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Thermodynamic Consistency Test for Experimental Data of Water Content of Methane

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Accurate knowledge of the water content of natural gases is an important factor to estimate the gas hydrate, ice, and condensed water formation conditions. However, the experimental data regarding the water content of gases in equilibrium with the gas hydrate, ice, or liquid water (near gas hydrate or ice formation region) are limited. This is partly because of the fact that concentration of water in the gaseous phase in equilibrium with gas hydrate, ice or liquid water (near gas hydrate or ice formation region) is very low considering that reaching the equilibrium conditions near and inside gas hydrate or ice formation region is time consuming process. The measurement difficulties may consequently result in generating unreliable experimental data. This work aims at performing a thermodynamic consistency test based on area approach to study the reliability of some experimental data reported in the literature on the water content of methane (the main component of natural gases) in equilibrium with the gas hydrate, ice, or liquid water (near gas hydrate or ice formation region). A discussion is made on the studied experimental data according to the performed consistency test. © 2010 American Institute of Chemical Engineers *AIChE J,* 57: 2566–2573, 2011

Keywords: thermodynamic consistency test, area test, water content, natural gas, gas hydrate, ice, liquid water

Introduction

Natural gases may contain some quantities of undesired dissolved water, which may condense during production, transportation, and processing operations altering the physical state from vapor to condensed water, gas hydrates, and/or ice. Condensed phase may lead to corrosion and/or two-phase flow problems. The formation of gas hydrates and/or ice could result in equipment blockage and shutdown. 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. However, gas hydrate/ice formation process from the dissolved water in the gas phase (in the absence of free water) is a very time consuming process.[1,2] Moreover, because of the low concentration of dissolved water in the gaseous phase, the determination of water content of gas in equilibrium with gas hydrate, ice, or liquid water (near gas hydrate or ice formation region) is

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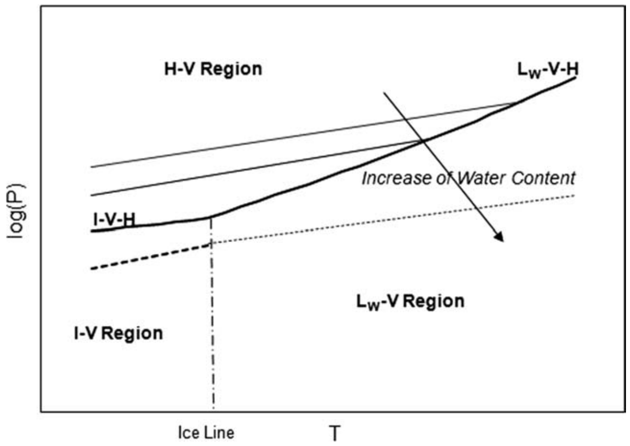

Figure 1. Typical hydrate (*H*)–gas (*G*), ice (*I*)–gas and liquid water (L_W)–gas equilibria regions for water (limiting reactant) + single (pure and supercritical) hydrate former system.[12,15]

Bold solid lines: L_W-*G*-*H* and *I*-*G*-*H* equilibria; Solid lines: water content of gas inside hydrate stability zone; Dashed line: water content of gas outside hydrate or ice stability zone; Bold dashed line: water content of gas inside ice stability zone; Solid-dashed line: Ice line representing L_W-*G*-*I* equilibrium.

difficult.[1–18] Figure 1 shows the typical Pressure-Temperature phase diagram for the methane + water system.[12,15]

Unfortunately, most of the experimental data for water content of natural gas components in equilibrium with gas hydrate, ice, or liquid water (near gas hydrate or ice formation region) were found to be scarce and often rather dispersed.[1,2] Literature survey reveals the availability of few sets of experimental data for water content of gases in equilibrium with gas hydrates/ice.[1] Therefore, few predictive methods for the water content of gases in equilibrium with gas hydrates/ice have been recommended in the literature as these methods are generally based on experimental data.[1–18]

To present accurate thermodynamic models for estimation of the water content of natural gases, reliable experimental data sets are required. This communication aims at testing the thermodynamic consistency of literature data for methane (the main component of natural gases) water content at conditions of equilibrium with gas hydrate, ice, or liquid water (near gas hydrate or ice formation region) to verify their reliability.

Thermodynamic Consistency Test

The thermodynamic relationship, which is frequently used to analyze thermodynamic consistency of experimental phase equilibrium data is the fundamental "Gibbs-Duhem equation."[19–21] This equation, as normally presented in the literature, interrelates the activity/fugacity coefficients of all components in a given mixture. If the equation is not obeyed within the defined criteria then the data are declared to be thermodynamically inconsistent. It means that this relation imposes a constraint on the activity/fugacity coefficients that is not satisfied by the experimental data.[19,20] This is due to various errors occurring during experimental works especially those dealing with high pressure and low temperature conditions.

The ways in which the "Gibbs-Duhem equation"[19–21] is arranged and applied to the experimental data have given origin to several "consistency test methods," most of them designed for low-pressure data. Among these, are the "slope test," the "integral test," the "differential test," and the "tangent-intercept test."[19–24] Good reviews of these methods are given elsewhere.[22,23]

In recent years, Valderrama and coworkers[24–28] have investigated the applications of numerical thermodynamic consistency methods to various systems including incomplete phase equilibrium data of high-pressure gas–liquid mixtures,[24] high pressure ternary mixtures of compressed gas and solid solutes,[25] high pressure gas–solid solubility data of binary mixtures,[26] vapor-liquid equilibrium data for mixtures containing ionic liquids,[27] and high pressure gas–liquid equilibrium data including both liquid and gas phases.[28]

A method especially employed for determining thermodynamic consistency of high pressure gas-solid data by Valderrama and Alvarez,[24] which is based on rewriting the "Gibbs-Duhem equation"[19–21] in terms of fugacity coefficients[29] has been used in our work. The consistency method employed here can be considered as a modeling procedure. This is because a thermodynamic model that can reliably fit the experimental data must be used to apply the consistency test. The fitting of the experimental data requires the calculation of some model parameters using a defined objective function that must be minimized.

As stated by Valderrama and Alvarez,[24] a good consistency test method to analyze high pressure data must fulfill 10 basic requirements: (i) use the "Gibbs-Duhem equation"[19–21]; (ii) use the fundamental equation of phase equilibrium; (iii) use for testing all the experimental *P*-*T*-*y* data available; (iv) does not necessarily require experimental data for the whole concentration range and be applicable for data in any range of concentration; (v) be able to correlate the data within acceptable limits of deviations, deviations that must be evenly distributed; (vi) requires few additional calculated properties; (vii) be able to detect erroneous experimental points; (viii) makes appropriate use of necessary statistical parameters; (ix) be simple to be applied, with respect to the complexity of the problem to be solved; and (x) be able to conclude about consistency with regard as defined criteria.

Equations

The "Gibbs-Duhem"[19–21] equation for a binary homogeneous mixture at constant temperature can be written as:[20,25]

$$\left[\frac{v^{\mathrm{E}}}{RT}\right]dP = y_1 d(\ln\gamma_1) + y_2 d(\ln\gamma_2), \qquad (1)$$

where v^{E} is the excess molar volume, T represents temperature, R stands for universal gas constant, γ is activity coefficient, y represents the solute mole fraction, P stands for pressure, and d is the derivative symbol. In this equation, subscripts 1 and 2 refer to Components 1 and 2 in the gas phase, respectively. Eq. 1 can be written in terms of the fugacity coefficients as follows:[24]

$$\left[\frac{Z-1}{P}\right]dP = y_1 d(\ln\varphi_1) + y_2 d(\ln\varphi_2), \qquad (2)$$

where Z is the compressibility factor of the gas mixture and φ stands for the fugacity coefficient.

This equation can be written in terms of the water content of the gas phase. If the water is considered as Component 2 in the binary mixture of methane + water, the latter equation becomes:

$$\frac{1}{P}\frac{dP}{dy_2} = \frac{y_2}{(Z-1)}\frac{d(\ln\varphi_2)}{dy_2} + \frac{(1-y_2)}{(Z-1)}\frac{d(\ln\varphi_1)}{dy_2}, \quad (3)$$

or in integral form as follows:

$$\int \frac{1}{Py_2}dP = \int \frac{1}{(Z-1)\varphi_2}d\varphi_2 + \int \frac{(1-y_2)}{y_2(Z-1)\varphi_1}d\varphi_1, \quad (4)$$

The properties φ_1, φ_2, and Z can be calculated using an equation of state and suitable mixing rules.

In Eq. 4, the left-hand side is designated by A_{p} and the right-hand side by A_φ, as follows:[24]

$$A_{\mathrm{p}} = \int \frac{1}{Py_2}dP, \quad (5)$$

$$A_\varphi = A_{\varphi 1} + A_{\varphi 2}, \quad (6)$$

$$A_{\varphi 1} = \int \frac{(1-y_2)}{y_2(Z-1)\varphi_1}d\varphi_1, \quad (7)$$

$$A_{\varphi 2} = \int \frac{1}{(Z-1)\varphi_2}d\varphi_2, \quad (8)$$

Thus, if a set of data is considered to be consistent, A_{p} should be equal to A_φ within acceptable defined deviations. To set the margins of errors, an individual percent area deviation ($\%\Delta A_i$) between experimental and calculated values is defined as:[12,15,16]

$$\%\Delta A_i = 100\left[\frac{A_{\varphi_i} - A_{\mathrm{p}_i}}{A_{\mathrm{p}_i}}\right], \quad (9)$$

where i refers to the data set number. The maximum values accepted for these deviations regarding the proposed systems are discussed later.

Hydrate-Gas Equilibrium. The water content of a single hydrate former in equilibrium with its gas hydrate up to intermediate pressures can be estimated using the following expression:[12,15,16]

$$y_2 = \frac{P_2^{MT}}{\varphi_2 P} \times \exp\left[\frac{v_2^{MT}(P - P_2^{MT})}{RT}\right] \times \left[(1 + C_{small}P)^{-v'_{small}} \times (1 + C_{l\arg e}P)^{-v'_{l\arg e}}\right], \quad (10)$$

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. 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.[30]

For pentagonal dodecahedra (Small cavity):[12,15,16,30]

$$C_{\mathrm{small}} = \frac{3.7237 \times 10^{-2}}{T}\exp\left(\frac{2.7088 \times 10^3}{T}\right). \quad (11)$$

For tetrakaidecahedra (Large cavity):[12,15,16,30]

$$C_{\mathrm{large}} = \frac{1.8373 \times 10^{-1}}{T}\exp\left(\frac{2.7379 \times 10^3}{T}\right), \quad (12)$$

where T is in K and C has unit of reciprocal MPa. Dharmawardhana et al.[31] obtained the following equation for the vapor pressure of the empty hydrate structure I:[1,12,15,16]

$$P_2^{\mathrm{MT}} = 0.1 \times \exp\left(17.440 - \frac{6003.9}{T}\right), \quad (13)$$

where P_2^{MT} is in MPa and T in K. In the above equation, the following values can be used:[12,15,16]

$v_2^{\mathrm{MT}} = 0.022655$ m^3/kgmol (von Stackelberg and Müller[32])
$v'_{\mathrm{small}} = \frac{1}{23}$ (Sloan and Koh[1])
$v'_{\mathrm{large}} = \frac{3}{23}$ (Sloan and Koh[1])

Liquid Water/Ice-Gas Equilibrium. The water content of a gas in equilibrium with liquid water up to intermediate pressures can be estimated using the following expression:[12,15,16]

$$y_2 = \frac{P_2^{\mathrm{sat}}}{\varphi_2 P}\exp\left(\frac{v_2^L(P - P_2^{\mathrm{sat}})}{RT}\right) \quad (14)$$

where P_2^{sat} and $v_{\mathrm{L}}^{\mathrm{L}}$ are saturation pressure of water and molar volume of liquid water, respectively. As can be seen, water content is determined primarily by the fugacity coefficient of water in the gas phase, temperature and pressure. In other word, the nonideality of the gas phase is the critical factor determining water content in the intermediate pressure range.[4,12,15,16]

To estimate vapor pressure and molar volume of water in Eq. 14, the relations reported by Daubert and Danner[33] and McCain[34] can be used, respectively:[12,15,16]

$$P_2^{\mathrm{sat}} = 10^{-6}\exp(73.649 - 7258.2/T - 7.3037\ln(T) + 4.1653 \times 10^{-6}T^2), \quad (15)$$

$$v_2^L = 18.015 \times (1 - 1.0001 \times 10^{-2} + 1.33391 \times 10^{-4} \times [1.8(T - 273.15) + 32] + 5.50654 \times 10^{-7} \times [1.8(T - 273.15) + 32]^2) \times 10^{-3}, \quad (16)$$

where, T, P_2^{sat}, v_2^{L} are, respectively, in K, MPa and m^3/kgmol. Equations. 15 and 16 are valid at $T < 400\ K$, and $P < 34.5$ MPa even over a wide range of salt concentration in aqueous solution.[3,10,12,15,16]

Ice-gas equilibrium normally reaches at low-intermediate pressures and therefore Eq. 14 can be used for estimating water content of gases in equilibrium with ice.[12,15,16] For this purpose, the following relations for molar volume of ice and ice vapor pressure can be used:[3,10,15,16,35]

$$v_2^I = (19.655 + 0.0022364 \times (T - 273.15)) \times 10^{-3}, \quad (17)$$

$$P_I^{\mathrm{sat}} = \frac{\left[10^{(-1032.558/T + 51.056 \times log(T) - 0.0977 \times T + 7.0357 \times 10^{-5} \times T^2 - 98.512)}\right]}{7600}, \tag{18}$$

where v_2^I and P_I^{sat} stand for molar volume and saturation pressure of ice, respectively. In the above equations, T, v_2^I, and P_2^I are in K, m^3/kgmol, and MPa, respectively.

Equation 14 can be applied directly to estimate the water content of gas in equilibrium with liquid water or ice using an appropriate expression for the fugacity coefficient of water in the gas phase.[12,15,16] The ice-gas equilibrium normally reaches at relatively low-pressures, as mentioned earlier, and therefore the fugacity coefficient of water in the gas phase can be set to unity as a good approximation. In other words, the Ideal model (Raoult's law) or ideal model + Poynting correction can be used to estimate water content of a gas in equilibrium with ice.[12,15,16]

Methodology

To evaluate the parameters for the consistency test method, a previously tuned thermodynamic model[35–38] was applied. The Valderrama modification of the Patel and Teja equation of state (*VPT-EoS*)[39] with non-density-dependent (NDD) mixing rules[40] was used to calculate the compressibility factor, fugacity coefficients of components in the gas phase, and the water content of methane.[35–40] The *VPT-EoS*[39] with the NDD mixing rules[40] is given in the Appendix and the detailed description of the thermodynamic model can be found elsewhere.[37]

The following algorithm was then applied for the thermodynamic consistency test:[24]

1. Determine A_{p} from Eq. 5 using the experimental P-T-y data. Use a numerical integration for this purpose. In this work, Simpson's 3/8 rule[41] was used. Valderrama and Alvarez[24] have demonstrated that the deviations between the calculated values of the integrals by the simple trapezoidal integration rule and a fitted polynomial function are below 2%. Therefore, a simple numerical integration method e.g., trapezoidal rule can be applied for the cases that there are only two available experimental data points.

2. Evaluate A_φ by Eqs. 6–8 using the obtained values for φ_2 and Z from the thermodynamic model[35–38] for the proposed system and y_2 from experimental data.

3. For every set of the experimental data, determine $\Delta A_i\%$ between experimental and calculated values as mentioned earlier:

$$\%\Delta A_i = 100\left[\frac{A_{\varphi_i} - A_{\mathrm{p}_i}}{A_{\mathrm{p}_i}}\right] \tag{9}$$

Consistency criteria

First and perhaps most importantly is the fact that the thermodynamic model should lead the average absolute deviations of the results from experimental values to be within the acceptable range. Generally, the accepted absolute deviations (AD) in gas phase mole fraction predictions (defined by the following equation), lies between 0 and 20%:[24]

$$\%\mathrm{AD} = 100\frac{\left|y_i^{\mathrm{cal}} - y_i^{\mathrm{exp}}\right|}{y_i^{\mathrm{exp}}}, \tag{19}$$

where superscripts cal and exp refer to calculated and experimental values, respectively.

It was shown in previous works[4,9,15] that the ADs% of the model results used in this work are <20% for all the experimental data points. Therefore, the model is acceptable for this purpose.

For determination of the acceptable percentages of the two evaluated areas deviations from each other, the error propagation was performed on the existing experimental data. This was done using the general equation of error propagation,[42] considering the temperature and water content as the independent measured variables.[24] The calculated A_φ is the dependent variable of interest. The error in the calculated areas, E_{A} and the percent error $\%E_{\mathrm{A}}$ are calculated as follows:[25]

$$E_{\mathrm{A}} = \left[\frac{\partial A_{\varphi j}}{\partial T}\right]\Delta T + \left[\frac{\partial A_{\varphi j}}{\partial y}\right]\Delta y, \tag{20}$$

$$E_{\mathrm{A}}\% = 100\left[\left|\frac{E_{\mathrm{A}}}{A_{\varphi j}}\right|\right], \tag{21}$$

where subscript j refers to jth individual calculated area. We assumed maximum uncertainties of 0.1 K for the experimental temperature and 10% for the experimental water content data. However, these uncertainties depend on the method of experimental measurements. The maximum acceptable errors are much dependent on uncertainty of water content measurements and one can also neglect the first right-hand side term of Eq. 20. But the uncertainty for the measurements of the water content of the gas is high and that is why we imperatively need the thermodynamic consistency test of such data.

The partial derivatives of the two preceding equations have been evaluated using Central Finite Difference[41] method. It results in the relative average absolute deviations range between 0 to 58%. Therefore, the range [0,60]% is established as the maximum acceptable error for the calculated areas ([A_i]). The high uncertainty in measurements of the water content data and also very low concentrations of water in gas phase contribute this wide range of acceptable individual area deviations for the data to be thermodynamically consistent.

Regarding these facts, the thermodynamic consistency test criteria are applied through the following instructions:[24–28]

1. Check the percentage Δy_2 not to be outside of the margins of errors [0,20]%. If it is so, change the thermodynamic model or eliminate the weak predictions until the absolute deviations of the results from experimental values would be within the acceptable range.

2. If the model correlates the data within the acceptable error ranges of the predictions and the area test is fulfilled for all points in the data set, the proposed model is reliable and the data are thermodynamically consistent.

3. In the case that the model correlates the data acceptably and the area test is not accomplished for most of the data set calculated areas (more than 75% of the individual areas), the applied model is conclusive but the experimental data are considered to be thermodynamically inconsistent.

4. In the case that the model acceptably correlates the data and some of the area deviations (equal or <25% of the areas)

Table 1. The Experimental Data Ranges Used for Consistency Test in This Work

System	Set No.	T/K	Number of experimental data	Range of pressure/MPa	Range of water content of methane/mole fraction $\times 10^8$	Reference
H-G-E*						
	1	240.00	3	3.450–10.340	272–1230	43
	2	250.00	3	3.450–10.340	846–3217	
	3	260.00	3	3.450–10.340	2423–7824	
	4	270.00	3	3.450–10.340	6422–17,809	
	5	283.08	2	10.010–14.240	15,000–21,300	44
	6	288.11	3	17.490–34.460	9200–16,700	
	7	293.11	2	24.950–35.090	16,800–22,500	
L_W-G-E**						
	8	283.08	2	1.006–6.030	10,800–124,000	18
	9	288.11	3	1.044–10.030	8760–178,000	
	10	293.11	4	0.992–17.680	7990–236,000	
	11	298.11	6	1.010–34.420	7790–330,000	
	12	303.11	6	1.100–34.560	15,100–390,000	
	13	308.11	6	1.100–34.580	28,000–582,000	
	14	313.12	6	1.100–34.610	42,400–746,000	
	15	318.12	6	1.003–34.610	56,000–989,000	
	16	283.08	2	1.006–6.030	29,200–124,000	45
	17	288.11	3	1.044–10.030	27,300–178,000	
	18	293.11	4	0.992–17.680	33,800–236,000	
	19	298.11	6	1.010–34.420	26,500–330,000	
	20	303.11	6	1.100–34.560	33,100–444,000	
	21	308.11	6	1.100–34.580	44,700–111,400	
	22	313.12	6	1.100–34.610	57,500–746,000	
	23	318.12	6	1.003–34.610	69,100–989,400	
	24	254.00	2	3.450–6.900	2070–4240	44
	25	293.01	2	0.510–0.992	241,000–464,000	4
	26	298.01	2	0.608–2.846	121,800–519,300	
I-G-E***						
	27	258.15	2	0.500–1.500	11000–31000	46
	28	263.15	2	0.500–1.500	19000–52000	
	29	268.15	2	0.500–1.500	28000–83000	

*Hydrate-Gas Equilibria.
**Liquid Water-Gas Equilibria.
***Ice-Gas Equilibria.

are outside the error range [0,60]%, the applied method declares the experimental values as being not fully consistent.

5. The determined data in the previous step could be further analyzed to check, if after eliminating some points, the remaining data fulfill the criteria described before and these remaining data are consistent or inconsistent.

Results and Discussion

As discussed earlier, the experimental data for the water content of gas in equilibrium with gas hydrate, ice or liquid water (near gas hydrate or ice formation region) are limited. In this work, 29 (isothermal) experimental data sets have been selected for consistency test. Table 1 summarizes the ranges of the data along with the references. These data contain various pressure, temperature and water content values available in the literature.[12,15] Previous studies have shown that the thermodynamic model used in this work results in reliable predictions of water content of various gas samples, as pointed out earlier.[3,10,12,15,16]

Table 2 indicates the results of the thermodynamic consistency test for all of the experimental data sets presented in Table 1. As can be seen, almost all of the deviations lie near the maximum acceptable limit for being thermodynamically consistent. This is partly because of the difficulty of experimental measurements for such systems.[1] The percentage of the consistent data, inconsistent data, and not fully consistent data are 48, 28, and 24%, respectively. It can also be

Table 2. Results of the Consistency Test

Set No.	ΔA_i%	Test result
1	62.5	TI
2	35.2	TC
3	62.5	TI
4	63.6	TI
5	49.5	NFC
6	49.0	TC
7	65.2	TI
8	74.9	TI
9	58.6	NFC
10	53.4	TC
11	48.9	TC
12	63.8	TI
13	67.2	TI
14	51.2	NFC
15	49.1	TC
16	57.9	NFC
17	46.5	TC
18	53.1	TC
19	50.0	TC
20	52.1	TC
21	61.7	TI
22	52.3	NFC
23	46.2	TC
24	52.3	TC
25	51.6	TC
26	58.7	NFC
27	50.7	TC
28	52.4	NFC
29	49.8	TC

TI: Thermodynamically Inconsistent Data.
TC: Thermodynamically Consistent Data.
NFC: Not Fully Consistent Data.

Table 3. Typical Detailed Calculation Results for the Data Set 4

T/K	P/MPa	$y_2^{\mathrm{exp}} \times 10^8$	$y_2^{\mathrm{cal}} \times 10^8$	%AD	Z	φ_1^{G}	φ_2^{G}	Ap	$A\varphi$	$\Delta A\%$
270	3.45	17,809	15,700	11.8	0.91000	0.91200	0.86300	1.08×10^4	1.77×10^4	63.6
	6.9	9443	8340	11.7	0.83071	0.83571	0.74224			
	10.34	6422	6210	3.3	0.77396	0.77396	0.63883			

indicated that the thermodynamic consistency test is a useful procedure to determine the accuracy of the measurements. For instance, the sets 16–23 are the revised data measured by Chapoy et al.[44] that previously reported as the data sets 8–15.[18] The results show that the revised data are reported with more accuracy and this has leaded the experimental data to be more thermodynamically consistent. Typical calculation results for the forth data set are shown in Table 3.

It is also obvious that using more developed experimental apparatus can cause more reliable experimental data. As for this, consider the data sets 1–4 reported by Aoyagi et al.[43] in 1980. Although, three of these four sets are thermodynamically inconsistent, measurements of such data were acknowledgeable in that period. Additionally, the results of such a test introduce a procedure to select the experimental data by which a thermodynamic model is supposed to be tuned and optimal values of the model parameters are supposed to be obtained. Thermodynamically inconsistent data (sometimes not fully consistent data) used for tuning of the models will bring about inaccurate predictions of the model in further applications and the cause of such deviations may not be easily figured out.

Another element to consider is that the data on which the thermodynamic consistency test was applied by the presented procedure, should be reported as isotherms because the main assumption in development of Eqs. 1–8 is similar to that assumed in developing the original "Gibbs-Duhem equation"[19–21] at constant temperature. This fact assigns some limitations to choose the experimental data sets for consistency test by the presented procedure especially for this kind of scarce data. One way of solving the problem of few data is generating more data in a statistical form. The generated data is treated as pseudo-experimental. But this is very doubtful and seems to be incorrect for the data of water content in equilibrium with gas hydrate, because there is the possibility of structure change of the gas hydrate and these would result in inaccurate generated data. Apart from that, it is not recommended to generate data based on the doubtful data, which are not yet theoretically tested. Therefore, one has to perform such a test following the proposed procedure using the existed available data, even if only two isothermal data points are available.

Conclusions

A thermodynamic consistency test was applied on the isothermal experimental data for water content of methane in equilibrium with gas hydrate, ice, or liquid water (near gas hydrate or ice formation region). A previously tuned thermodynamic model,[35–38] which contains *VPT-EoS*[39] with non-density-dependent (NDD) mixing rules[40] was applied to predict the required parameters of the gas phase for the test, which was based on the area test approach derived from the original "Gibbs-Duhem equation"[19–21] at constant temperature.[24–29] The results showed that 48% of the investigated experimental data are thermodynamically consistent meanwhile this percentage is 27% for inconsistent data and 25% for not fully consistent data. In addition, the results indicated that the measurements of such data must be done accurately and deliberately to be able to use in tuning of the future models for predictions of water contents of gas samples.

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Notation

A = area, (m^2)
AD = absolute deviation
a = attractive parameter of the equation of state, ($MPa.m^6/mol^2$)
b = repulsive parameter of the equation of state, (m^3/mol)
C = Langmuir constant
c = third parameter of the equation of state, (m^3/mol)
d = derivative
E = error or equilibrium
F = coefficient of the equation of state defined by Eq. A7
f = fugacity, (MPa)
G = gas
H = hydrate
I = Ice
k = binary interaction parameter
L = liquid
l = binary interaction parameter for the asymmetric term of *VPT-EoS*[39]
NFC = not fully consistent
P = pressure, (MPa)
R = universal gas constant, ($MPa.m^3/mol.K$)
T = temperature, (K)
TC = thermodynamically consistent
TI = thermodynamically inconsistent
V = vapor
v = molar volume, (m^3/mol)
v' = number of cavities per water molecule in a unit hydrate cell
y = mole fraction in gas phase/mixture
Z = compressibility factor

Greek letters

α = alpha function of the equation of state
γ = activity coefficient
φ = fugacity coefficient
Δ = difference value
Ψ = coefficient used in Eq. A6
ω = acentric factor
Ω = coefficients defined by Eqs. A8–A10

Subscripts

A = area
c = critical state
I = ice
i = ith component in a mixture or ith experimental data set
j = jth component in a mixture or jth individual calculated area
large = large type of cavities in water molecule
p = refers to experimental P-T-y data or the index of polar components
r = reduced property

small = small type of cavities in water molecule
W = water
φ = refers to calculated parameters of the model for evaluations of the integrals in Eqs. 6–8
1 = refers to methane
2 = refers to water

Superscripts

A = refers to asymmetric interaction
C = Attractive term of the *VPT-EoS*[39] defined by classical quadratic mixing rules
cal = calculated value
E = excess property
exp = experimental value
G = gas
L = liquid
MT = empty hydrate lattice
sat = saturated state
Ψ = parameter in Eq. A6
0 = first parameter of asymmetric binary interaction parameter
1 = second parameter of asymmetric binary interaction parameter
I = ice

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Appendix

The *VPT-EoS*[39] along with NDD mixing rule is used for modeling gas/vapor phase, as it is believed that this combination is a strong tool for modeling systems containing water and polar compounds.[40] This equation of state is written as follows:[4,37,39]

$$P = \frac{RT}{v-b} - \frac{a}{v(v+b)+c(v-b)} \tag{A1}$$

where P is pressure, T is temperature, R denotes the universal gas constant, v stands for the molar volume, and a, b, and c are the parameters of the *VPT-EoS*[39].

In Eq. A1:

$$a = \bar{a}\alpha(T_{\mathrm{r}}), \tag{A2}$$

$$\bar{a} = \frac{\Omega_a R^2 T_{\mathrm{c}}^2}{P_{\mathrm{c}}}, \tag{A3}$$

$$b = \frac{\Omega_b R T_{\mathrm{c}}}{P_{\mathrm{c}}}, \tag{A4}$$

$$c = \frac{\Omega_{\mathrm{c}} R T_{\mathrm{c}}}{P_{\mathrm{c}}}, \tag{A5}$$

where the alpha function $\alpha(T_r)$ is given as:

$$\alpha(T_r) = \left[1 + F\left(1 - T_r^{\Psi}\right)\right]^2, \tag{A6}$$

where $\Psi = 0.5$ and the coefficient F is given by:

$$F = 0.46286 + 3.58230(\omega Z_c) + 8.19417(\omega Z_c)^2 \tag{A7}$$

The subscripts c and r in the preceding equations denote critical and reduced properties, respectively, and ω is the acentric factor. Besides, the coefficients Ω_a, Ω_b, Ω_c are calculated by:

$$\Omega_a = 0.66121 - 0.76105 Z_c, \tag{A8}$$

$$\Omega_b = 0.02207 + 0.20868 Z_c, \tag{A9}$$

$$\Omega_{\mathrm{c}} = 0.57765 - 1.87080 Z_c, \tag{A10}$$

where Z_c is the critical compressibility factor, and ω is the acentric factor. Avlonitis et al.[40] relaxed the constraints on F and Ψ for water in order to improve the predicted vapor pressure and saturated volume for this compound:

$$F = 0.72318, \qquad \Psi = 0.52084. \tag{A11}$$

Later, Tohidi-Kalorazi[35] relaxed the alpha function for water, $\alpha_{\mathrm{w}}(T_{\mathrm{r}})$, using experimental water vapor pressure data in the range of 258.15–374.15 K, to improve the predicted water fugacity:

$$\alpha_{\mathrm{w}}(T_{\mathrm{r}}) = 2.4968 - 3.0661\, T_{\mathrm{r}} + 2.7048\, T_{\mathrm{r}}^2 - 1.2219\, T_{\mathrm{r}}^3. \tag{A12}$$

Nonpolar-nonpolar binary interactions in fluid mixtures are described by applying classical mixing rules as follows:

$$a = \sum_i \sum_j y_i y_j a_{ij}, \tag{A13}$$

$$b = \sum_i y_i b_i, \tag{A14}$$

$$c = \sum_i y_i c_i, \tag{A15}$$

$$a_{ij} = \left(1 - k_{ij}\right)\sqrt{a_i a_j}, \tag{A16}$$

where k_{ij} is the standard binary interaction parameter and y stands for the mole fraction of the species.

For polar-nonpolar interaction, however, the classical mixing rules are not satisfactory and therefore more complicated mixing rules are necessary. In this work the NDD mixing rules developed by Avlonitis et al.[40] are applied to describe mixing in the a-parameter:[4,37,40]

$$a = a^C + a^A, \tag{A17}$$

where a^C is given by the classical quadratic mixing rules (Eqs. A13 and A16). The term a^A corrects for asymmetric interaction, which cannot be efficiently accounted for by classical mixing rules:[4,37,40]

$$a^{\mathrm{A}} = \sum_{\mathrm{p}} x_{\mathrm{p}}^2 \sum_i x_i a_{pi} l_{pi}, \tag{A18}$$

$$a_{pi} = \sqrt{a_p a_i}, \tag{A19}$$

$$l_{pi} = l_{pi}^0 - l_{pi}^1 (T - T_0), \tag{A20}$$

where p is the index of polar components, and l represents the binary interaction parameter for the asymmetric term.

Using the above *EoS*[39] and the associated mixing rules, the fugacity of each component in gas/vapor phase is calculated from:

$$f_i = y_i \varphi_i P, \tag{A21}$$

where y_i and φ_i are the mole fraction and the fugacity coefficient of component i, respectively.

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