase equilibria. The knowledge of vapour liquid equilibrium behaviour is necessary for synthesis, design and optimization of distillation processes and selection of solvent. Experimental error vary differently in each test so it is advisable not to depend on single consistency

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test alone therefore use of other test also permit validity of the data.

METHODS

Area test

The area or integral test was first proposed by Herington in 1947 and Redlich and Kister 1948. The area or integral test is relatively simple and provide sufficient condition for the evaluation of thermodynamic consistency. This test come positive only when the area above the curve equals the area below the curve. This test is widely used in thermodynamic consistency. Integral or area test has disadvantage that the cancellation of errors may occur due to the point by point test of the data. The integration of the equation is,

$$\sum_i x_i d \ln \gamma_i - \frac{V^E}{RT} dp + \frac{H^E}{RT^2} dT = 0 \quad \dots (1)$$

Over composition x_1 at constant T or P gives

$$A^* = 100 \left(\int_0^1 \ln \frac{\gamma_1}{\gamma_2} dx + \int_0^1 \epsilon dx \right) \quad \dots (2)$$

Where

$$\epsilon = \left(\frac{V^E}{RT} \right) \left(\frac{\partial p}{\partial x_1} \right)_T \quad (T \text{ constant}) \quad \dots (3)$$

And

$$\epsilon = - \left(\frac{H^E}{RT^2} \right) \left(\frac{\partial T}{\partial x_1} \right)_P \quad (P = \text{constant}) \quad \dots (4)$$

According to this method the experimental data is thermodynamically consistent if $\ln \left(\frac{\gamma_1}{\gamma_2} \right)$ v/s x_1 plots the value of (D-J) is less than 10, D and J can be calculated using the equation as follows

$$D = 100 * \left(\frac{s_1 - s_2}{s_1 + s_2} \right) \quad \dots (5)$$

$$J = 150 * \left(\frac{T_{Max} - T_{Min}}{T_{Min}} \right) \quad \dots (6)$$

Where, S_1 is the area under the curve above the x axis
 S_2 is the area below the x axis under curve

Point test

It is also known as differential test. It was first introduced by Kojima and co-workers

$$\delta = \frac{100 \sum_{k=1}^N \delta^{*-1}}{N} \quad \dots (7)$$

Where

$$\delta^* = \left\| \left[\frac{d(G^E/RT)}{dx_1} - \ln \left(\frac{\gamma_1}{\gamma_2} \right) - \epsilon \right]_k \right\| \quad \dots (8)$$

Where δ^* is the deviation for individual experimental point
 δ is an overall deviation in percent

Value of ϵ can-not neglected for isobaric system. The values of γ_1 and γ_2 are calculated from the experimental values of T-p-x-y. The calculated values of $G^E/RT = x_1 \ln \gamma_1 + x_2 \ln \gamma_2$ is fitted by Pade equation. For activity coefficient it is as follows

$$\frac{G^E}{RT} = x_1 x_2 * \left(\frac{a_0 + \sum_{n=1}^N a_n + (x_1 - x_2)n}{1 + \sum_{m=1}^M b_m (x_1 - x_2)m} \right) \quad \dots (9)$$

this research M=1 and N=3. This expression minimises to Redlich-kister expansion when M=0. The criteria given by Kojima and Co-workers is if value of delta is less than 5 ($\delta < 5$) the VLE data is consistence otherwise it fails.

Infinite Dilution Test

This test is for the consistency in limiting behaviour of γ_1 and γ_2 and $\left(\frac{G^E}{x_1 x_2 RT} \right)$.

The percent deviation can be calculated as

$$I_1 = 100 \left(\frac{\left(\frac{G^E}{x_1 x_2 RT} \right) - \ln \left(\frac{\gamma_1}{\gamma_2} \right)}{\ln \left(\frac{\gamma_1}{\gamma_2} \right)} \right) x_1 = 0 \quad \dots (10)$$

$$I_2 = 100 \left(\frac{\left(\frac{G^E}{x_1 x_2 RT} \right) - \ln \left(\frac{\gamma_1}{\gamma_2} \right)}{\ln \left(\frac{\gamma_1}{\gamma_2} \right)} \right) x_2 = 0 \quad \dots (11)$$

When $I_1 < 30$ and $I_2 < 30$ the data set is consistence, otherwise it fails. The quality factor for infinite dilution calculated with I_1 and I_2 is as follows.

$$F_{\text{test}} = \frac{60}{(I_1 + I_2)} \quad \dots (12)$$

With limits $30 < I_1, I_2 < 300$. For the regression of activity coefficient γ_1, γ_2 and $\left(\frac{G^E}{x_1 x_2 RT} \right)$ the Pade approximation is used.

Van Ness Test

This test is known as modelling capability test. The test indicate how a mathematical activity coefficient model can accurately reproduce experimental data. Here NRTL model was used to found bubble pressure for given temperature and liquid composition. The NRTL equation is represent below

$$\ln \gamma_i = \sum_i \frac{\tau_{ji} G_{ji} x_j}{\sum_i G_{ij} x_i} + \sum_j \frac{G_i x_{ij}}{\sum_i \tau_{ij} G_{ij} x_i} \left(\tau_{ij} - \frac{\sum_n \tau_n G_n x_n}{\sum_m G_m x_m} \right) \quad \dots (13)$$

Where

$$\tau_{ji} = \exp \left(- \frac{(G_{ji} - u_{ii})}{RT} \right) \quad \dots (14)$$

And

$$G_{ij} = e^{(-\alpha_{ji} \tau_{ji})}, A_{ji} = u_{ji} - u_{ii} \quad \dots (15)$$

For isothermal data sets binary interaction parameters are taken to be composition dependent:

$$A_{ji} = A_{ji}^A + A_{ji}^B (x_i - x_j) \quad \dots (16)$$

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

$$A_{ji} = A_{ji}^A + \frac{A_{ji}^B}{T} \quad \dots (17)$$

Partial Pressure data

At low pressure, the fugacity of a gas equals the pressure and therefore, Gibbs – Duhem equation in term of fugacity can be written as

$$x_1 \frac{d \ln p_1}{dx_1} - x_1 \frac{d \ln p_2}{dx_1} \quad \dots (18)$$

$$\frac{x_1 dp_1}{p_1 dx_1} = - \frac{x_2 dp_2}{p_2 dx_1} \quad \dots (19)$$

The partial pressure of both component are plotted against mole fraction x_1 . The slope $\left(\frac{dp_1}{dx_1} \right)$ and $\left(\frac{dp_2}{dx_1} \right)$ are determined at any selected composition. Then according to equation (19) the values of these quantities should be the same if data are thermodynamically consistency.

Coexistence equation

It is one of the method for calculating thermodynamic consistency test for binary vapour-liquid equilibrium data. If

vapour is in equilibrium with binary liquid mixture which behaves as an ideal gas then equation $y_i = \gamma_i x_i P_i^s$ can be used to describe the equilibrium. Rearranging the above equation we get

$$\gamma_1 = \frac{y_1 P}{x_1 P_1^s} \quad \gamma_2 = \frac{y_2 P}{x_2 P_2^s}$$

When we substitute the γ_1 and γ_2 in Gibbs Duhem equation we get the following form

$$x_1 d \ln \left(\frac{y_1 P}{x_1 P_1^s} \right) = -(1 - x_1) d \ln \frac{y_2 P}{x_2 P_2^s} \quad \dots (20)$$

P_1^s and P_2^s are constants at constant temperature when above equation is simplified we get equation as follows

$$\frac{dP}{dy_i} = \frac{P(y_1 - x_1)}{y_i(1 - y_1)} \quad \dots (21)$$

Above equation is known as Coexistence equation and can be used to test the consistency of the measured data.

Redlich – Kister Method

The method also known as ‘Zero area method’. This method can be used when activity coefficient values over entire concentration range is available to test consistency of experimental data. It is based on excess free energy of mixing. For binary solution excess free energy of mixing can be written as follows

$$\Delta G^E = RT \sum x_i \ln \gamma_i + x_2 \ln \gamma_2 \quad \dots (22)$$

After Differentiating and substitution of Gibbs – Duhem equation leads to

$$\frac{d(\Delta G^E)}{dx_1} = RT \ln \frac{\gamma_1}{\gamma_2} \quad \dots (23)$$

This can be integral of the limits $x_1 = 0$ and $x_1 = 1$. At this point $\Delta G = 0$ since only pure components involved at two ends and no mixing effect occur, Therefore

$$\int_0^1 \ln \frac{\gamma_1}{\gamma_2} dx_1 = 0 \quad \dots (24)$$

$\ln \left(\frac{\gamma_1}{\gamma_2} \right)$ values are calculated and plotted against x_1 on x-axis. If the data is thermodynamically consistent then net area should equal to zero.

Slope of ln γ curves

Gibbs-Duhem equation in terms of activity coefficient provide simple test for thermodynamic consistency.

$$x_1 \left(\frac{\partial \ln \gamma_1}{\partial x_1} \right)_{T,P} = x_2 \left(\frac{\partial \ln \gamma_2}{\partial x_2} \right)_{T,P} \quad \dots (25)$$

The above equation can be reduced to following form

$$x_1 \left(\frac{\partial \ln \gamma_1}{\partial x_1} \right)_{T,P} = -(1 - x_1) \left(\frac{\partial \ln \gamma_2}{\partial x_1} \right)_{T,P} \quad \dots (26)$$

In equation (26) if Gibbs-Duhem equation is to be satisfied then slope of $\ln \gamma_1$ and $\ln \gamma_2$ both slope must have opposite sign, if not then generated data is inconsistent. In addition to this according to equation number (25) we can make following generalised observation.

1. If one $\ln \gamma$ curve has maximum at certain concentration, the other curve must have a minimum (or maximum) at the same composition.

2. If there is no minimum or maximum point, then both curves must be negative or must be positive over the entire range.

Apparatus

For the generation of vapour liquid equilibrium data hundreds of static, recirculating and other types of equipment have been proposed and published in literature. For low pressure vapour liquid equilibrium measurement the first recirculating still is developed by Jamaguchi [1913] and then by Sameshima [1918]^[4].

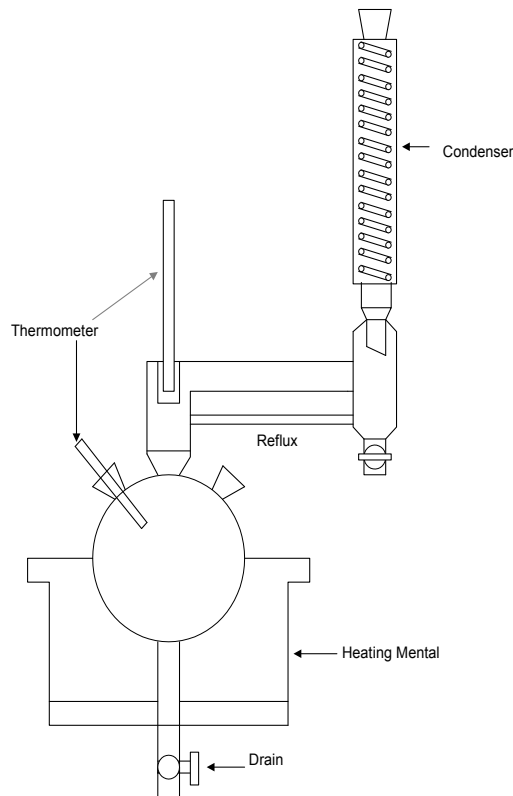


Fig Vapour liquid equilibrium setup

Procedure

1. Prepare mixture of binary component of approximately known composition
2. Take mixture in still and start heater and condenser water supply
3. As temperature increases the vapours formation begins, distillate collect in distillate chamber and excess of distillate is recirculate to still
4. Continue this operation till temperature in thermometer 1 and thermometer 2 will be same. This will require 30 – 45 minutes
5. Stop heating, collect the distillate and residue from the still and analyse them for their composition.
6. Report the equilibrium liquid and vapour composition.

Vapour liquid equilibrium laws^[5]

Vapour liquid equilibrium are understood with the help of simple empirical laws which may applies in certain limits

Raoult's Law

Raoult's law give relation for the partial pressure P_i' of component i over a liquid mixture

$$P_i' = x_i p_i^o \quad \dots (18)$$

According to equation (18) the partial pressure P_i' depends on vapour pressure P_i^o of pure component i and mole fraction x_i ; is not affected by concentration and nature of other substance in mixture. Non-ideal liquid phase behaviour is described with the help of activity coefficient γ_i which is define as follows.

$$p_i' = \gamma_i x_i p_i^o \quad \dots (19)$$

Equation 18 and 19 are valid for mole fractions only. Activity coefficient γ_i also called as Raoult's law correction factor which is highly concentration dependant. Equation 18 and 19 only apply at temperature below the critical temperature.

Dalton's law

It describe vapour phase

$$\frac{p_i''}{p_t} = \frac{n_i''}{n_t} \quad \dots (20)$$

Where n is the number of moles of substance and P is the pressure and subscript i denotes component i. $\frac{n_i''}{n_t} = \gamma_i$. And γ_i is the mole fraction of component i in the vapour. This law applies at low pressure, for higher pressure the equation needs modification and can be written in terms of fugacity

$$f_i'' = \gamma_i f_t'' \quad \dots (21)$$

Vapour liquid equilibrium in ideal systems Binary systems

At constant Pressure

$$P = P_A + P_B = x_A P_A^o(T) + (1 - x_A) P_B^o(T) \quad \dots (22)$$

P_i^o - Vapour pressure of pure component i depends on the temperature. The relation that gives the dependency between the compositions of the vapour and liquid phases is given by following equation

$$y_A = \frac{\alpha x_A(T)}{1 + x_A \alpha(T) - 1} \quad \dots (23)$$

α - Relative volatility and is equal to $\frac{P_A^o(T)}{P_B^o(T)}$

Calculation of phase equilibrium from excess enthalpy

For calculating phase equilibrium in the given system that are non-ideal in liquid phase is only based on the activity coefficient models such as Margules, Van Laar, Wilson, NRTL, UNIQUAC and UNIFAC on the other hand for higher pressure, non-ideality in vapour phase is described by equations of state.

Margules equation

Max Margules introduced this in 1895 which is simple thermodynamic model for calculating excess Gibbs free energy of a liquid mixture. After that Lewis had introduced the concept of activity coefficient, the model is used to derive an expression for the activity coefficients γ_i of compound i in a liquid thus activity coefficient is measure for deviation from ideal solubility. The model has features to describe extrema in the activity coefficient while NRTL, UNIQUAC modern models can-not.

For excess Gibbs free energy of binary mixture Margules express following expression

$$\frac{g^E}{RT} = x_1 x_2 (A_{21} x_1 + A_{12} x_2) \quad \dots (24)$$

Activity coefficient of component i is found by differentiation of the excess Gibbs energy tends to x_1

Van Laar Equation

It is an activity model, developed by Johannes Van Laar in 1910-1913 for describing phase equilibria of liquid mixtures. This equation is derived from Van der Waals equation. The equation as follows

$$\frac{g^E}{RT} = \frac{A_{12} x_1 x_2}{x_1 \left(\frac{A_{12}}{A_{21}} \right) + x_2} \quad \dots (25)$$

A_{12} and A_{21} are constants and obtained by regression of experimental vapour-liquid equilibrium data. The activity coefficient of component i derived from differentiation of x_2

$$\ln \gamma_1 = A_{12} \left(\frac{A_{21} x_2}{A_{12} x_1 + A_{21} x_2} \right)^2$$

$$\ln \gamma_2 = A_{21} \left(\frac{A_{21} x_2}{A_{12} x_1 + A_{21} x_2} \right)^2$$

Wilson Equation

Wilson presented this equation for excess Gibbs energy of a binary solution in 1964

$$\frac{g^E}{RT} = -x_1 \ln(x_1 + A_{12} x_2) - x_2 \ln(x_2 + A_{21} x_1) \quad \dots (26)$$

Activity coefficient derived from this equation are

$$\ln \gamma_1 = -\ln(x_1 + A_{12} x_2) + x_2 \left(\frac{A_{12}}{x_1 + A_{21} x_2} - \frac{A_{21}}{x_2 + A_{21} x_1} \right)$$

$$\ln \gamma_2 = -\ln(x_2 + A_{21} x_1) - x_1 \left(\frac{A_{12}}{x_1 + A_{12} x_2} - \frac{A_{21}}{x_2 + A_{21} x_1} \right)$$

The Wilson equation has A_{12} and A_{21} adjustable parameter and these related to pure component molar volumes and characteristic energy differences by

$$A_{21} = \frac{v_2}{v_1} \exp \left(\frac{-\lambda_{12} - \lambda_{11}}{RT} \right)$$

$$A_{12} = \frac{v_1}{v_2} \exp \left(\frac{-\lambda_{21} - \lambda_{22}}{RT} \right)$$

Wilson equation can be used only for liquid system that are completely miscible

Analysis of vapour liquid equilibrium data⁶¹

Before proceeding to calculation we need to make some assumption. For the binary vapour equilibrium the criteria for phase equilibrium is

$$f_i^L = f_i^V \quad i = 1, 2$$

f_i represents fugacity of component i in the solution and subscript L and V represent vapour and liquid phases. The fugacity are split into several contribution each for the analysis.

$$f_i^{-L} = x_i \gamma_i \phi_i^{sat} p_i^{sat} \exp \left(\int_{P_{isat}}^P \frac{v_{iL}}{RT} dP \right) = y_i \phi_i^v P = f_i^{-v}$$

In above equation the pointing factor $\exp \left(\int_{P_{isat}}^P \frac{v_{iL}}{RT} dP \right)$ is the effect of pressure on fugacity of pure liquid. For low pressure it is close to unity, another good assumption for low pressure is that fugacity coefficient of pure saturated liquid is near unity

and fugacity coefficient of each species in the mixture. Therefore above equation reduced to

$$x_i \gamma_i p_i^{sat} = y_i P$$

In the experiment the pressure is near to 1 standard atm so assumption made above are valid. The last step is to fit the needed parameter in activity coefficient model. Here we need to use more than one simple models, for low pressure recommended to use Van Laar and Margules equations. These models are limited to binary system only, therefore cannot be used in real process simulator.

A solution behaving ideally has following characteristics

1. The components will be chemically similar. The intermolecular forces of attraction and repulsion in of magnitude.
2. There is no volume change in mixing or volume of mixture varies linearly with composition.
3. When solution are mixed neither absorption nor evolution of heat pure and solution (mixture) are approximately same order
4. i.e. there is no temperature change on mixing.
5. Components in ideal solution obeys Raoult's law

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How to cite this article:

Shrikrishna Bobde S B *et al* (2018) 'Thermodynamic Consistency Test For Thevapour- Liquid Equilibrium (Vle) Data: A Review', *International Journal of Current Advanced Research*, 07(2), pp. 9941-9945.
DOI: <http://dx.doi.org/10.24327/ijcar.2018.9945.1660>
