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Thermodynamic Consistency Test for Experimental Data of Sulfur Content of Hydrogen Sulfide

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ABSTRACT: Accurate knowledge of the sulfur content of hydrogen sulfide vapor is an important factor for prediction of the sulfur precipitation conditions in production of many sour natural gases. However, limited data regarding the sulfur content of hydrogen sulfide are available in the open literature. This is partly because of the fact that the concentration of sulfur in the vapor phase is very low. The measurement difficulties may consequently result in generating inaccurate and sometimes unreliable experimental data. This work aims at performing a thermodynamic consistency test based on area approach to study the reliability of some selected experimental data from the literature on the sulfur content of hydrogen sulfide vapor. The Peng−Robinson equation of state along with conventional mixing rules is used for thermodynamic modeling. In this model, sulfur molecules are treated as single molecules S_8. The results show that almost 45% of all of the investigated experimental data are thermodynamically consistent, 45% are inconsistent, and 10% are not fully consistent.

1. INTRODUCTION

A serious problem in production of sour natural gases is precipitation of sulfur in the formation, in well bores, and in production facilities, especially at high temperatures, pressures, and hydrogen sulfide concentrations.[1,2] Sulfur deposition can cause a substantial and drastic reduction in the permeability of the formation near the well bore. As the gas flows up the tubing string, the temperature and pressure are decreased, causing further sulfur deposition. The occurrence of sulfur precipitation has also been reported when transporting natural gases.[1−5] Details of the most probable locations where sulfur deposition occurs in natural gas transportation and its impact on the equipment is given elsewhere.[5]

Vapor and liquid phases of sulfur are composed of different molecules.[1,6−13] Sulfur may exist as a number of polymeric species ranging up to S_8 in the gas and combines with other gases to produce polysulfides or sulfanes such as H_2S_9.[1,14−16] The amount of each molecule depends on both pressure and temperature.[2,10−13] Sulfur vapors are mainly constituted of light sulfur molecules (typically S_2−S_8) around the critical point, whereas the most abundant vapor sulfur species, below 400 K and at saturation pressure, seems to be S_8.[2,6−13,17,18] Under atmospheric pressure and at temperatures greater than the fusion temperature, liquid sulfur is composed of about 99% (mole basis) of S_8 and traces of lighter molecules.[1,9−13,18] Nevertheless, if temperature increases, the ring molecules of sulfur polymerize. Liquid sulfur begins to polymerize at about 430 K.[1,10−13,19] Two thermodynamically stable forms of solid sulfur can also exist. If liquid sulfur is slightly cooled, it becomes monoclinic sulfur (or β sulfur) at fusion temperature. If monoclinic sulfur is cooled again, it converts into orthorhombic sulfur (or α sulfur).[1,10−13,19] On the other hand, it has been argued that during the transportation of natural gas, the solubility of sulfur is very low. Although the composition of natural gas when transported can vary according to its origins, sulfur's solubility under transportation conditions does not greatly differ with gas composition. It can partially be explained by the fact that after natural gas treatment the amount of hydrogen sulfide, the quantity that greatly influences the sulfur solubility, is very low.[1,10−13]

Thus far, several researchers have attempted to measure the sulfur content in gas samples. Kennedy and Wieland[19] measured the equilibrium sulfur content in pure methane, carbon dioxide, hydrogen sulfide, and mixtures of these gases at temperatures of 339, 367, and 394 K and in the pressure range of 6.9−41.3 MPa. Later, Roof[20] measured the solubility of sulfur in hydrogen sulfide in the range of temperature between 317 and 394 K and at pressures up to 31 MPa.

Another attempt has been made by Swift et al.,[23] who reported the solubility of sulfur in hydrogen sulfide at pressures between 35 and 140 MPa and temperatures between 390 and 450 K, conditions that may be encountered in high-pressure natural gas reservoirs. Brunner and Woll[21] measured the sulfur solubility in pure hydrogen sulfide and in four gas mixtures composed of H_2S, CO_2, CH_4, and N_2 between 373 and 433 K at pressures up to 60 MPa.[1]

Later, Brunner et al.[24] measured the sulfur solubility in sour gas mixtures of various compositions at pressures up to 155 MPa between 394 and 486 K. Woll[25] examined the effect of hydrogen sulfide on depression of the freezing point of sulfur. Davis et al.[26] measured the solubility of sulfur in sour gases of high hydrogen sulfide content (up to 90%) at four temperatures, 333, 363, 393, and 423 K, between 5 and 55 MPa.

In addition, Gu et al.[27] measured the solubility of sulfur in two rich-H_2S natural gases at 363 K, where the mole fractions of H_2S

Table 1. Experimental Studies on Sulfur Content of Various Gases

author(s)	system	T/K	P/MPa	remarks
Sun and Chen[29]	7 (CH_4 + H_2S + CO_2) ternary mixtures	303–363	20–45	mole fraction of H_2S in sour gas mixture ranges from 0.0495 to 0.2662 and that of CO_2 ranges from 0.0086 to 0.1039
Migdisov et al.[28]	gaseous hydrogen sulfide	323–563	up to 20	
Gu et al.[27]	two rich-H_2S natural gases	363	up to 34.7 and 32.8	mole fractions of H_2S are 0.4411 and 0.9509
	H_2S, CO_2, and methane	363 (for the solubility of sulfur in H_2S)	up to 36.2 (for the solubility of sulfur in H_2S)	
		363 and 383 (for the solubility of sulfur in CO_2)	up to 40.5 (for the solubility of sulfur in CO_2)	
		and 383 (for the solubility of sulfur in methane)	up to 50.2 (for the solubility of sulfur in methane)	
Davis et al.[26]	sour gases	333, 363, 393, and 423	5–55	high hydrogen sulfide content (up to 90%)
Brunner et al.[24]	sour gas mixtures of various compositions	394–486	up to 155	
Brunner and Woll[21]	hydrogen sulfide and four gas mixtures composed of H_2S, CO_2, CH_4, and N_2	373–433	up to 60	
Swift et al.[23]	hydrogen sulfide	390–450	35–140	
Roof[20]	hydrogen sulfide	317–394	up to 31	
Kennedy and Wieland[19]	methane, carbon dioxide, hydrogen sulfide, and mixtures of these gases	339, 367, and 394	6.9–41.3	

were 0.4411 and 0.9509 and the pressures were up to 34.7 and 32.8 MPa, respectively.[1] Gu et al.[27] also measured the solubility of sulfur in pure H_2S at 363 K and pressures up to 36.2 MPa, in pure CO_2 at 363 and 383 K at pressures up to 40.5 MPa, and in pure methane at 383 K and pressures up to 50.2 MPa. Migdisov et al.[28] carried out experiments for the solubility of sulfur in gaseous hydrogen sulfide in the H_2S–S system at temperatures between 323 and 563 K and pressures up to 20 MPa.[1] Sun and Chen[29] measured the solubility of elemental sulfur in seven (CH_4 + H_2S + CO_2) ternary mixtures with a temperature range of 303–363 K and pressure range of 20–45 MPa.[1] Table 1 summarizes almost all of the experimental studies to date about the aforementioned concept.[1,15]

Modeling sulfur + sour/acid gas-phase equilibrium by conventional thermodynamic models requires the use of unknown parameters considering the complex chemical behavior of sulfur,[15] although there are other numerical methods which have solved this drawback.[1,15] The various thermodynamic models reported in the literature[14,17] typically use the Peng–Robinson equation of state (PR EoS)[30] and focus on ranges of pressure, temperature, and hydrogen sulfide content at gas production conditions, typically greater than those of gas transportation conditions.[15]

To present more accurate thermodynamic models for estimation of the sulfur content of sour natural gases, reliable experimental data sets, especially for the sulfur content of hydrogen sulfide, are required. Measurements of such data are difficult due to the low sulfur content of gases. Another important point to consider is that the sulfur content is generally measured at high temperatures and pressures to simulate the natural gas operation conditions.

This article aims at testing the thermodynamic consistency of literature data for the sulfur content of hydrogen sulfide at conditions of natural gas production and transportation in order to verify their reliability.

2. 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".[31–34] 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.[31–34] This is due to various errors occurring during experimental measurements, especially those dealing with high pressures and high temperatures.

The ways in which the "Gibbs–Duhem equation"[31–34] 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".[32–35] Good reviews of these methods are given elsewhere.[33]

In recent years, Valderrama and co-workers[35–39] investigated the applications of numerical thermodynamic consistency test methods to various systems including incomplete phase equilibrium data of high-pressure gas–liquid mixtures,[35] high-pressure ternary mixtures of compressed gas and solid solutes,[36] high-pressure gas–solid solubility data of binary mixtures,[37] vapor–liquid

equilibrium data for mixtures containing ionic liquids,[38] and high-pressure gas−liquid equilibrium data including both liquid and vapor phases.[39] Recently, Eslamimanesh et al.[40] applied almost the same approach for performing the thermodynamic consistency test on a significant system encountered in the natural gas industry: the water content of methane in equilibrium with gas hydrate, liquid water, or ice.

A method especially employed for determining the thermodynamic consistency of high-pressure gas−solid data by Valderrama and Alvarez,[35] which is based on rewriting the "Gibbs−Duhem equation"[31−34] in terms of fugacity coefficients,[41] 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 accurately fit the experimental data must be used to apply the consistency test. The fitting of the experimental data requires calculation of some model parameters using a defined objective function that must be minimized.

As stated by Valderrama and Alvarez,[35] a good consistency test method to analyze high-pressure data must fulfill 10 basic requirements:

(i)   use the "Gibbs−Duhem equation";[31−34]
(ii) use the fundamental equation of phase equilibrium;
(iii) use for testing all the experimental $P-T-y$ (pressure-temperature-vapor phase composition) 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 to the defined criteria.

2.1. Equations. The "Gibbs−Duhem equation"[31−34] for a binary homogeneous mixture at constant temperature can be written as[35−40]

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

where v^E is the excess molar volume, T is the temperature, R is the Universal gas constant, γ is the activity coefficient, y is the solute mole fraction, P is the 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. Equation 1 can be written in terms of the fugacity coefficients as follows[35,40]

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

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

This equation can be written in terms of the sulfur content of the gas phase. If sulfur is considered as component 2 in the binary mixture of hydrogen sulfide + sulfur, the latter equation becomes

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

or in integral form as follows

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

The properties φ_1, φ_2, and Z can be calculated using suitable thermodynamic models.

In eq 4, the left-hand side is designated by A_P and the right-hand side by A_φ as follows[35,40]

$$A_p = \int \frac{1}{Py_2} dP \tag{5}$$

$$A_\varphi = A_{\varphi_1} + A_{\varphi_2} \tag{6}$$

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

$$A_{\varphi_2} = \int \frac{1}{(Z-1)\varphi_2} d\varphi_2 \tag{8}$$

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[35,40]

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

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

3. SULFUR SOLUBILITY MODEL

In this work, the thermodynamic model proposed by Karan et al.[14] has been used to predict the solubility of sulfur in hydrogen sulfide. The Peng−Robinson[30] equation of state along with conventional mixing rules is used for this purpose as follows

$$P = \frac{RT}{v-b} - \frac{a}{v(v+b)+b(v-b)} \tag{10}$$

where a and b are the EoS attractive and repulsive parameters, respectively, which are evaluated by the expressions below

$$a = a_c \times \alpha \tag{11}$$

where

$$a_c = \frac{0.457235R^2T_c^2}{P_c} \tag{12}$$

$$\alpha = \left(1+m\left(1-T_r^{0.5}\right)\right)^2 \tag{13}$$

where

$$m = 0.37464 + 1.54226\omega - 0.26992\omega^2 \tag{14}$$

$$b = \frac{0.077796RT_c}{P_c} \tag{15}$$

In the preceding equations, ω stands for the acentric factor and subscripts c and r refer to the critical and reduced property, respectively. The term m has been later modified for heavier components as follows[42]

$$m = 0.3796 + 1.485\omega - 0.1644\omega^2 + 0.01667\omega^3 \tag{16}$$

To extend the EoS to the mixture, the common random (van der Waals one) mixing rules have been applied

$$a = \sum_{i=1} \sum_{j=1} y_i y_j (a_{ij})(1 - k_{ij}) \tag{17}$$

$$b = \sum_{i=1} y_i b_i \tag{18}$$

where y is the mole fraction, i and j refer to ith and jth components, respectively, and a_{ij} is given by

$$a_{ij} = (a_i a_j)^{0.5} \tag{19}$$

In this model, sulfur is treated as single molecule S_8 under all conditions.[15] Due to the fact that the sulfur critical property values are far from the values encountered for petroleum reservoir fluids (P_c = 20.7 MPa and T_c = 1314 K) and also the chemical complexity of sulfur, Karan and co-workers[14] recommend the following expressions for evaluating the parameters of the PR EoS[30] for vapor and liquid sulfur instead of using sulfur critical property values[14]

$$b = 0.13122 (\mathrm{m^3/kmol}) \tag{20}$$

$$a(T) = 6.1051 + 2568.1/T (\mathrm{MPa\ m^6/kmol^2}) \tag{21}$$

The above relations result in acceptable deviations in prediction of vapor pressures and saturated liquid and vapor densities in a wide temperature range of experimental data reported in the literature.[14] In addition, the calculations show that the heat of vaporization of sulfur can be well predicted by this method.[14]

It should be noted that liquid sulfur has undergone phase transition to become solid sulfur as a monoclinic structure. Karan et al.[14] used the following expression for evaluation of the fugacity of solid sulfur

$$\ln f_s = A/T + B + P v_s/(RT) \tag{22}$$

where the first two terms define the fugacity of sulfur at its sublimation pressure and the third term is the Poynting correction factor for higher pressures. In eq 22, v_s is the volume of solid sulfur, which is considered to be independent of pressure. The values of the aforementioned parameters have been fitted to the experimental hydrogen sulfide–sulfur three-phase points, and the following values have been obtained[14]

$$\ln f_s = 22.83572 - 13846.797/T + 0.122479 P/(RT) \tag{23}$$

where the fugacity of solid sulfur is calculated in MPa.

4. METHODOLOGY

The described model has been applied to evaluate the required parameters for the consistency test method. In order to tune the model for accurate calculation of the sulfur content of hydrogen sulfide, the following procedure has been used.

(1) Determine a set of sulfur-content P–T–y experimental (isothermal) data for consistency test.

(2) Consider the gaseous/vapor mixture consisting of hydrogen sulfide and an amount of solute (sulfur), which is a preliminary guess at this step.

(3) Define the state of the sulfur component in the proposed conditions from the experimental data.

(4) Evaluate the fugacity of the components in every phase present applying the previously described equations.

Table 2. Experimental Data Used for the Thermodynamic Consistency Test

| | | | | | range of data | |
| | | | | | | |
system	set no.	T/K	N^a	P/MPa	$y_2 \times 10^6$/mole fraction	ref
solid sulfur-H$_2$S	1	316.3	5	7.028–31.143	1669–2196	20
solid sulfur-H$_2$S	2	338.7	5	7.028–31.143	2620–4494	
solid sulfur-H$_2$S	3	366.5	4	10.473–31.143	3641–9778	
liquid sulfur-H$_2$S	4	374.8	4	10.473–31.143	2746–10243	
liquid sulfur-H$_2$S	5	383.2	3	17.363–31.143	5473–10060	
solid sulfur-H$_2$S	6	363.2	6	11.83–36.21	4832–10540	27
liquid sulfur-H$_2$S	7	373.15	8	10–50	2372–14145	24
liquid sulfur-H$_2$S	8	393.15	8	12–60	1790–20304	
liquid sulfur-H$_2$S	9	413.15	8	15–60	1883-21451	
liquid sulfur-H$_2$S	10	433.15	12	15–60	1406–22848	

^{a} N = Number of experimental data.

(5) Check whether the difference between the fugacity of sulfur in the gaseous phase and its fugacity in other phases (liquid or solid) present is within the defined tolerance.

(6) If not, change the sulfur content of hydrogen sulfide according to the ratio of the fugacity coefficient of sulfur in the liquid or solid phase to the one in the gas phase.

(7) Whenever $f_2^{s/1} = f_2^{v}$, compare the values of calculated solubilities with experimental sulfur content data. If the absolute average deviation (ADD %) is not within the acceptable range, choose an optimization algorithm to obtain the optimum values of the adjustable parameter (here, k_{ij}). The following objective function has been considered to be minimized

$$\mathrm{OF} = \frac{100}{N} \sum_{i=1}^{N} \left| \frac{y_{2i}^{calc} - y_{2i}^{exp}}{y_{2i}^{exp}} \right| \tag{24}$$

where N is the number of experimental data and superscripts calc and exp refer to calculated and experimental values.

Selecting the most efficient optimization strategy has been always of great interest for researchers. Almost all of the traditional optimization algorithms have the possibility of getting trapped at the local optimum depending upon the degree of nonlinearity and initial guess. There is no guarantee for these optimization methods to find the global optimum solution. Valderrama and Alvarez[35] applied a nonlinear regression program applying the Marquardt method[35] to describe the phase behaviors of gas–liquid mixtures. However, the population-based search algorithms, which are supposed to converge to the global optimum,[43,44] can be used instead. Such optimization techniques, which are designed based on natural phenomena, are the simulated annealing (SA),[45] evolution strategies (ES),[46] genetic algorithms (GA),[47,48] and differential evolution (DE) techniques.[49] Recently, Eslamimanesh,[50] Eslamimanesh and Shariati,[51] Eslamimanesh and Esmaeilzadeh,[52] and Yazdizadeh et al.[53] demonstrated that the DE optimization technique[49] has high capabilities in evaluation of the thermodynamic model parameters, especially those dealing with phase equilibrium calculations. Therefore, this optimization strategy has been used in this study for obtaining the optimum values of the model parameter. Details of this technique can be found elsewhere.[49–54]

Once the model is tuned for the proposed purpose, the following algorithm is applied for the thermodynamic consistency test:[35]

Table 3. Results of Tuning the Thermodynamic Model[14] for Calculation of Sulfur Content of Hydrogen Sulfide

Table 3. Continued

T/K	P/MPa	$y_2^{exp} \times 10^6$ /mole fraction	$y_2^{calc} \times 10^6$ /mole fraction	k_{ij}^c	ARD[a] %	ref[b]
316.3	7.028	1669	1660	0.0805	0.5	20
	10.473	1846	1817	0.0805	1.6	
	17.363	1977	2066	0.0805	4.5	
	24.253	2078	2084	0.0805	0.3	
	31.143	2196	2205	0.0805	0.4	
338.7	7.028	2620	2620	0.0810	0.0	20
	10.473	2926	3249	0.0810	11.0	
	17.363	3670	3690	0.0810	0.5	
	24.253	4189	4332	0.0810	3.4	
	31.143	4494	4484	0.0810	0.2	
366.5	10.473	3641	2581	0.0844	29.1	20
	17.363	6128	5578	0.0844	9.0	
	24.253	8176	7920	0.0844	3.1	
	31.143	9778	9816	0.0844	0.4	
374.8	10.473	2746	1228	0.1020	55.3	24
	17.363	5893	3184	0.1020	48.0	
	24.253	8144	4634	0.1020	43.1	
	31.143	10 243	5721	0.1020	44.1	
383.2	17.363	5473	2186	0.1300	60.1	20
	24.253	8191	3393	0.1300	58.6	
	31.143	10 060	4253	0.1300	57.7	
363.2	11.83	4832	4020	0.0780	16.8	27
	14.79	5081	5444	0.0780	7.1	
	19.14	7313	7302	0.0780	0.2	
	25.86	8053	9697	0.0780	20.4	
	31.03	9523	11 355	0.0780	19.2	
	36.21	10 540	12 727	0.0780	20.8	
373.15	10	2373	1394	0.1100	41.2	24
	10	2862	1394	0.1100	51.3	
	12	3416	2486	0.1100	27.2	
	18	6166	5090	0.1100	17.5	
	30	9814	9490	0.1100	3.3	
	30	9957	9490	0.1100	4.7	
	40	11 738	12 897	0.1100	9.9	
	50	14 146	16 295	0.1100	15.2	
393.15	12	1790	342	0.1200	80.9	24
	15	3218	1658	0.1200	48.5	
	15	3574	1658	0.1200	53.6	
	20	5904	3813	0.1200	35.4	
	32	11 141	8349	0.1200	25.1	
	40	13 060	11 139	0.1200	14.7	
	51	16 464	14 894	0.1200	9.5	
	60	20 305	18 028	0.1200	11.2	
413.15	15	1883	636	0.1200	66.2	24
	24	6494	4644	0.1200	28.5	
	24	6573	4644	0.1200	29.3	
	33	11 777	9257	0.1200	21.4	
	40	14 301	13 004	0.1200	9.1	
	40	14 339	13 004	0.1200	9.3	
	44	15 306	15 260	0.1200	0.3	
	50	17 491	18 916	0.1200	8.1	
	60	21 451	26 517	0.1200	23.6	
433.15	19.6	2835	473	0.1200	67.1	24
	24	5785	1676	0.1200	40.9	
	24	5917	3714	0.1200	35.8	
	30	8810	7200	0.1200	18.3	
	30	9058	7200	0.1200	18.3	
	40	14 016	14 160	0.1200	1.0	
	40	14 533	14 160	0.1200	2.6	
	45	17 107	18 361	0.1200	7.3	
	52	19 539	25 994	0.1200	33.0	

[a] $ARD = 100 \times ((|y_2^{calc} - y_2^{exp}|)/y_2^{exp})$. [b] References of experimental data. [c] k_{ij} = Binary interaction parameter.

(1) Determine A_P by eq 5 applying the experimental $P-T-y$ data. Use a numerical integration for this purpose. In this work, Simpson's 3/8 rule was used. Valderrama and Alvarez[35] 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 can be also applied for this purpose.

(2) Evaluate A_φ by eqs 6-8 using the obtained values for φ_2 and Z by the tuned thermodynamic model for the proposed system and y_2 from experimental data.

(3) For every set of experimental data, determine an individual absolute percent area deviation ($\Delta A_i\%$) between experimental and calculated values using eq 9.

5. CONSISTENCY CRITERIA

First and perhaps most importantly is the fact that the used thermodynamic model should lead to average absolute deviations of the results from experimental values to be within the acceptable range, which depends highly on the type of measured data and the difficulty of getting satisfactory experimental values. Generally, the accepted deviations in vapor-phase mole fraction predictions lie between 0 and 20%.[35]

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,[55] considering the temperature and sulfur content as the independent measured variables. The calculated individual area (A_φ) is the dependent variable of interest. The error in the calculated areas E_A and the percent error $E_A\%$ are calculated as follows[35,40]

$$E_A = \left[\frac{\partial A_{\varphi j}}{\partial T}\right]\Delta T + \left[\frac{\partial A_{\varphi j}}{\partial y}\right]\Delta y \qquad (26)$$

$$E_A\% = 100\left[\left|\frac{E_A}{A_{\varphi j}}\right|\right] \qquad (27)$$

where subscript j refers to the jth individual calculated area. We assume maximum uncertainties of 0.1 K for the experimental temperature and 10% for the experimental sulfur content data. However, these uncertainties depend on the method of experimental measurements. The maximum acceptable errors are much more dependent on the uncertainty of sulfur content measurements, and one can also neglect the first right-hand side term of eq 26. The

Table 4. Results of Thermodynamic Consistency Test on the Experimental Data Investigated in This Work[a]

T/K	P/MPa	Z	$\varphi_2^{s/l}$	$f_2^{s/l}$	f_2^{v}	A_P	A_φ	$\Delta A\%$	consistency test result	ref[b]
316.3	7.0278	0.11625	9.6×10^{-8}	1.1×10^{-9}	1.1×10^{-9}	2.106	1.128	46.4	TC	20
	10.4728	0.16982	6.9×10^{-8}	1.3×10^{-9}	1.3×10^{-9}					
	17.3628	0.27275	5×10^{-8}	1.8×10^{-9}	1.8×10^{-9}					
	24.2528	0.37156	4.9×10^{-8}	2.5×10^{-9}	2.5×10^{-9}					
	31.1428	0.46743	5×10^{-8}	3.4×10^{-9}	3.4×10^{-9}					
338.7	7.0278	0.12319	1.1×10^{-6}	2×10^{-8}	2×10^{-8}	2.109	1.907	9.5	TC	20
	10.4728	0.17651	6.7×10^{-7}	2.3×10^{-8}	2.3×10^{-8}					
	17.3628	0.27753	4.8×10^{-7}	3.1×10^{-8}	3.1×10^{-8}					
	24.2528	0.37357	4×10^{-7}	4.2×10^{-8}	4.2×10^{-8}					
	31.1428	0.46613	4×10^{-7}	5.6×10^{-8}	5.6×10^{-8}					
366.5	17.3628	0.29475	6.7×10^{-6}	6.5×10^{-7}	6.5×10^{-7}	0.622	1.091	75.4	TI	20
	24.2528	0.38504	4.5×10^{-6}	8.6×10^{-7}	8.6×10^{-7}					
	31.1428	0.47346	3.7×10^{-6}	1.1×10^{-6}	1.1×10^{-6}					
363.2	11.83	0.21635	7.8×10^{-6}	3.7×10^{-7}	3.7×10^{-7}	2.828	3.281	16	TC	27
	14.79	0.25643	5.2×10^{-6}	4.2×10^{-7}	4.2×10^{-7}					
	19.14	0.31506	3.6×10^{-6}	5×10^{-7}	5×10^{-7}					
	31.03	0.47116	2.3×10^{-6}	8.1×10^{-7}	8.1×10^{-7}					
373.15	30	0.46273	1.1×10^{-5}	3.2×10^{-6}	3.2×10^{-6}	1.129	2.288	87.7	TI	24
	30	0.46273	1.1×10^{-5}	3.2×10^{-6}	3.2×10^{-6}					
	40	0.58703	9.7×10^{-6}	5×10^{-6}	5×10^{-6}					
	50	0.71001	9.6×10^{-6}	7.8×10^{-6}	7.8×10^{-6}					
393.15	40	0.59473	4.6×10^{-5}	2×10^{-5}	2×10^{-5}	0.422	0.125	70.4	NFC	24
	51	0.72151	4.3×10^{-5}	3.3×10^{-5}	3.3×10^{-5}					
	60	0.8254	4.4×10^{-5}	4.8×10^{-5}	4.8×10^{-5}					
413.15	40	0.6095	1.3×10^{-4}	6.9×10^{-5}	6.9×10^{-5}	14.9	0.599	95.97	TI	24
	40	0.6095	1.3×10^{-4}	6.9×10^{-5}	6.9×10^{-5}					
	44	0.65277	1.2×10^{-4}	8.1×10^{-5}	8.1×10^{-5}					
	50	0.71901	1.1×10^{-4}	1×10^{-4}	1×10^{-4}					
433.15	40	0.62933	3.5×10^{-4}	2×10^{-4}	2×10^{-4}	43.8	2.489	94.3	TI	24
	40	0.62933	3.5×10^{-4}	2×10^{-4}	2×10^{-4}					
	45	0.6787	3×10^{-4}	2.4×10^{-4}	2.4×10^{-4}					

[a] The parameters are defined in the Nomenclature list. [b] References of experimental data.

uncertainty for the measurements of the sulfur 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 the central finite difference[56] method. It results in a relative average absolute deviations range between 0 and 50%. Therefore, the 0−50% range is established as the maximum acceptable error for the individual areas ($\Delta A_i \%$). The high uncertainty in measurements of the sulfur content data and also low concentrations of sulfur in the gas phase contribute to 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:[35−40]

(1) Check that the percentage Δy_2 is not outside of the margins of errors 0−20%. If it is, then 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 calculation results 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 to or less than 25% of the areas) are outside the 0−50% error range, 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.

6. RESULTS AND DISCUSSION

As discussed earlier, the experimental data for the sulfur content of hydrogen sulfide are limited. In this work, 10 (isothermal) experimental data sets have been treated for consistency test. Table 2 summarizes the ranges of the data along with the references. These data contain various pressures, temperatures, and sulfur content values available in the literature.[1,15]

The results of tuning the thermodynamic model for these data are indicated in Table 3. As can be seen, the deviations of the model results for several points are not within the acceptable range for the thermodynamic consistency test procedure. Therefore, the test has been done on the data points for which the model leads to acceptable results.

Table 4 shows the detailed results of the thermodynamic consistency test for all of the experimental data sets investigated in this work. The percentage of consistent data, inconsistent data, and not fully consistent data is almost 45%, 45%, and 10%, respectively. It is observed that the percentage of thermodynamically inconsistent data is high. This may be because of the difficulty of the experimental measurements for such systems.

It is also shown that the thermodynamic consistency test is a useful procedure to determine the accuracy of the measurements. 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 is applied through using the described 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"[31−34] at constant temperature. This fact assigns some limitations to choose the experimental data sets for consistency testing, especially for this kind of scarce data. One way of solving the problem of few data is generating more data in a statistical form.[40] The generated data is treated as pseudoexperimental. However, this is very doubtful and seems to be incorrect for some thermodynamic data. For instance, as for data on the water content of gases in equilibrium with hydrate because there is the possibility of a structure change of the clathrate hydrate, and these would result in inaccurate generated data,[40] and in the case of the solubility of sulfur in hydrogen sulfide, there is the possibility of liquid−solid phase transitions, which affect the experimental measurements. Apart from that, we may not be able to generate data based on the doubtful data that are not already proven to be thermodynamically consistent. Therefore, the only possible solution is considering the existing isothermal data for the test using the aforementioned procedure.

7. CONCLUSIONS

A thermodynamic consistency test was applied on the isothermal experimental data for the sulfur content of hydrogen sulfide. A thermodynamic model proposed by Karan et al.[14] was used to predict the required parameters for the test, which was based on the area test approach derived from the original "Gibbs−Duhem equation"[31−34] at constant temperature.[35−41] The DE optimization strategy[49] was used as an efficient technique for obtaining the global optimum of the adjustable parameter. The results showed that almost 45% of the investigated experimental data are thermodynamically consistent; meanwhile, this percentage is around 45% for inconsistent data and 10% for not fully consistent data. In addition, the results indicated that the measurements of such data must be done carefully to be able to be used in tuning of the future models for predictions of the sulfur content of gas/vapor samples.

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■ NOMENCLATURE

A = area (m^2) or parameter in the fugacity expression in eq 22
ARD = absolute relative deviation, %
B = parameter in the fugacity expression in eq 22
a = attractive parameter of the equation of state $(MPa \cdot m^6/mol^2)$
b = repulsive parameter of the equation of state (m^3/mol)
d = derivative operator
E = error
f = fugacity (MPa)
k = binary interaction parameter
m = parameter of the equation of state defined by eqs 14 and 16
N = number of experimental data
OF = objective function
P = pressure (MPa)
R = universal gas constant $(MPa \cdot m^3/mol \cdot K)$
T = temperature (K)
v = molar volume (m^3/mol)
y = mole fraction in the vapor phase
Z = compressibility factor

Greek Letters

α = alpha function of the equation of state
γ = activity coefficient
φ = fugacity coefficient
Δ = difference value
ω = acentric factor

Subscripts

A = area
c = critical property
i = ith component in a mixture or ith experimental data set
j = jth component in a mixture or jth individual calculated area
p = refers to experimental $P-T-y$ data
r = reduced property
s = solid
φ = refers to calculated parameters of the model for evaluations of the integrals in eqs 6−8
1 = refers to hydrogen sulfide
2 = refers to sulfur

Superscripts

calc = calculated
E = excess property
exp = experimental
l = liquid
s = solid
v = vapor

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