A Semiempirical Approach for Estimating the Water Content of Natural Gases

4 AUTHORS:

Amir H. Mohammadi

558 PUBLICATIONS   4,819 CITATIONS

SEE PROFILE

Antonin Chapoy

Heriot-Watt University

105 PUBLICATIONS   1,666 CITATIONS

SEE PROFILE

Bahman Tohidi

Heriot-Watt University

216 PUBLICATIONS   3,094 CITATIONS

SEE PROFILE

Dominique Richon

Aalto University

533 PUBLICATIONS   6,595 CITATIONS

SEE PROFILE

A Semiempirical Approach for Estimating the Water Content of Natural Gases

Amir H. Mohammadi,[†] Antonin Chapoy,[‡] Bahman Tohidi,*,[†] and Dominique Richon[‡]

Centre for Gas Hydrate Research, Institute of Petroleum Engineering, Heriot-Watt University, Edinburgh EH14 4AS, Scotland, U.K., and Centre d'Energétique, Ecole Nationale Supérieure des Mines de Paris, CENERG/TEP, 35 Rue Saint Honoré, 77305 Fontainebleau, France

A semiempirical approach for estimating the equilibrium water content of natural gases in the liquid water−vapor and ice−vapor regions has been developed. This method estimates the water content of natural gases using water/ice vapor pressure and water/ice molar volume as well as pressure and temperature of the system. The approach has been developed using the experimental water content data for methane at a temperature range of 273.15 and 377.59 K and pressures up to 13.81 MPa. Experimental data for the water content of a hydrocarbon gas mixture (94% methane + 4% ethane + 2% *n*-butane) have been generated at a temperature range of 288.15 to 313.14 K and pressures up to 17.56 MPa using a static-analytic apparatus, taking advantage of a pneumatic capillary sampler for fluid sampling. These independent data have been used in examining the reliability of the semiempirical approach. The predictions of this approach are in good agreement with the experimental data generated in this work and those reported in the literature.

1. Introduction

Natural gases are normally saturated with water at reservoir conditions. During production, transportation, and processing, dissolved water in the gas phase may form liquid water phase, ice, and/or gas hydrates. Forming a liquid water phase may lead to corrosion and/or two-phase flow problems. Gas hydrates and/or ice formation may cause blockage during production and transportation. To predict and avoid such problems, predictive methods are necessary. On the other hand, estimating the water content by predictive techniques is crucial to design and selection of operating conditions in natural gas facilities. General methods for calculation include the following: (1) empirical or semiempirical correlations and charts of the water content and corrections for the presence of acid gases (such as hydrogen sulfide and carbon dioxide), heavy hydrocarbons, and salts in the system and (2) thermodynamic models which are based on equality of chemical potential of various components in different phases.

The main advantage of empirical or semiempirical correlations and charts is the availability of input data and the simplicity of the calculations, which can be performed by using charts or hand-held calculators. The correlations/charts have still kept their popularity among engineers in the petroleum industry. Although most available thermodynamic models could be installed on typical laptop computers, there seem to be a need for simple, yet robust, predictive methods for quick estimation of the water content of natural gases.

The available correlations and charts are generally based on limited data and with limited application. In general, the available correlations/charts can predict the water content of gases with good accuracy at high-temperature conditions. While in predicting the water content at low-temperature conditions, the available methods have lower accuracy and need further verification at low-temperature conditions. In fact, during the development of the original correlations/charts, experimental data describing the phase equilibrium in water−hydrocarbons systems for temperatures typically lower than 298.15 K were not available. Due to this shortcoming, the water content for low temperatures calculated by the correlations/charts might not be accurate.

To develop new correlations/charts and to improve the accuracy of the estimated water content of gases, experimental data are required (which could also be used for validation of correlations/charts). Mohammadi et al.[1] gathered most of the water content data for the main components of natural gases from literature and concluded that most of the water content data for hydrocarbons and for non-hydrocarbon gases (e.g. N_2, CO_2, and H_2S) at low-temperature conditions are often inconsistent. These types of uncertainties can lead to large deviations for correlations, when using these scattered data for regressing.

The aim of this work is to develop a semiempirical approach based on equality of water fugacity in equilibrium phases for estimating the water content of natural gases in equilibrium with liquid water or ice. For this purpose, a quick review is made on the most famous correlations/charts existing in the open literature. Then a set of experimental data for the water content of a hydrocarbon gas mixture (94% methane + 4% ethane + 2% *n*-butane) is generated at a temperature range of 288.15 to 313.14 K and pressures up to 17.56 MPa using a static-analytic apparatus, taking advantage of a pneumatic capillary sampler for fluid sampling.[1−3]

To develop the approach, experimental data for the water content of methane are used; however, as mentioned earlier, most of the water content data at low-temperature conditions are inconsistent, and further

* To whom correspondence should be addressed. Tel.: +44 (0)131 451 3672. Fax: +44 (0)131 451 3127. E-mail: Bahman.Tohidi@pet.hw.ac.uk.
† Institute of Petroleum Engineering.
‡ Ecole Nationale Supérieure des Mines de Paris.

experimental work is necessary for developing new predictive methods at low-temperature conditions. To evaluate the capability of this approach, the results are compared with the experimental data generated in this work and other literature data as well as other predictive tools. The results are in good agreement demonstrating the capability of the approach and data generated in this work.

2. Predictive Methods

Many thermodynamic models and correlations/charts are available, which can calculate the phase equilibrium in water–hydrocarbon systems. Thermodynamic models use different approaches in order to model the fluid, ice, and gas hydrates phases. For example, some thermodynamic models use activity coefficient and Henry's constant approaches for modeling the aqueous phase; however, other models use the equation of state (*EoS*) approach. Although thermodynamic models are useful tools in phase behavior calculations, they may not be available easily. Correlations and charts are more simple tools, and because of their ease of use, they are of interest to engineers in petroleum industry. Various correlations and charts with different capabilities have been reported for estimating the water content/water dew point of gases. The original correlations/charts are normally applicable to dry and sweet gases. Generally, these correlations/charts have been developed for the liquid water–vapor (L_w–V) region and interpolating the results to the hydrate–vapor (H–V) and ice–vapor (I–V) regions may be questionable. In this section, a review of the most famous correlations and charts in the natural gas industry are presented:

(1) The *Ideal* model (Raoult's law) is expressed by the following expression

$$y_w = \frac{(1 - x_g)P_w^{sat}}{P} \tag{1}$$

where *y*, *x*, and *P* are the mol fraction in the vapor phase, mol fraction in the liquid phase, and pressure, respectively, subscripts *w* and *g* relate to water and gas, and the superscript *sat* relates to the saturation state. In this equation, the gas solubility in the water x_g can be ignored for hydrocarbons, as hydrocarbons are weakly soluble in water and solubility will decrease by increasing the molecular weight of hydrocarbons; however, for acid gases (CO_2 and H_2S) the solubility can be significant, even at relatively low pressure.[4,5] In this case, the water content can be expressed by the following expression:

$$y_w = \frac{P_w^{sat}}{P} \tag{2}$$

The above relation assumes the water content of a gas equals to the ratio of the water vapor pressure and total pressure of the system.

A more accurate form of the *Ideal* model can be expressed by taking into account the *Poynting* correction

$$y_w = \frac{P_w^{sat}}{P} \exp\left(\frac{v_w^L(P - P_w^{sat})}{RT}\right) \tag{3}$$

where *v, R,* and *T* are molar volume, universal gas constant, and temperature of the system, respectively,

and the superscript *L* stands for the liquid state. The *Ideal model* and its *Poynting correction* are simple tools for predicting the water content of natural gases. However, these methods can be used at low-pressure conditions (typically up to 1.4 MPa[4]).

(2) Bukacek[6] developed a method similar to the *Ideal* model, which only requires information on the water vapor pressure and the temperature and pressure of the system. This correlation is one of the most used methods in the natural gas industry for calculating the water content of dry and sweet natural gases. This correlation in *American Engineering units* is given as follows[4,5]

$$y_w = 47484\frac{P_w^{sat}}{P} + B \tag{4}$$

$$log(B) = \frac{-3083.87}{459.6 + t} + 6.69449 \tag{5}$$

where the water content (y_w) and *t* are in *lbm/MMscf* and the temperature is in °*F*. As can be seen, this correlation uses an ideal contribution and a deviation factor. The above relation is reported to be accurate for temperatures between 288.15 and 511.15 K and for pressures from 0.1 to 69 MPa.[4,5] This correlation is accurate to about ±5% within the stated range,[4,5,7] as this is about as accurate as the water content can be measured.

(3) Sharma and Campbell[8–10] provided a relatively complicated method in order to calculate the equilibrium water content of sweet and sour gases in the L_W–V region. In this method, the water content is calculated as below

$$y_w = k\left(\frac{f_w^{sat}}{f_g}\right)^Z \tag{6}$$

where *k, Z,* and *f* are a correction factor, the compressibility factor, and the fugacity, respectively, and subscript *g* refers to the gas phase. The compressibility factor *Z* should be calculated using a suitable method. The correction factor *k* can be calculated from a figure (provided by the authors) or by the following equation

$$k = \left(\frac{P_w^{sat}}{P}\right)\left(\frac{f_w^{sat}/P_w^{sat}}{f_w/P}\right)\left(\frac{P}{P_w^{sat}}\right)^{0.0049} \tag{7}$$

where f_w^{sat} and f_w are fugacity of water at saturation conditions (*T* and P_w^{sat}) and the fugacity of water at pressure and temperature of the system (*T* and *P*). They provided a chart for calculating the fugacity of water. As mentioned before, this method is relatively complicated; however, Campbell[10] mentioned that the consistency of the results of this method is high.

(4) Behr[11] proposed the following equation for pressure ranging from 1.379 to 20.679 MPa

$$y_w = \exp(A_0 + A_1(1/T)^2 + A_2(1/T)^3 + A_3(lnP) + A_4(lnP)^2 + A_5(lnP)^3 + A_6(lnP/T)^2 + A_7(lnP/T)^3) \tag{8}$$

where y_w is in *lbm/MMscf* and A_0 to A_7 are constants based on fitting the natural gas dew point versus the water content data of ref 6.

(5) Later Kazim[12] proposed an analytical expression for calculating the water content of sweet natural gases. The expression in the *American Engineering units* is

$$y_w = A \times B^t \tag{9}$$

$$A = \sum_{i=1}^{4} a_i \left(\frac{p - 350}{600}\right)^{i-1} \tag{10}$$

$$B = \sum_{i=1}^{4} b_i \left(\frac{p - 350}{600}\right)^{i-1} \tag{11}$$

where y_w is in *lbm/MMscf* and *p* is the pressure in *psia*, and a_is and b_is are constants reported in the original publication. These two correlations are similar as in which, they originate from regression methods to express the water content of natural gases as a function of temperature and pressure and require many constants, which may reduce their applications for calculating the water content of natural gases in comparison with the Bukacek[6] correlation.

(6) Several charts have been reported in order to calculate the equilibrium water content of gases. The most commonly used is the McKetta-Wehe[13] chart, which is used for sweet natural gases containing over 70% methane and small amounts of heavy hydrocarbons.[13,14] This chart was first published in 1958[15] and was based on experimental data available at that time.[13] Gas Processors Associations (*GPA*) and Gas Processors Supplier Associations (*GPSA*) have reproduced this chart for many years. In this chart the water content of a sweet gas is presented in a semilogarithmic plot versus temperature at different pressures. Two correction factors have been provided in order to take into account the presence of heavy hydrocarbons in the gas phase and salts in the liquid water. In this chart, the meta-stable $L_W - V$ equilibrium is assumed rather than the $H - V$ equilibrium in the hydrate formation region with limited justification.[16] However the actual water content in the $H - V$ region is lower than the calculated water content by assuming the $L_W - V$ equilibrium. Furthermore, reading the water content from this semilogarithmic chart may be slightly difficult. If used with care, this chart can calculate the water content of sweet gases with less than 5% error.[4]

(7) Ning et al.[17] proposed the following correlation based on the McKetta-Wehe[13] chart:[4,5]

$$y_w = \exp(a_0 + a_1 T + a_2 T^2) \tag{12}$$

For the above equation, a complicated figure and table have been provided in order to calculate the pressure dependent coefficients a_0, a_1, and a_2 for pressures up to 100 MPa. It seems that this correlation is not a simple tool due to the complicated dependency of coefficients to the pressure. Their correlation takes into account the effect of gas gravity by the following correction factor[4]

$$F_{HC} = 1.01532 + 0.011\,(T\text{-}273.15) - 0.0182\,SG_g - 0.0142\,SG_g\,(T\text{-}273.15) \tag{13}$$

$$y_{w,heavy} = F_{HC} y_{w,light} \tag{14}$$

where *F* and *SG* are correction factors due to the presence of heavy hydrocarbons and gas gravity, and subscripts *HC*, *heavy*, and *light* relate to hydrocarbon, heavy, and light components, respectively.

The above correlations/charts (except for the Sharma and Campbell method[8−10]) assume that the water content of dry and sweet natural gases is independent of the gas composition. However, when acid gases and heavy hydrocarbons and/or salts are present in the system, their accuracy is reduced, and some corrections should be used in addition to the above correlations/ charts.

Both hydrogen sulfide and carbon dioxide contain more water at saturation than methane or sweet natural gas mixtures, and the relative amounts vary considerably with temperature and pressure.[13] The water content of carbon dioxide and hydrogen sulfide plays an important role in phase equilibria calculations, e.g., enhanced oil recovery (*EOR*) processes, corrosion prevention, flow assurance, gas hydrates inhibition, etc. There are some methods for estimation of the water content due to the presence of acid gases in the gas phase. The correlations should be applied when the gas mixture contains more than 5% hydrogen sulfide and/ or carbon dioxide, especially at high pressures.[13]

Several graphs are reported for estimating the water content of pure carbon dioxide[5,13,18−23] and pure hydrogen sulfide.[5,13,20,24] There are also other graphs for estimating the water content of different mixtures containing acid gases.[13,22,25−29]

The Robinson et al.,[25−27] Maddox et al.,[28] and Wichert−Wichert[29] methods correct the water content of sweet gases due to the presence of acid gases.

Robinson et al.[25−27] reported a series of charts to estimate the water content of sour natural gases. These charts were calculated based on an equation of a state based model. They used an equivalent mol fraction for H_2S for their charts, which is calculated by the following expression[26,27]

$$z_{H2S}{}^{equi} = z_{H2S} + 0.75 z_{CO2} \tag{15}$$

where *z* is the mol fraction in the natural gas, the subscripts CO_2 and H_2S refer to carbon dioxide and hydrogen sulfide, respectively, and the superscript *equi* refers to equivalent H_2S. This method is applicable for $z_{H2S}{}^{equi} < 0.4$ (mol fraction), $283.15 < T < 450.15$ K and $2.07 < P < 69$ MPa. In addition, using these charts is slightly difficult due to the need for interpolations.

In the Maddox et al.[28] method, the water content of sour gases is calculated using the following expression

$$y_w = \\ y_{w,HC} \times z_{HC} + y_{w,CO2} \times z_{CO2} + y_{w,H2S} \times z_{H2S} \tag{16}$$

where subscript *HC* refers to hydrocarbon. In the above equation, the contribution to the sweet gas can be calculated using an appropriate correlation or chart. The acid gas contributions can be calculated by either the corresponding charts or equations. The above correlation is applicable to acid gas concentrations of less than 40 mol %, a pressure range of $0.7 < P < 20.7$ MPa, and a temperature range of $300.15 < T < 344.15$ K for CO_2 and $300.15 < T < 411.15$ K for H_2S.

Wichert and Wichert[29] proposed a new chart based on temperature, pressure, and equivalent H_2S content in order to calculate a correction factor (F_{sour}). They used the definition of Robinson et al.[26,27] for the equivalent H_2S content. Using this correction factor, the water content of sour natural gases can be calculated by using the following expression:

$$y_{w,sour} = F_{sour} y_{w,sweet} \tag{17}$$
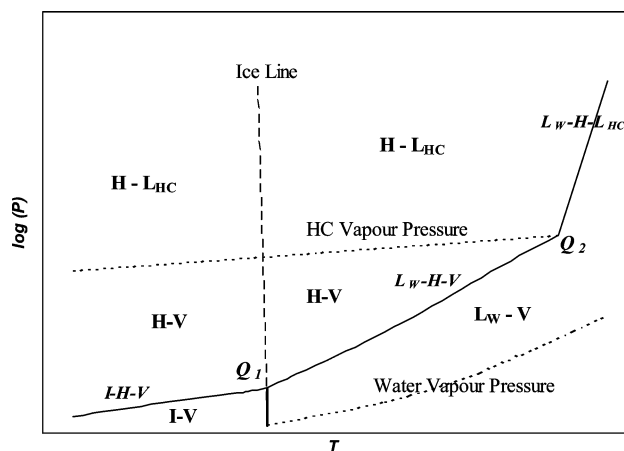
Figure 1. Typical pressure–temperature diagram for a water (limiting reactant)–single (pure) hydrocarbon system.[1,30]

In the above equation, the subscripts *sour* and *sweet* relate to the sour and sweet natural gases. The McKetta-Wehe[13] chart is recommended for calculating y_{sweet} in the above equation. This method is applicable for $z_{H2S}^{equi} < 0.55$ (mol fraction), $283.15 < T < 450.15$ K, and $1.4 < P < 69$ MPa. In addition, using this method is easier than the method suggested by Robinson et al.,[25–27] as there is no need for interpolation.

In addition, determining the water content in acid/sour gases is a very complex topic. According to *GPSA*,[13] an accurate determination of the water content requires a careful study of the existing literature and available experimental data. In most cases, additional experimental data is the best way to verify the predicted values. Even the most sophisticated *EoS* techniques may give results of questionable reliability.

Figure 1 shows a typical pressure-temperature diagram for a water–hydrocarbon system.[1,30] As can be seen, the $I-V$ equilibrium for sweet natural gases with very low nitrogen content can be reached at relatively low-pressure conditions. The maximum pressure at which the $I-V$ equilibrium can be reached is around 2.563 MPa, which corresponds to hydrate formation conditions for methane at around quadruple point. The *Poynting* correlation can be used for estimating the water content of sweet natural gases with very low nitrogen content in equilibrium with ice. Katz[31,32] also reported a chart in the temperature and pressure range of $222.04 < T < 273.15$ K and $0.1 < P < 2.757$ MPa for calculating the water content of natural gases in equilibrium with ice.

The water content of natural gases in equilibrium with gas hydrates is lower (typically less than 0.001 mol fraction[16]) than the water content of natural gases in equilibrium with meta-stable liquid water and therefore difficult to measure, as hydrate formation is a time-consuming process and the water content of gases in the hydrate region is a strong function of composition.[13,16] In other words, a gas-phase saturated with water can form gas hydrates in the $H-V$ region from a strict thermodynamic stand point; however, the question of the accumulation of a hydrate phase is a question of kinetics, dependent upon the time necessary for hydrate nuclei to attain a critical size.[16] This time may be in excess of that available for laboratory study but may occur in processes, which operate over extended periods of days, months, or years.[16] On the other hand, limited experimental data have been reported in this region. Therefore, a comprehensive correlation/chart for calcu-

lating the water content of gases in equilibrium with gas hydrates would be problematic.[16] Few mathematical relations/charts for this region have been developed in the literature.[4,16,32–36] Where experimental data are limited, utilization of a thermodynamic model can provide an estimate of the water content in equilibrium with hydrates.

In addition, in many standards, the Bukacek[6] correlation and the McKetta-Wehe[13] chart are recommended to estimate the water content of sweet natural gases in equilibrium with liquid water. However, the Bukacek[6] correlation and the McKetta-Wehe[13] chart may not describe real phase behavior in water–hydrocarbon systems at low-temperature conditions. In other words, the Bukacek[6] correlation should be used at temperatures higher than 288.15 K,[4,5] and the water contents obtained from the McKetta-Wehe[13] chart at temperatures below hydrate formation conditions correspond to the meta-stable L_W-V equilibrium rather than the $H-V$ equilibrium.

3. Experimental Section

A description of the commonly used methods for measuring the water content/water dew point of gases is reported elsewhere.[1] Based on the laboratory experience and on the existing laboratory equipment a method based on gas chromatography (*GC*) is selected to perform the analyses in this study. A detailed description of the experimental setup and experimental procedure has been reported previously.[1–3]

3.1. Materials. The gas mixture, 94% methane, 4% ethane ($\pm$ 2%, i.e., 3.92–4.08), and 2% *n*-butane ($\pm$ 2%, i.e., 1.96–2.04) was purchased by *Messer Griesheim*. Helium from *Air Liquide* is pure grade with traces of water (3 *ppm*) and of hydrocarbons (0.5 *ppm*). Furthermore, helium was dried by means of molecular sieves placed at the outlet of the cylinder.

3.2. Apparatus. The apparatus used in this work is based on a static-analytic method with vapor phase sampling. The analytical work was carried out using a *GC* (*VARIAN model CP-3800*) equipped with two detectors connected in series, a thermal conductivity detector (*TCD*) and a flame ionization detector (*FID*), connected to a data acquisition system (*BORWIN* ver. 1.5, from *JMBS, Le Fontanil*, France). The *FID* was utilized to detect the hydrocarbons. It was repeatedly calibrated by introducing known amounts of the gas mixture through a gas syringe in the injector of the *GC*. The calculation of the amount of water is carried out using equilibrium (equality of fugacity) and mass balance relations as summarized by the following expressions

$$y_w = \gamma_w^L x_w \frac{P_w^{sat} \phi_w^{sat}}{P_{dilutor} \phi_w^V} \exp\left(\left(\frac{v^L}{RT}\right)(P - P^{sat})\right) \quad (18)$$

with

$$y_w = \frac{n_w}{n_T} \quad (19)$$

An exact relationship is obtained:

$$n_w =$$

$$\gamma_w^L x_w \frac{P_w^{sat} \phi_w^{sat}}{P_{dilutor} \phi_w^V}\left(\frac{PVol}{ZRT}\right)^{loop} \exp\left(\left(\frac{v^L}{RT}\right)(P - P^{sat})\right) \quad (20)$$

In the above relations, γ, φ, n, Z, and Vol are activity coefficient, fugacity coefficient, number of moles, compressibility factor, and volume of the loop, respectively. The superscripts and subscripts V, $loop$, T, and $dilutor$ correspond to the vapor phase, loop, total, and dilutor, respectively.

3.3. Experimental Uncertainty. The temperature uncertainty is estimated to be not higher than ± 0.02 K. The uncertainty in the pressure measurements is estimated to be ± 5 kPa in the operating pressure range. The experimental accuracy of the TCD water calibration (from 9×10^{-10} mol to 1.2×10^{-8}) is estimated in the worst case at $\pm 5\%$. The methane, ethane, and n-butane calibration uncertainty are estimated to be within $\pm 1\%$, $\pm 3\%$, and $\pm 3\%$, respectively.

3.4. Experimental Procedure. The equilibrium cell and its loading lines are evacuated down to 0.1 Pa, and the necessary quantity of the preliminary degassed water (approximately 10 cm^3) is introduced using an auxiliary cell. Afterward, the desired amount of gas is introduced into the cell directly from the cylinder or via a gas compressor. The sampling is carried out using a capillary sampler injector[37] for each phase. The withdrawn samples are swept to a *Varian 3800 GC* for analysis. For each equilibrium condition, at least 10 points are withdrawn using the pneumatic samplers *ROLSI* and analyzed in order to check for measurement repeatability. As the volume of the withdrawn samples is very small compared to the volume of the vapor phase present in the equilibrium cell, it is possible to withdraw many samples without disturbing the phase equilibrium.

4. Semiempirical Approach

The vapor−liquid equilibrium (*VLE*) of a system is calculated, using the following equation

$$f_i^V = f_i^L \quad i = 1, N \tag{21}$$

where N is the number of components. The equality of fugacities can be calculated using the following relationship:

$$y_i \phi_i P = x_i \gamma_i P_i^{sat} exp \int_{P_i^{sat}}^{P} \frac{v_i^L dP}{RT} \tag{22}$$

In the intermediate pressure range, liquid water is an incompressible fluid, and gas solubility is very small compared to unity for hydrocarbons and some gases such as nitrogen (solubility of hydrocarbons in water are, in general, considerably less than water in hydrocarbons[13]) and to an approximation activity coefficient of water can be taken unity. However, the nonideality of the liquid phase and gas solubility become important at high-pressure conditions. Therefore, the mol fraction of water in the gas phase can be estimated, using the following equation:

$$y_w = \frac{(1 - x_g)P_w^{sat}}{\phi_w P} exp\left(\frac{v_w^L(P - P_w^{sat})}{RT}\right) \tag{23}$$

As can be seen, the water content is determined primarily by the fugacity coefficient of water (ϕ_w) in the gas phase, temperature, and pressure. In other words, the nonideality of the gas phase is the critical factor determining the water content in the intermediate

pressure range. The fugacity coefficient of water (ϕ_w) in the gas phase up to intermediate pressures may be calculated as below

$$\phi_w = exp(BP + CP^2) \tag{24}$$

where B and C are a function of temperature. The following relations for B and C seem to be satisfactory

$$B = a + \frac{b}{T} \tag{25}$$

$$C = c + \frac{d}{T} \tag{26}$$

where a, b, c, and d are constants and can be calculated for every water−gas system by regressing the water content data for that system. To estimate the vapor pressure and the molar volume of water in eq 23, the relations reported by Daubert and Danner[38] and McCain[7] are used, respectively where, T, t, p, P_w^{sat}, and v_w^L are

$$P_w^{sat} = 10^{-6} exp(73.649 - 7258.2/T - 7.3037 \ln(T) + 4.1653 \times 10^{-6} T^2) \tag{27}$$

$$v_w^L = 18.015/\rho_w \tag{28}$$

$$\rho_w = 62.368/D_w \tag{29}$$

$$D_w = (1 + \Delta V_{wt}) \tag{30}$$

$$\Delta V_{wt} = -1.0001 \times 10^{-2} + 1.33391 \times 10^{-4} t + 5.50654 \times 10^{-7} t^2 \tag{31}$$

in K, °F, psia, MPa, and ft^3/lbmol, respectively, and ρ_w, D_w, and ΔV_{wt} are water density in lb_m/ft^3, formation volume factor, and volume change due to temperature, respectively. Eqs 30 and 31 are valid at $t < 260$ °F, and $p < 5000$ psia even over a wide range of salt concentration.[39] To find constants a, b, c, and d in eqs 25 and 26, the water content data are used as input for a multidimension regression procedure, to reduce the average absolute deviation (*AAD*) between experimental and calculated data.

The above approach can be used for estimating the water content of gases in equilibrium with ice. For this purpose, the following relations for the molar volume of ice and ice vapor pressure can be used[40]

$$v_w^I = (19.655 + 0.0022364 \times (T - 273.15))/10^3 \tag{32}$$

$$\log (P_w^{sub}) = -1032.5576407/T + 51.0557191 \times \log(T) - 0.0977079751 \times T + 7.035711316 \times 10^{-5} \times T^2 - 98.5115496 \tag{33}$$

where superscript I and sub refer to ice and sublimation, respectively. In the above equations, T, v_w^I, and P_w^{sub} are in K, m^3/kgmol, and mmHg, respectively.

5. Results and Discussions

To find the constants a, b, c, and d for the methane−water system, the data reported in Table 1 are used. As can be seen, the temperature range is from 273.15 to 377.59 K, and the pressures are up to 13.81 MPa, respectively. The *AAD%* among all the experimental and

Table 1. Experimental Data Used for Developing This Approach in the L_W-V Region

reference	T_{min}/K	T_{max}/K	P_{min}/MPa	P_{max}/MPa	no. of points	AAD%
Althaus[30]	273.15	293.15	0.5	10	17	4.43
Rigby and Prausnitz[41]	298.15	373.15	2.35	9.35	12	1.07
Yokoyama et al.[42]	298.15	323.15	3	8	6	3.03
Gillespie and Wilson[20]	323.15	348.15	1.379	13.786	6	2.25
Kosyakov et al.[43]	273.16	283.16	1.01	6.08	5	7.52
Olds et al.[44]	310.93	377.59	2.67	13.81	11	8.65

Table 2. Constants a, b, c, and d in Eqs 25 and 26 for a Methane−Water System

constant	value
a	0.069355849
b/K	−30.90480919
c	−0.000765359
d/K	0.317895764

Table 3. Comparison between the Experimental Data and the Predictions of This Approach in the $I-V$ Region

reference	T/K	P/MPa	water content experimental (mol fraction)	water content this work (mol fraction)	AD%
Althaus[30]	253.15	0.500	0.00021	0.00021	0.00
	258.15	1.500	0.00011	0.00012	9.09
	258.15	0.500	0.00031	0.00034	9.68
	263.15	1.500	0.00019	0.00019	0.00
	263.15	0.500	0.00052	0.00053	1.92
	268.15	1.500	0.00028	0.00029	3.57
	268.15	0.500	0.00083	0.00083	0.00
Kosyakov et al.[43]	263.15	1.013	0.00028	0.00027	3.57
	253.15	1.013	0.00011	0.00011	0.00
	243.15	1.013	0.00004	0.00004	0.00

calculated data is 4.43%. These constants are reported in Table 2. On the other hand, the saturated water content of a natural gas depends on pressure, temperature, and composition. The effect of composition increases with pressure and is particularly important if the gas contains carbon dioxide and hydrogen sulfide.[13] For lean and sweet natural gases containing over 70 mol % methane and small amounts of heavy hydrocarbons, the effect of composition can be ignored, and the water content can be assumed as a function of temperature and pressure. Therefore, the constants a, b, c, and d for the methane−water system can be used with a good approximation for the dry and sweet natural gases−water system.

These constants can also be used for predicting the water content of methane and dry and sweet natural gases in the $I-V$ region. Table 3 shows a comparison between the experimental and predicted water content of methane in this region. The agreements between the experimental and predicted data are satisfactory, and the *AAD%* among all the experimental and predicted data is 2.78%.

Table 4 shows the experimental data measured for the water content of the gas mixture (94% methane + 4% ethane + 2% *n*-butane) prepared in this laboratory.

This table also shows the predictions of the Bukacek[6] correlation, *Ideal* model, *Ideal* model + *Poynting* correction, and the approach developed in this work. As can be seen, the *Ideal* model and *Ideal* model + *Poynting* correction show large deviations due to relatively high-pressure conditions and high nonideality of the system. However, the results of other predictive methods are nearly in good agreement with the experimental data.

In Tables 5 and 6, the capabilities of this approach are tested with data from the literature. As it can be observed for all references not used in the tuning of a, b, c, and d parameters, the predictions of this approach are in good agreement with the reported results. It is particularly noticeable that the influence of the gas composition/gas gravity (in all of these cases the gas gravity is close to the one of methane, 0.554) is negligible, and even high concentrations of nitrogen (10.35%) have little effect on the quality of the predictions. However, this latest assumption is true if the gas is mainly composed of methane and light hydrocarbons, and therefore its gas gravity is close to that of pure methane. The presence of heavy hydrocarbons in natural gases increases the water content. To take into account the effect of gas composition, the correction factor of the McKetta-Wehe[13] chart can be used. The presence of high quantities of nitrogen in natural gases can shift the hydrate phase boundaries to higher pressures. To estimate the water content in systems composed mainly of nitrogen, it is advised to use the values of the a, b, c, and d parameters in Table 2 for the L_W-V region, as the water contents for the methane and nitrogen systems are nearly identical.[30] Table 7 shows a comparison between the experimental and predicted water content of nitrogen in the L_W-V region.

Sour natural gases will contain a higher water content than sweet natural gases. The effect of acid gases has not been taken into account, as in eq 23 the gas solubility in the water phase is assumed to be negligible (which may not be true if high concentrations of acid gases are present). However at low pressure conditions (up to 0.5 MPa) this approach as well as some other correlations can be used, as the solubilities of acid gases are relatively small. Table 8 shows the predictions of this approach for the water content of some sour natural gases with low and intermediate concentrations of acid gases. As it can be seen, at low and intermediate concentrations of acid gases, this approach is capable

Table 4. Comparison between New Experimental Data and the Predictions of This Approach as Well as Other Predictive Methods[a]

T/K	P/MPa	$y_{w,exp}$	this work	AD %	Bukacek[6]	AD %	Ideal model	AD %	Ideal+ Poynting	AD %
288.15	6.020	0.314	0.368	17.20	0.401	27.71	0.283	9.87	0.296	5.73
297.93	6.000	0.710	0.662	6.76	0.706	0.56	0.522	26.48	0.545	23.24
297.95	10.050	0.418	0.460	10.05	0.497	18.90	0.312	25.36	0.335	19.86
303.13	17.560	0.444	0.445	0.23	0.474	6.76	0.242	45.50	0.274	38.29
308.12	17.500	0.565	0.576	1.95	0.608	7.61	0.321	43.19	0.364	35.58
313.14	10.030	1.131	1.033	8.66	1.088	3.80	0.736	34.92	0.789	30.24
313.14	17.500	0.777	0.738	5.02	0.773	0.51	0.422	45.69	0.477	38.61

[a] Values are in mol fraction × 10^3.

Table 5. Comparison between the Predictions of This Approach and the Bukacek[6] Correlation for the Water Content of Methane and Different Natural Gases (*NG*)

T/K	P/MPa	SG_g	experimental water content	predicted water content, this work	AD %	predicted water content, Bukacek[6]	AD %
			NG_1[30]				
273.15	0.500	0.5654	1.169E−03	1.25E−03	6.93	1.24E−03	6.07
273.15	1.500	0.5654	4.26E−04	4.39E−04	3.05	4.62E−04	8.45
278.15	0.500	0.5654	1.68E−03	1.79E−03	6.55	1.82E−03	8.33
278.15	1.500	0.5654	6.05E−04	6.25E−04	3.31	6.53E−04	7.93
283.15	1.500	0.5654	8.42E−04	8.78E−04	4.28	9.11E−04	8.19
283.15	6.000	0.5654	2.51E−04	2.68E−04	6.77	2.97E−04	18.33
288.15	1.500	0.5654	1.16E−03	1.22E−03	5.17	1.25E−03	7.76
288.15	6.000	0.5654	3.56E−04	3.69E−04	3.65	4.02E−04	12.92
288.15	10.000	0.5654	2.50E−04	2.60E−04	4.00	2.88E−04	15.20
			NG_2[30]				
273.15	0.500	0.598	1.19E−03	1.25E−03	5.04	1.24E−03	4.20
278.15	0.500	0.598	1.68E−03	1.79E−03	6.55	1.82E−03	8.33
278.15	1.500	0.598	5.99E−04	6.25E−04	4.34	6.53E−04	9.02
288.15	1.500	0.598	1.16E−03	1.22E−03	5.17	1.25E−03	7.76
288.15	4.000	0.598	4.68E−04	5.09E−04	8.76	5.44E−04	16.24
288.15	6.000	0.598	3.56E−04	3.69E−04	3.65	4.02E−04	12.92
293.15	6.000	0.598	4.65E−04	5.00E−04	7.53	5.39E−04	15.91
293.15	10.000	0.598	3.26E−04	3.50E−04	7.36	3.83E−04	17.48
			NG_3[30]				
273.15	0.500	0.628	1.20E−03	1.25E−03	4.17	1.24E−03	3.33
278.15	0.500	0.628	1.72E−03	1.79E−03	4.07	1.82E−03	5.81
283.15	1.500	0.628	8.26E−04	8.78E−04	6.30	9.11E−04	10.29
288.15	1.500	0.628	1.15E−03	1.22E−03	6.09	1.25E−03	8.70
			NG_4[30]				
273.15	0.500	0.6326	1.19E−03	1.25E−03	5.04	1.24E−03	4.20
278.15	0.500	0.6326	1.71E−03	1.79E−03	4.68	1.82E−03	6.43
278.15	1.500	0.6326	5.91E−04	6.25E−04	5.75	6.53E−04	10.49
283.15	1.500	0.6326	8.50E−04	8.78E−04	3.29	9.11E−04	7.18
288.15	1.500	0.6326	1.17E−03	1.22E−03	4.27	1.25E−03	6.84
288.15	4.000	0.6326	4.85E−04	5.09E−04	4.95	5.44E−04	12.16
293.15	6.000	0.6326	4.70E−04	5.00E−04	6.38	5.39E−04	14.68
293.15	8.000	0.6326	3.62E−04	4.06E−04	12.15	4.41E−04	21.82
			NG_5[30]				
273.15	0.500	0.6672	1.16E−03	1.25E−03	7.76	1.24E−03	6.90
278.15	0.500	0.6672	1.69E−03	1.79E−03	5.92	1.82E−03	7.69
283.15	1.500	0.6672	8.36E−04	8.78E−04	5.02	9.11E−04	8.97
288.15	1.500	0.6672	1.17E−03	1.22E−03	4.27	1.25E−03	6.84
			NG_6[30]				
273.15	0.500	0.6395	1.22E−03	1.25E−03	2.46	1.24E−03	1.64
278.15	0.500	0.6395	1.72E−03	1.79E−03	4.07	1.82E−03	5.81
278.15	1.500	0.6395	6.03E−04	6.25E−04	3.65	6.53E−04	8.29
283.15	1.500	0.6395	8.55E−04	8.78E−04	2.69	9.11E−04	6.55
288.15	1.500	0.6395	1.16E−03	1.22E−03	5.17	1.25E−03	7.76
288.15	6.000	0.6395	3.49E−04	3.69E−04	5.73	4.02E−04	15.19
			NG_7[30]				
278.15	0.500	0.8107	1.76E−03	1.79E−03	1.70	1.82E−03	3.41
			Synthetic Mixture Containing 96.94 Mol % of Methane and 3.06 Mol % of Ethane[30]				
278.15	1.500	0.569	6.12E−04	6.25E−04	2.12	6.53E−04	6.70
288.15	4.000	0.569	4.94E−04	5.09E−04	3.04	5.44E−04	10.12
288.15	6.000	0.569	3.52E−04	3.69E−04	4.83	4.02E−04	14.20
288.15	8.000	0.569	2.86E−04	3.00E−04	4.90	3.31E−04	15.73
288.15	10.000	0.569	2.48E−04	2.60E−04	4.84	2.88E−04	16.13

of predicting the water content with reasonable accuracy. It should be noted that measuring the water content of gases especially at low temperature conditions is very difficult, and an accuracy of 10% is generally acceptable. The presence of acid gases can be taken into account, using an appropriate correction such as in refs 28 or 29 in addition to this approach.

Dissolved solids (salts) in the water can change water properties such as reducing the water vapor pressure and changing water density and therefore reducing the water content of natural gases. To take into account the presence of salts, the extrapolation of the salinity correction factor in the McKetta-Wehe[13] chart to high salt concentrations is believed to underpredict the water content of a gas in equilibrium with brine.[39] The graphical correlation of ref 31 for the salinity correction factor is recommended instead.[39] The graphical correlation, developed from water vapor pressure depression due to the presence of salt, can be expressed as[7,39]

$$F_{salt} = 1 - 4.920 \times 10^{-3} \, w_{salt} - 1.7672 \times 10^{-4} \, w_{salt}^{2} \quad (34)$$

where w is the weight percent of salt in brine and the subscript *salt* refers to salt.

Table 6. Composition (Mol %) of Different Natural Gases[30]

| | gas gravity | | | | | | |
| | 0.5654 (NG₁) | 0.598 (NG₂) | 0.628 (NG₃) | 0.6326 (NG₄) | 0.6672 (NG₅) | 0.6395 (NG₆) | 0.8107 (NG₇) |
component							
helium	0.015	0.028		0.152	0.004	0.043	0.038
nitrogen	0.840	1.938	0.912	4.863	0.800	10.351	1.499
carbon dioxide	0.109	0.851		0.167	1.732	1.291	25.124
methane	98.197	93.216	88.205	86.345	84.339	83.847	70.144
ethane	0.564	2.915	8.360	6.193	8.724	3.460	2.520
propane	0.189	0.715	1.763	1.550	3.286	0.657	0.394
i-butane	0.029	0.093	0.293	0.214	0.311	0.093	0.067
n-butane	0.038	0.135	0.441	0.314	0.584	0.126	0.074
C₅	0.014	0.058	0.027	0.130	0.163	0.067	0.054
C₆₊	0.007	0.049	-	0.064	0.049	0.069	0.118

Table 7. Experimental and Predicted Water Content of Nitrogen in the L_W-V Region

reference	T/K	P/MPa	water content experimental (mol fraction)	water content this work (mol fraction)	AD %
Maslennikova et al.[45]	298.15	5.000	0.00066	0.00078	18.18
	298.15	7.500	0.00050	0.00057	14.00
	298.15	10.000	0.00045	0.00047	4.44
	323.15	5.000	0.00275	0.00290	5.45
	323.15	7.500	0.00199	0.00208	4.52
	323.15	10.000	0.00158	0.00168	6.33
	348.15	5.000	0.00835	0.00874	4.67
	348.15	7.500	0.00605	0.00619	2.31
	348.15	10.000	0.00500	0.00492	1.60
	373.15	5.000	0.02150	0.02227	3.58
	373.15	7.500	0.01500	0.01555	3.67
	373.15	10.000	0.01170	0.01220	4.27
Sidorov et al.[46]	373.15	5.066	0.02130	0.02200	3.29
	373.15	10.133	0.01170	0.01206	3.08
Althaus[30]	273.15	0.500	0.00125	0.00125	0.00
	273.15	1.500	0.00043	0.00044	2.33
	273.15	4.000	0.00017	0.00019	11.76
	273.15	6.000	0.00013	0.00014	7.69
	273.15	8.000	0.00011	0.00011	0.00
	273.15	10.000	0.00009	0.00010	11.11
	278.15	0.500	0.00178	0.00179	0.56
	278.15	1.500	0.00060	0.00063	5.00
	278.15	6.000	0.00018	0.00019	5.56
	278.15	8.000	0.00015	0.00016	6.67
	278.15	10.000	0.00012	0.00014	16.67
	283.15	0.500	0.00250	0.00251	0.40
	283.15	1.500	0.00084	0.00088	4.76
	283.15	4.000	0.00035	0.00037	5.71
	283.15	6.000	0.00025	0.00027	8.00
	283.15	8.000	0.00020	0.00022	10.00
	283.15	10.000	0.00018	0.00019	5.56
	293.15	1.500	0.00163	0.00166	1.84
	293.15	4.000	0.00065	0.00069	6.15
	293.15	6.000	0.00047	0.00050	6.38
	293.15	8.000	0.00038	0.00041	7.89
	293.15	10.000	0.00033	0.00035	6.06
Rigby and Prausnitz[41]	298.15	2.249	0.001529	0.00155	1.37
	298.15	3.090	0.001149	0.00116	0.96
	298.15	3.870	0.000941	0.00096	2.02
	323.15	2.109	0.00626	0.00626	0.00
	323.15	3.742	0.00368	0.00372	1.09
	323.15	5.982	0.00242	0.00250	3.31
	323.15	7.700	0.001956	0.00204	4.29
	348.15	4.221	0.01009	0.01016	0.69
	348.15	6.115	0.00721	0.00734	1.80
	348.15	8.972	0.00523	0.00535	2.29
	373.15	5.717	0.01994	0.01974	1.00
	373.15	7.948	0.01503	0.01479	1.60
	373.15	10.152	0.01218	0.01205	1.07

In summary, the predictive method developed in this work can predict the water content of natural gases near hydrate forming conditions. It is recommended to use this approach at temperature and pressure ranging 273.15−377.59 K and 0.1−13.81 MPa, as the experimental data at these ranges have been used to find the constants. Therefore, using this approach at higher pressures and temperatures may result in unreasonable predictions as at these conditions, water may be a compressible liquid, eq 24 for the fugacity coefficient

Table 8. Comparison between the Experimental Water Content Data of Different Sour Gases (with Low and Intermediate Concentrations of Acid Gases) and Predictions of the Approach Developed in This Work[a]

T/K	P/MPa	gas composition (mol fraction)			experimental	predictions, this work	AD%
		methane	CO_2	H_2S			
GPA Engineering Databook[13]							
311.15	13.800	0.89	0.11		8.08E−04	7.63E−04	5.57
311.15	13.800	0.8	0.2		8.08E−04	7.63E−04	5.57
327.15	10.300	0.92		0.08	2.21E−03	1.98E−03	10.41
344.15	6.900	0.89	0.11		5.67E−03	5.64E−03	0.53
344.15	6.900	0.8	0.2		5.59E−03	5.64E−03	0.89
344.15	6.900	0.83		0.17	5.79E−03	5.64E−03	2.59
344.15	9.430	0.725		0.275	4.90E−03	4.39E−03	10.41
Lukacs and Robinson[47]							
344.26	2.468	0.79		0.21	1.50E−02	1.41E−02	6.00
344.26	4.212	0.81		0.19	9.30E−03	8.67E−03	6.77
344.26	6.376	0.71		0.29	6.90E−03	6.05E−03	12.32
344.26	6.962	0.83		0.17	6.16E−03	5.62E−03	8.77
344.26	9.595	0.725		0.275	5.20E−03	4.35E−03	16.35
344.26	9.616	0.84		0.16	4.75E−03	4.34E−03	8.63
Ng et al.[48]							
322.04	1.379	0.75[c]	0.0625	0.1875	9.367E−03	8.87E−03	5.31
322.04	1.379	0.75[c]	0.1875	0.0625	8.74E−03	8.87E−03	1.49
322.04	10.339	0.75[c]	0.1875	0.0625	1.871E−03	1.56E−03	16.62
322.04	10.339	0.75[c]	0.0625	0.1875	1.814E−03	1.56E−03	14.00
366.48	1.379	0.75[b]	0.1875	0.0625	5.93E−02	5.93E−02	0.00
366.48	1.379	0.75[b]	0.0625	0.1875	5.9674E−02	5.93E−02	0.63
366.48	4.136	0.75[c]	0.1875	0.0625	2.9922E−02	2.09E−02	30.15
366.48	10.339	0.75[b]	0.1875	0.0625	1.1179E−02	9.45E−03	15.47
366.48	10.339	0.75[b]	0.0625	0.1875	1.0448E−02	9.45E−03	9.55
366.48	10.339	0.75[c]	0.1875	0.0625	1.0053E−02	9.45E−03	6.00

[a] Values are in mol fraction. [b] This mixture consists of methane and propane with a molar ratio equal to 95:5. [c] Composition of this mixture is 90% methane, 6% ethane, 2.5% propane, 0.6% i-butane, and 0.9% n-butane.

may not be acceptable, the solubilities of gases in water may not be negligible, and also the activity coefficient of water may not be taken unity. Using this approach for pure CO_2 and H_2S is not recommended. In addition, using more reliable water content data, especially at low-temperature conditions in the future, can increase the accuracy of this approach.

6. Conclusions

A review was made on the most commonly used predictive methods for the water content of natural gases.

A semiempirical approach based on the equality of fugacity concept was proposed for the estimation of the water content of natural gases in the temperature range 273.15−377.59 K and pressures up to 13.81 MPa.

New experimental data for the water content of a hydrocarbon gas mixture (94% methane + 4% ethane + 2% n-butane) were generated in the temperature range 288.15 to 313.14 K and pressures up to 17.56 MPa using a static-analytic apparatus, taking advantage of a pneumatic capillary sampler for fluid sampling.

The results of the predictive method developed in this work are in good agreement with the experimental data generated in this laboratory as well as other experimental data and predictive methods.

The developed correlation was able to estimate the water content of a natural gas containing up to 10% nitrogen. The presence of carbon dioxide as a minor component of the natural gas was also taken into account, and no degradation of the prediction was observed for a small amount of carbon dioxide.

Acknowledgment

Nomenclature

AAD = average absolute deviation
AD = absolute deviation
EOR = enhanced oil recovery
EoS = equation of state
FID = flame ionization detector
GC = gas chromatography
NG = natural gas
SG = specific gravity
TCD = thermal conductivity detector
VLE = vapor−liquid equilibrium
Vol = volume of the loop
min = minimum
max = maximum
A = parameter in eqs 8 and 9
B = parameter in eq 4, 9 and 24
C = parameter in eq 24
D = formation volume factor
F = correction factor
G = gas
H = hydrate
I = ice
L = liquid
N = number of components
P = pressure
Q = quadruple point
R = universal gas constant
T = temperature
V = vapor
Z = compressibility factor
a = parameter of eqs 10 and 25

b = parameter of eqs 11 and 25
c = parameter of eq 26
d = parameter of eq 26
f = fugacity
k = correction factor in eq 6
n = mol
p = pressure in psia
t = temperature in °F
v = molar volume
w = weight percent of salt in brine
x = mol fraction in the liquid phase
y = mol fraction in the vapor state
z = mol fraction in natural gas

Greek Letters

ΔV = volume change
γ = activity coefficient
ρ = density
ϕ = fugacity coefficient

Superscripts

I = ice state
L = liquid state
V = vapor state
sat = properties at saturation
sub = sublimation properties

Subscripts

HC = hydrocarbon
T = total
exp = experimental property
$salt$ = salt
g = gas
t = temperature
w = water
1 = first quadruple point
2 = second quadruple point

Literature Cited

(1) Mohammadi, A. H.; Chapoy, A.; Richon, D.; Tohidi, B. Experimental Measurement and Thermodynamic Modeling of Water Content in Methane and Ethane Systems. *Ind. Eng. Chem. Res.* **2004**, in press.

(2) Chapoy, A.; Coquelet, C.; Richon, D. Solubility measurement and modeling of water in the gas phase of the methane/water binary system at temperatures from 283.08 to 318.12 K and pressures up to 34.5 MPa. *Fluid Phase Equilibria* **2003**, *214*, 101−117.

(3) Chapoy, A.; Coquelet, C.; Richon, D. Measurement of the Water Solubility in the Gas Phase of the Ethane + Water Binary System near Hydrate Forming Conditions. *J. Chem. Eng. Data* **2003**, *48*, 957−966.

(4) Carroll, J. J. *Natural Gas Hydrates: A Guide for Engineers*; Gulf Professional Publishing: 2003.

(5) Carroll, J. J. The Water Content of Acid Gas and Sour Gas from 100° to 220 °F and Pressures to 10000 psia. *Presented at the 81st Annual GPA Convention*, Dallas, Texas, 11−13 March 2002.

(6) Bukacek, R. F. Equilibrium Moisture Content of Natural Gases. *Institute of Gas Technology, Research Bulletin 8*. 1955 (quoted in refs 4 and 5).

(7) McCain, W. D., Jr. *The Properties of Petroleum Fluids*, 2nd ed.; Pennwell Publishing Company: Tulsa, OK, 1990.

(8) Sharma, S. Equilibrium Water Content of Gaseous Mixtures, Ph.D. Thesis, University of Oklahoma, 1969.

(9) Sharma, S.; Campbell, J. M. Predict natural-gas water content with total gas usage. *Oil Gas J.* 4 Aug 1969, 136−137.

(10) Campbell, J. M. *Gas Conditioning and Processing, Volume 1: The Basic Principles*; Campbell Petroleum Series, Oklahoma, 1994.

(11) Behr, W. R. Correlation eases absorber-equilibrium-line calculations for TEG-natural gas dehydration. *Oil Gas J.* 7 Nov **1983**, 96−98.

(12) Kazim, F. M. A. Quickly calculate the water content of natural gas. *Hydrocarbon Process.* March **1996**, 105−108.

(13) *GPSA Engineering Data Book*, 11th ed.; Tulsa, OK, 1998.

(14) Arnold, K.; Stewart, M. *Surface Production Operations, Volume 2: Design of Gas-Handling Systems and Facilities*, 2nd ed.; Gulf Publishing Company: Houston, Texas, 1999.

(15) McKetta, J. J.; Wehe, A. H. Use This Chart for Water Content of Natural Gases. *Pet. Refiner (Hydrocarbon Process.)* August **1958**, *37(8)*, 153.

(16) Sloan, E. D., Jr. *Clathrate Hydrates of Natural Gases*, 2nd ed.; Marcel Dekker: New York, 1998.

(17) Ning, Y.; Zhang, H.; Zhou, G. Mathematical simulation and program for water content chart of natural gas. *Chem. Eng. Oil Gas* **2000**, *29*, 75−77 (in Chinese, quoted ref 4).

(18) Wiebe, R.; Gaddy, V. L. Vapor Phase Composition of Carbon Dioxide-Water Mixtures at Various Temperatures and at Pressures to 700 Atmospheres. *J. Am. Chem. Soc.* February **1941**, *63*, 475−477 (quoted in ref 13).

(19) Coan, C. R.; King, A. D., Jr. Solubility of Water in Compressed Carbon Dioxide, Nitrous Oxide, and Ethane. Evidence for Hydration of Carbon Dioxide and Nitrous Oxide in the Gas Phase. *J. Am. Chem. Soc.* April 21, **1971**, *93(8)*, 1857−1862.

(20) Gillespie, P. C.; Wilson, G. M. *Vapor-Liquid and Liquid−Liquid Equilibria: Water−Methane, Water−Carbon Dioxide, Water-Hydrogen Sulfide, Water-nPentane, Water−Methane-nPentane*; GPA Research Report 48; Tulsa, OK, April 1982.

(21) Song, K. Y.; Kobayashi, R. *The Water Content of CO_2 − rich Fluids in Equilibrium with Liquid Water and/ or Hydrates*; GPA Research Report 99; Tulsa, OK, June 1986.

(22) Song, K. Y.; Kobayashi, R. *Water Content Values of a CO_2 − 5.31 Mol Percent Methane Mixture*; GPA Research Report 120; Tulsa, OK, January 1989.

(23) King, M. B.; Mubarak, A.; Kim, J. D.; Bott, T. R. The Mutual Solubilities of Water with Supercritical and Liquid Carbon Dioxide. *J. Supercrit. Fluids* **1992**, *5*, 296−302.

(24) Selleck, F. T.; Carmichael, L. T.; Sage, B. H. Phase Behavior in the Hydrogen Sulfide − Water System. *Ind. Eng. Chem.* September **1952**, *44(9)*, 2219−2226 (quoted in ref 13).

(25) Robinson, J. N.; Moore, R. G.; Heideman, R. A.; Wichert, E. Estimation of the Water Content of Sour Natural Gases. *SPE J.* August **1977**, 281−286.

(26) Robinson, J. N.; Wichert, E.; Moore, R. G.; Heidemann, R. A. Charts help estimate H_2O content of sour gases. *Oil Gas J.* 6 February **1978**, 76−78.

(27) Robinson, J. N.; Moore, R. G.; Heidemann, R. A.; Wichert, E. Estimation of the Water Content of Sour Natural Gas. *Laurance Reid Gas Conditioning Conference*, 1980, Norman, OK.

(28) Maddox, R. N.; Lilly, L. L.; Moshfeghian, M.; Elizondo, E. Estimating Water Content of Sour Natural Gas Mixtures. *Laurance Reid Gas Conditioning Conference*, March 8, 1988, Norman, OK.

(29) Wichert, G. C.; Wichert, E. Chart estimates water content of sour natural gas. *Oil Gas J.* 29 March **1993**, 61−64.

(30) Althaus, K. *Fortschritt − Berichte VDI* **1999**, Reihe 3, 350 (in German), Oellrich, L. R.; Althaus, K. GERG − Water Correlation (GERG Technical Monograph TM14) Relationship Between Water Content and Water Dew Point Keeping in Consideration the Gas Composition in the Field of Natural Gas. *Fortschritt − Berichte VDI* **2000**, Reihe 3- Nr. 679 (in English).

(31) Katz, D. L.; Cornell, D.; Kobayashi, R.; Poettmann, F. H.; Vary, J. A.; Elenbaas J. R.; Weinaug, C. F. *Handbook of Natural Gas Engineering*; McGraw-Hill Book Company: 1959.

(32) Kobayashi, R.; Song, K. Y.; Sloan, E. D. *Petroleum Engineering Handbook*; Chapter 25: Phase Behavior of Water/Hydrocarbon Systems, Society of Petroleum Engineers: Richardson, Texas, 1987.

(33) Sloan, E. D.; Khoury, F. M.; Kobayashi, R. Water Content of Methane Gas in Equilibrium with Hydrates. *Ind. Eng. Chem. Fundam.* **1976** *15(4)*, 318−323.

(34) Song, K. Y.; Kobayashi, R. Measurement and Interpretation of the Water Content of a Methane-Propane Mixture in the Gaseous State in Equilibrium with Hydrate. *Ind. Eng. Chem. Fundam.* **1982**, *21(4)*, 391−395.

(35) Aoyagi, K.; Song, K. Y.; Kobayashi, R.; Sloan, E. D.; Dharmawardhana P. B. (*I*). The Water Content and Correlation of the Water Content of Methane in Equilibrium with Hydrates (II). The Water Content of a High Carbon Dioxide Simulated Prudhoe Bay Gas in Equilibrium with Hydrates; GPA Research Report 45; Tulsa, OK, December 1980.

(36) Aoyagi, K.; Song, K. Y.; Sloan, E. D.; Dharmawardhana, P. B.; Kobayashi, R. Improved Measurements and Correlation of the Water Content of Methane Gas in Equilibrium with Hydrate. *58th Annual GPA Convention* 1979, Denver, CO, March.

(37) Guilbot, P.; Valtz, A.; Legendre, H.; Richon, D. Rapid On-Line Sampler Injector. *Analusis* **2000**, *28*, 426−431.

(38) Daubert, T. E.; Danner, R. P. *DIPPR Data Compilation Tables of Properties of Pure Compounds*; AIChE, New York, 1985 (quoted in ref 39).

(39) Danesh, A. *PVT and Phase Behaviour of Petroleum Reservoir Fluids*; Elsevier Science B.V.: 1998.

(40) Tohidi-Kalorazi, B. *Gas Hydrate Equilibria in the Presence of Electrolyte Solutions*, Ph.D. Thesis, Heriot-Watt University, 1995.

(41) Rigby, M.; Prausnitz, J. M. Solubility of Water in Compressed Nitrogen, Argon, and Methane. *J. Phys. Chem.* January **1968**, *72(1)*, 330−334.

(42) Yokoyama, C.; Wakana, S.; Kaminishi, G. I.; Takahashi, S. Vapor − Liquid Equilibria in the Methane − Diethylene Glycol − Water System at 298.15 and 323.15 K. *J. Chem. Eng. Data* **1988**, *33*, 274−276.

(43) Kosyakov, N. E. et al. *Vopr Khim. Tekhnol.* **1982**, *47*, 33 (in Russian, data from Dortmund Data Base).

(44) Olds, R. H.; Sage, B. H.; Lacey, W. N. Phase Equilibria in Hydrocarbon Systems. Composition of the Dew-Point Gas of the Methane-Water System. *Ind. Eng. Chem.* October **1942**, *34(10)*, 1223−1227.

(45) Maslennikova, V. Ya.; Vdovina, N. A.; Tsiklis, D. S. Solubility of Water in Compressed Nitrogen. *Russ. J. Phys. Chem.* (*Zh. Fiz. Khim.*: *In Russian*) **1971**, *45(9)*, 1354.

(46) Sidorov, I. P.; Kazarnovsky, Y. S.; Goldman, A. M. *Tr. Gosudarst. Nauch.-Issled. I Proekt. Inst. Azot. Prom.* **1953**, *1*, 48 (data from Dortmund Data Base).

(47) Lukacs, J.; Robinson, D. B. Water Content of Sour Hydrocarbon Systems. *SPE J.* December **1963**, 293−297.

(48) Ng, H.-J.; Chen, C.-J.; Schroeder, H. *Water Content of Natural Gas Systems Containing Acid Gas*; GPA Research Report 174; Tulsa, OK, January 2001.