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Thermodynamic consistency test for isobaric experimental data of water content of methane

Javad Kondori[a], Jafar Javanmardi[a,*], Ali Eslamimanesh[b], Amir H. Mohammadi[c,d]

[a] *Department of Chemical Engineering, Shiraz University of Technology, 71555-313 Shiraz, Iran*
[b] *Department of Chemical & Biomolecular Engineering, Clarkson University, Potsdam, NY 13699-5705, USA*
[c] *Institut de Recherche en Génie Chimique et Pétrolier (IRGCP), Paris Cedex, France*
[d] *Thermodynamics Research Unit, School of Chemical Engineering, University of KwaZulu-Natal, Howard College Campus, King George V Avenue, Durban 4041, South Africa*

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ABSTRACT

An important factor to predict the gas hydrate formation conditions is accurate estimation of water content of natural gas. The water content of natural gas (mostly methane as the main component) is very low and consequently its measurement is difficult and time consuming. The experimental data for water content of methane (or other natural gas components) in equilibrium with gas hydrates/ice/liquid water (at low temperatures) are scarce. The measurement difficulties may eventually result in generating unreliable experimental data or at least the data with high uncertainties. As a result, the available data should be checked for consistency prior to further applications. The goal of this work is to present a new consistency test method for investigation of the corresponding phase equilibrium data at constant pressure (isobaric data). The proposed method is based on the Gibbs–Duhem equation and the area test technique. In this method, H^R (residual enthalpy) values are calculated at constant pressure. A thermodynamic model based on the Valderrama modification of the Patel–Teja equation of state along with non-density dependent mixing rules is applied for this purpose. The results show that the proposed consistency test can be applied with acceptable confidence, determining the quality of the investigated experimental data.

1. Introduction

Water is often associated with natural gas in the reservoirs. Thus, produced natural gas is, in most cases, saturated with water [1,2]. As the temperature and pressure change during the production of the gas, water can condense from the flow of the gas. Moreover, natural gas sweetening process (in order to remove hydrogen sulfide and carbon dioxide, the so-called “acid gases”) often employs aqueous solutions [1,2]. The subsequent sweet gas (i.e. the product of the sweetening process) can be saturated with water [2]. This association of water and natural gas means that gas hydrates may be encountered during the production and processing of natural gas. Gas hydrates (or clathrate hydrate) and/or ice formation may bring about pipelines blockage. A gas phase with dissolved water can form gas hydrates/ice at the gas hydrates/ice–gas boundaries without the presence of a free water phase from a thermodynamic standpoint [3]. However, gas hydrate/ice formation process from the dissolved water in the gas phase is a generally time consuming process [3]. In addition, the determination of water content of gas in equilibrium with gas hydrate, ice or liquid water is difficult mainly because of the low concentration of dissolved water in the gaseous phase [3].

Unfortunately, the corresponding experimental data at low temperatures are scarce and quite dispersed [1–3]. Inappropriate calibration of the pressure transducers, temperature probes, or gas chromatograph detectors, errors in design of the apparatuses, or non-suitable experimental techniques may be some reasons of producing experimental phase equilibrium data with high uncertainties.

Therefore, use of predictive methods for representation/prediction of water content of gases in equilibrium with gas hydrates/ice have attracted much attention in petroleum industry [1–3]. To present more accurate thermodynamic models for estimation of the water content of natural gases, reliable experimental data sets are required. In a previous work [3] a thermodynamic consistency test was performed on the isothermal literature data for methane (the main component of natural gases) water content in equilibrium with gas hydrate, ice or liquid water (near gas hydrate or ice formation region) in order to check for their reliability. However, application of the mentioned method

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* Corresponding author. Tel.: +98 711 7354520.
E-mail address: javanmardi@sutech.ac.ir (J. Javanmardi).

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was limited to merely isothermal data. In the present work, a thermodynamic consistency test algorithm is presented to verify the quality of the isobaric experimental datasets of water content of methane.

2. Thermodynamic consistency test

The "Gibbs–Duhem equation" [4–6] is generally applied to analyze thermodynamic consistency of experimental phase equilibrium data. As a matter of fact, if the values of the activity/fugacity coefficients of all of the components in the mixture do not satisfy this relation within an acceptable deviation, the experimental data are suspected to be thermodynamically inconsistent [3,7–11]. This is mainly because of various probable errors during experimental works especially those dealing with high pressure, low temperature, and low concentrations of particular species in the mixtures [3,7–11]. The consistency (or data assessment) tests generally include the following methods: the "Slope Test", the "Integral Test", the "Differential Test" and the "Tangent-Intercept Test" [3,7–11]. Good reviews of these methods can be found elsewhere [12].

2.1. Equations

The general "Gibbs–Duhem" [4–6] equation in terms of residual properties for a homogeneous mixture is written as follows [5]:

$$\sum y_i d\left[\frac{G_i^R}{RT}\right] = \frac{-H^R}{RT^2}dT + \frac{v^R}{RT}dP \tag{1}$$

where G_i^R is the residual Gibbs energy, T represents temperature, R stands for universal gas constant, y_i represents the mole fraction of species i in the mixture, H^R and v^R are the molar residual enthalpy and volume, respectively, P stands for pressure and d is the derivative symbol. Introducing $[G_i^R] = RT\ \ln\varphi_i$ into Eq. (1) gives:

$$\sum y_i d[\ln\varphi_i] = \frac{-H^R}{RT^2}dT + \frac{v^R}{RT}dP \tag{2}$$

where φ stands for the fugacity coefficient.

The Gibbs–Duhem equation [4–6] for a binary mixture at constant pressure can be written as:

$$-\left[\frac{h^R}{T}\right]dT = y_1 d(\ln\varphi_1) + y_2 d(\ln\varphi_2) \tag{3}$$

In Eq. (3), subscripts 1 and 2 refer to components 1 and 2 in the gas phase, respectively and h^R can be determined by the following equation [13]:

$$-h^R = \frac{-H^R}{RT} = T\int_{\infty}^{v}\left(\frac{\partial Z}{\partial T}\right)\frac{dv}{v} + (Z-1) \tag{4}$$

where Z is the compressibility factor of the gas mixture and v is molar volume. Appropriate mathematical re-arrangements of Eq. (3) leads to obtain Eq. (5):

$$\int_{T_f}^{T_l}\frac{1}{Ty_2}dT = \int_{\varphi_{2f}}^{\varphi_{2l}}\frac{1}{(-h^R)\varphi_2}d\varphi_2 + \int_{\varphi_{1f}}^{\varphi_{1l}}\frac{(1-y_2)}{(-h^R)y_2\varphi_1}d\varphi_1 \tag{5}$$

where subscripts f and l refer to first and last points of experimental data, respectively. The properties h^R, φ_1, φ_2, and Z can be calculated using a proper thermodynamic model.

In Eq. (5), the left hand side is designated by A_T and the right hand side by A_φ, as follows [14]:

$$A_T = \int\frac{1}{Ty_2}dT \tag{6}$$

$$A_\varphi = A_{\varphi 1} + A_{\varphi 2} \tag{7}$$

$$A_\varphi = \int\frac{(1-y_2)}{(-h^R)y_2\varphi_1}d\varphi_1 + \int\frac{1}{(-h^R)\varphi_2}d\varphi_2 \tag{8}$$

If a set of data is supposed to be thermodynamically consistent, a percent area deviation (% ΔA_i) between experimental and calculated values must be within the acceptable range [3,7–12,15]:

$$\%\Delta A_i = 100\left[\frac{|A_{\varphi_i} - A_{T_i}|}{A_{T_i}}\right] \tag{9}$$

where subscripts φ and T refer to the areas based on calculated and experimental values, respectively, and i refers to the data set number. For determination of the acceptable percentages of the two evaluated areas deviations from each other, the error propagation method [14] is used considering the pressure and water content as the independent measured variables. The calculated individual area (A_φ) is treated as the dependent variable. The error in the calculated areas, E_A and the percent error $\%E_A$ are calculated as follows [3,7–12,15]:

$$E_A = \left[\frac{\partial A_\varphi}{\partial P}\right]\Delta P + \left[\frac{\partial A_\varphi}{\partial y}\right]\Delta y \tag{10}$$

$$\%E_A = 100\left|\frac{E_A}{A\varphi_j}\right| \tag{11}$$

where subscript j refers to jth calculated area. We assumed maximum uncertainties of 0.1 MPa for the experimental pressure and 10% for experimental water content data. However, these uncertainties depend on the method of experimental measurements. The partial derivatives of the two preceding equations have been evaluated using Central Finite Difference method [16]. It results in the relative average absolute deviations range between 0 to 8%. Therefore, the range [0–8]% is established as the maximum acceptable error for the calculated areas (%ΔA_i).

2.2. Hydrate–gas equilibrium

The water content of methane in equilibrium with its gas hydrate (y_2^H) up to intermediate pressures can be estimated using the following expression [3,17–19]:

$$y_2^H = \frac{P_2^{MT}}{\varphi_2^G P}\times\exp\left[\frac{v_2^{MT}(P-P_2^{MT})}{RT}\right]\times\left[(1+C_{\text{small}}P)^{-v'_{\text{small}}}\times(1+C_{\text{large}}P)^{-v'_{\text{large}}}\right] \tag{12}$$

where P_2^{MT} and v_2^{MT} are the vapor pressure of the empty hydrate lattice and the partial molar volume of water in the empty hydrate, respectively φ_G^2. C denotes the Langmuir constant for methane's interaction with each type cavity, v' stands for the number of cavities per water molecule in a unit hydrate cell, and the subscripts *small* and *large* refer to two types of cavities. The Langmuir constants for methane's interaction with each type of cavity have been determined as a function of temperature, which are expressed from statistical mechanics as well as from data at the three-phase line by Parrish and Prausnitz [20].

For pentagonal dodecahedra (small cavity) [3,17–20]:

$$C_{\text{small}} = \frac{3.7237\times10^{-2}}{T}\exp\left(\frac{2.7088\times10^{3}}{T}\right) \tag{13}$$

For tetrakaidecahedra (large cavity) [3,17–20]:

$$C_{\text{large}} = \frac{1.8373\times10^{-1}}{T}\exp\left(\frac{2.7379\times10^{3}}{T}\right) \tag{14}$$