THE WATER CONTENT OF ACID GAS AND SOUR GAS FROM 100° TO 220°F AND PRESSURES TO 10,000 PSIA.

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ABSTRACT

The water content of natural gas is an important parameter in the design of facilities for the production, transmission, and processing of natural gas. It is important for natural gas engineers to accurately predict aqueous dew points.

This series of papers focuses on the water dew point of acid gases and sour gas over the range of temperatures from 100° to 220°F and for pressures up to 10,000 psia. In this the first paper, the water content of methane, carbon dioxide, and hydrogen sulfide is examined in detail.

First, the pertinent experimental data are reviewed. Then a few simple models for predicting the water content of natural gas will be discussed.. In addition, the application of the software package AQUAlibrium© will be investigated. AQUAlibrium is a model specifically designed for phase equilibrium involving water, acid gas, sweet and sour natural gas and is designed for use with both gas and non-aqueous liquid phases.

THE WATER CONTENT OF ACID GAS AND SOUR GAS FROM 100° TO 220°F AND PRESSURES TO 10,000 PSIA PART 1 – PURE COMPONENTS

INTRODUCTION

Water is associated with natural gas from the reservoir, through production and processing and is a concern in transmission.

Natural gas reservoirs always have water associated with them Thus gas in the reservoir is water saturated. When the gas is produced water is produced as well. Some of this water is produced water from the reservoir directly. Other water produced with the gas is water of condensation formed because of the changes in pressure and temperature during production.

In the sweetening of natural gas, the removal of hydrogen sulfide and carbon dioxide, aqueous solvents are usually used. The sweetened gas, with the H_2S and CO_2 removed, is saturated with water. In addition, the acid gas byproduct of the sweetening is also saturated with water. Furthermore, water is an interesting problem in the emerging technology for disposing of acid gas by injecting into a suitable reservoir - acid gas injection.

In the transmission of natural gas further condensation of water is problematic. It can increase pressure drop in the line and often leads to corrosion problems. Thus water should be removed from the natural gas before it is sold to the pipeline company.

For these reasons, the water content of natural gas and acid gas is an important engineering consideration.

It is the purpose of this paper to review the experimental data for the water content of pure methane, carbon dioxide, and hydrogen sulfide in the range of temperature 100° to 220°F and for pressure up to 10,000 psia. The pure components are examined not only because of their importance but also because they are a prerequisite for the study of the mixtures that are important in industrial practice.

In addition this paper will briefly review some methods for calculating water content and compare them with the experimental data from the literature.

In order to assess the accuracy of the various methods some method of estimating the error is required. The appendix gives the definitions of the average error (AE) and the absolute average error (AAE) as use in this paper.

LITERATURE REVIEW

In this section of the paper a discussion of the available experimental data is presented. Included in this discussion are some of the problems associated with the reported data.

Hydrogen Sulfide

The phase equilibria in the system hydrogen sulfide + water is the key to the discussion of the water content of sour gas. In addition, there is some controversy regarding the exact behavior of the system. Thus some time will be spent to review the data in the literature.

The Data of Selleck et al.

The benchmark study of the phase behavior in the system hydrogen sulfide + water is that of Selleck et al. [1]. This study included an investigation of vapor-liquid equilibrium (VLE) and liquid-

liquid equilibrium (LLE). Their data are for temperatures from 100° to 340°F and pressure up to about 5000 psia.

Carroll and Mather [2] re-evaluated the data of Selleck et al. and concluded that their raw data were valuable, but their smoothed data were dubious. Fig. 1 shows the water content of the H_2S-rich phases for three isotherms from the work of Selleck et al. This figure shows both the raw data and the smoothed curves. The behavior shown on this plot (and subsequent H_2S plots) is quite complicated and requires some explanation.

**Fig. 1 Water Content Hydrogen Sulfide at 120°, 160°F, and 220°F
Points and Smoothing from Selleck et al., (1952)**
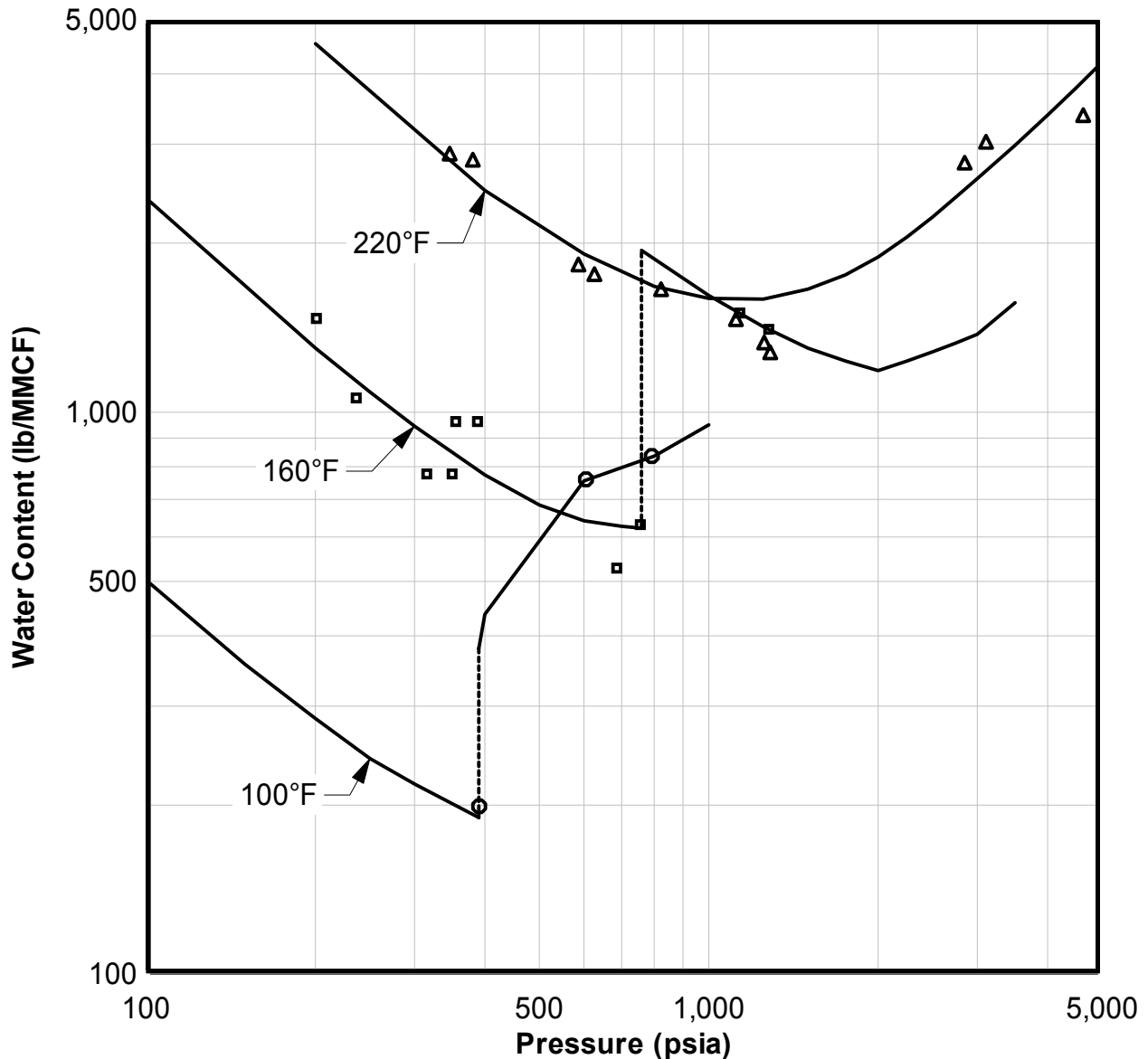
At low pressure the hydrogen sulfide + water mixture is in the gas phase. At low pressure the water content tends to decrease with increasing pressure, which is as expected.

Eventually a pressure is reached where the H_2S is liquefied. On this plot this is represented by the discontinuity in the curve and a broken line joins the phase transition. There is a step change in the water content when there is a transition from vapor to liquid. In the case of hydrogen sulfide the water content of the H_2S liquid is greater than the coexisting vapor. This is contrary to the behavior for light hydrocarbons where the water content in the hydrocarbon liquid is less than the coexisting vapor. As an example of the behavior in hydrocarbons see Kobayashi and Katz [3] for a description of the phase behavior in the system propane + water.

It is interesting to note that Selleck et al. did not believe that a three-phase transition occured at 220°F since this is at a temperature greater than the critical point of hydrogen sulfide. Therefore in Fig. 1 their smoothing of the 220°F isotherm does not show the phase transition. Subsequently Carroll and Mather demonstrated that a three-phase point _did_ occur at this temperature. This may seem impossible, but the reason is simple. It is because the mixture near the critical temperature contains enough water that the critical point is for a binary mixture and not simply for the pure component. The water is the non-aqueous phases cannot be neglected. Therefore the critical point of the binary mixture is at a temperature greater than the critical temperature of pure H_2S. Later in this paper predictions will be presented showing the phase transition at this temperature and how it fits the raw data of Selleck et al.

Another important observation is that there is a significant scatter in the raw data. The AAE from their smoothing is 10.0% for these temperatures. Even this value is a little low because Selleck et al. forced their smoothing through the few points for the water content of liquid H_2S and thus the error for these points is zero.

At 100°F there is only a single experimental point for the water content of the vapor. Based on this point a set of smoothed data was constructed. For the water content of the liquid at this temperature, only two points were measured.

The smoothed curve for the water content of liquid H_2S indicates that the water content is a strong function of the pressure. At 400 psia the water content from the smoothed values is 380 lb/MMCF and at 1000 psia it is 950 lb/MMCF. Although the two experimental points show a slight tendency to increase with pressure, they do not indicate the dramatic increases shown by the smoothing.

Ironically, at 160°F the two measured points for the water content of liquid H_2S show the water content decreases with increasing pressure – contrary to the observation discussed above for the 100°F isotherm. Based on these two points the smooth curve was constructed. This smoothed curve exhibits a minimum. It is difficult to justify a minimum in a function based on two points.

It would seem logical to conclude that the behavior at 100° and 160°F would be similar. It seems unlikely that there would be such a dramatic difference such as shown by the smoothed values. Thus a better conclusion based on the experimental data is that the water content of liquid H_2S, at temperatures removed from the critical point, is approximately independent of the pressure. Any variation in the water content is probably better explained as experimental error.

The main conclusion to be drawn from this discussion is that for the construction of a new model only the raw data of Selleck et al. should be used. Models based on their smoothed data have a built-in bias that is unnecessary and not supported by subsequent observations.

Other Data

Wright and Maass [4] reported some low-pressure (up to about 70 psia) data for the water content of the gas. These data were a part of their larger study on the solubility of hydrogen sulfide in water. These low-pressure data provide a lower limit for the testing a correlation. In addition, they are in the range of pressure of the amine regenerator and thus provide an important set of data for building models for estimating the water content of the acid gas off the regenerator.

In addition, Gillespie et al. [5] measured VLE and LLE data for this system. Their data are for pressures up to 3000 psia. These data will be examined in a subsequent section of this paper. As will be shown, these data are a key in revealing the true nature of the phase behavior in this system. It is the combination of the data of Gillespie et al and the raw data of Selleck et al. along with a rigorous thermodynamic model that reveals the true nature of the phase behavior in the system hydrogen sulfide + water.

Carbon Dioxide

In general the phase behavior of the system carbon dioxide + water is as complex as that of the system hydrogen sulfide + water. However for the range of temperature of this study a CO_2-rich liquid phase is not encountered; it only occurs for temperatures less than about 90°F. On the other hand, the water content of CO_2 does exhibit a minimum.

For carbon dioxide + water the landmark study is that of Wiebe and Gaddy [6]. Included in their study was the measurement of the water content of the CO_2-rich phase for pressures up to 10,300 psia.

Gillespie et al. [5] also measured phase equilibrium data for this system. In the range of interest in this study they measured the water content at two temperatures (167° and 200°F) and for pressure from 100 to about 3000 psia.

Two other important studies of the water content of CO_2 are those of Coan and King [7] and King et al. [8]. Coan and King included CO_2 in their study of the water content of gases. Their data are for temperatures up to 212°F and for pressure less than 750 psia. King et al. measured VLE in the region near the critical point of CO_2. Only one of their isotherms is in the region of interest in this study (104°F) and it was for pressures up to about 3000 psia. However the rest of their data are an important contribution as well.

There are a few low-pressure data for the water content of carbon dioxide in the temperature range of this study. Müller et al. [9] measured VLE at 212°F at pressures less than 340 psia. Zawisza and Malesinska [10] measured two aqueous dew points at 212°F. Both of these papers contain much more data, but it is beyond the range of temperature of this study. As with the low pressure H_2S data, these data are useful for testing low-pressure correlations, which in turn are useful for estimating the water content of the acid gas off the amine regenerator.

Another important study of the water content of carbon dioxide is that of Song and Kobayashi [11]. They measured a few points for the phase equilibria for this system, however their points are all out of the range of temperature of interest in this work.

Methane

The most important study of the aqueous dew points of pure methane is that of Olds et al. [12]. In this study they measured the dew point for pressures from 200 to 10,000 psia. Fortunately, the raw data of Olds et al. are included in the published paper and thus are readily available. Olds et al. also published tables of smoothed data.

There is some scatter in the raw data of Olds et al., the AE for their smoothing is 1.8% and the AAE is 5.2%. This provides a baseline for the comparison with other correlations.

In a study of the water content of gases Lukacs [13] measured the water content of pure methane at 160°F and pressures up to 1500 psia. Additional data from Lukacs will be examined in the second paper in this series.

As a part of their study, Gillespie at al. [5] also measured the water content of methane. In the range of interest in this study, they measured water content at 122° and 167°F and for pressures from 200 to 2000 psia.

Rigby and Prausnitz [14] studied what they termed the solubility of water in compressed gases. One of the gases they studied was methane. Three of the isotherms they studied were in the region of interest in this study (122°, 167°, and 212°F). Their measurements were for pressures up to about 1000 psia.

<p style="text-align:center">CALCULATING THE WATER CONTENT</p>

There are several models available for calculating the water content of natural gas. Only a few of them will be examined here.

In some of these models the vapor pressure of pure water is required as an input. Poor estimates of the vapor pressure will lead to poor estimates of the water content. In this paper the vapor pressure is calculated using the correlation of Saul and Wagner [15].

Ideal Model

In the Ideal Model, the water content of a gas is assumed to be equal to the vapor pressure of pure water divided by the total pressure of the system. This yields the mole fraction of water in the gas and this is value converted to lb water per MMCF by multiplying by 47,484. Mathematically this is:

$$w = 47484 \frac{P_{water}^{sat}}{P_{total}} \tag{1}$$

This equation yields w in lb/MMCF and the units on the two pressure terms must be the same; P_{water}^{sat} is the vapor pressure of pure water and P_{total} is the absolute pressure.

Clearly this model is very simple and should not be expected to be highly accurate except at very low pressures.

A more thermodynamically correct model is to include the effect of gases dissolved in the water. Mathematically this means:

$$w = 47484 \frac{x_{water} P_{water}^{sat}}{P_{total}} \tag{2}$$

In a typical application the solubility of the gas is not known and thus x_{water} is also unknown. Fortunately for hydrocarbons the solubility is so small that it is safe to assume that x_{water} equals unity. However, for acid gases, the solubility can be significant, even at relatively low pressure.

For the purposes of this paper, the Ideal Model is Eqn. (1).

McKetta-Wehe Chart

In 1958 McKetta and Wehe published a chart for estimating the water content of sweet natural gas. This chart has been modified slightly over the years and has been reproduced in many publications, most notably the *GPSA Engineering Data Book* [16].

To obtain the values in this study the original chart was photo-enlarged to two times its original size. Even so it is difficult to read the chart to an accuracy of more than two significant figures. Therefore the values reported here are only two significant figures.

The McKetta-Wehe chart is not applicable to sour gas, as will be clearly demonstrated here. Fortunately, most engineers who work in the natural gas industry are aware of this limitation. There

have been corrections proposed to make the chart applicable to these systems. Two will be discussed in the next paper in this series.

In addition, Kobayashi et al. [17] presented a correlation for the curves plotted in the McKetta-Wehe chart. Their equation is quite complicated and is only applicable for temperatures up to 120°F and to 2000 psia. Therefore, this equation will not be discussed further.

Sharma-Campbell Method

Sharma and Campbell [18] proposed a method for calculating the water content of natural gas, including sour gas. Although originally designed for hand calculations, this method is rather complicated. It is even rather complicated for computer applications.

The method will be described here. Given the temperature and the pressure, the procedure is as follows. Determine the fugacity if water at the saturation conditions (T and P_{water}^{sat}), which is designated f_{water}^{sat}, and the fugacity at the system conditions (T and P_{total}), designated f_{water}. A chart is provided to estimate the fugacity of water at the system conditions. Then the correlation factor, k, is calculated from the following equation:

$$k = \left(\frac{P_{water}^{sat}}{P_{total}} \right) \left(\frac{f_{water}^{sat}/P_{water}^{sat}}{f_{water}/P_{total}} \right) \left(\frac{P_{total}}{P_{water}^{sat}} \right)^{0.0049}$$

(3)

In this equation a consistent set of units should be used for the pressure and fugacity terms and then k is dimensionless. Then you must obtain the compressibility factor (z-factor), z, for the gas again at system conditions. They recommend using a generalized correlation for the compressibility. Finally the water content is calculated as:

$$w = 47484 k \left(\frac{f_{water}^{sat}}{f_{gas}} \right)^{z}$$

(4)

where f_{gas} is the fugacity of the dry gas calculated at system conditions. Again if a consistent set of units is used for the fugacity terms, then the calculated water content, w, is in lb/MMCF.

This method is rather difficult to use for hand calculations. First it requires the compressibility factor of the gas mixture. Next it requires the fugacity of pure water at system conditions. The chart given to estimate this value is only valid for temperatures between 80° and 160°F and for pressure less than 2000 psia. It is unclear how this method will behave if extrapolated beyond this range. Typically the calculation of a single fugacity is enough to scare away most process engineers. This method requires three fugacity calculations for a single water content estimate.

The pressure and temperature limitations make this method less useful for this study, where the pressure of interest ranges up to 10,000 psia and temperatures to 220°F. In addition, although this is intended to be a hand calculation method, it is a little difficult to use.

Bukacek

Bukacek [19] suggested a relatively simple correlation for the water content of sweet gas. The water content is calculated using an ideal contribution and a deviation factor. In equation form the correlation is as follows:

$$w = 47484 \frac{P_{water}^{sat}}{P_{total}} + B \tag{5}$$

$$log B = \frac{-3083.87}{459.6 + t} + 6.69449 \tag{6}$$

where w is in lb/MMCF and t is in °F.

This correlation is reported to be accurate for temperatures between 60° and 460°F and for pressure from 15 to 10,000 psia. Again, it is only applicable to sweet gas.

The pair of equations in this correlation is simple in appearance. The added complexity that is missing is that it requires an accurate estimate of the vapor pressure of pure water.

Ning et al.

Recently Ning et al. [20] proposed a correlation based on the McKetta-Wehe chart. This correlation merits a brief discussion because it further reveals how difficult it can be to correlate something that is as seemingly simple as the water content of natural gas.

Their basic equation is quite simple in appearance:

$$ln w = a_0 + a_1 T + a_2 T^2 \tag{7}$$

The coefficients a_0, a_1, and a_2, are are tabulated as a function of pressure, for pressures up to 14,500 psia (100 MPa). Unfortunately, the coefficients are not smooth functions of the pressure. Furthermore, there appears to be no simple correlations for this pressure function and the authors recommend interpolating between the tabular values. They recommend calculating the water content at pressures that span the values in the tables and then linearly interpolate to the pressure of interest.

AQUAlibrium

AQUAlibrium is a software package developed specifically for calculating equilibrium in systems containing acid gas or sour gas and water. In addition to calculating the water content of the gas, AQUAlibrium can be used to estimate the water content of the non-aqueous liquid. This is significant because occasionally the sour gas is in a liquid state. In addition, he software can be used to calculate the solubility of gases and liquids in water.

AQUAlibrium is based on a rigorous thermodynamic model, rather than mere empiricism. Thus it should be useful for extrapolating to conditions where no data exist. This is particularly true for the pressure.

The calculations presented in this paper were performed using AQUAlibrium Version 2.0i.

COMPARISON WITH DATA

For the pure components only four methods were examined: (1) the Ideal Model, (2) the McKetta-Wehe chart, (3) the Bukacek method, and (4) AQUAlibrium.

Methane

Since it should be the simplest gas to calculate the water content, methane will be considered first. Table I summarizes the errors from several prediction methods when compared with the experimental data from several sources. With the exception of the Ideal Model, all of the models accurately estimate the water content of pure methane.

Table I – Comparison of the Models for Estimating the Water Content of Methane

Source of Data	Ideal		McKetta		Bukacek		AQUAlibrium	
	AE	AAE	AE	AAE	AE	AAE	AE	AAE
Olds et al. [12]	45.22	45.22	-2.87	6.97	-1.66	5.16	-4.58	7.68
Lukacs [13]	12.86	12.86	3.61	3.78	-0.63	2.08	0.72	1.18
Rigby and Prausnitz [14]	12.79	12.79	-1.43	1.57	-3.58	3.58	-2.24	2.24
Gillespie et al. [5]	16.78	16.78	3.07	4.27	-3.29	4.00	-2.41	4.25
overall	33.13	33.13	-1.22	5.44	-2.01	4.41	-3.33	5.67

Fig. 2 shows the raw experimental data from Old et al. and their smoothing. Also shown on this plot are the predictions based on the ideal model outlined above.

At the pressure of the experimental data the Ideal Model is clearly not sufficiently accurate (the AE is 33% and the maximum error is around 75%, which occurs at the highest pressure). From Fig. 2 it can be seen that only for pressures below about 200 psia is the Ideal Model sufficiently accurate for design calculations.

The McKetta-Wehe chart is surprisingly accurate, AE of only 1.2% and the AAE is 5.4%, considering the difficulties reading the chart. Perhaps there is some bias the reading chart, however the accuracy remains very good. On the other hand, great effort was expended to read the chart as accurately as possible.

The Bukacek method is also very accurate for this range of temperatures and pressures, the AE is 2.0% and the AAE is 4.4%.

The errors for the McKetta-Wehe chart and Bukacek method are comparable to the smoothing of Olds et al. For all intents and purposes, these methods are equivalent to the smoothed data of Olds et al.

AQUAlibrium is slightly worse than either the McKetta-Wehe chart or the Bukacek equation, but it is still highly accurate. The AE for AQUAlibrium is -3.3% and the AAE is 5.7%, which is still a good prediction of the raw data.

Carbon Dioxide

The next most complex substance is carbon dioxide. Unlike methane, CO_2 exhibits a minimum in the water content. As will be demonstrated, these minima cannot be predicted by the relatively simple methods. Furthermore, it is well known that the simple methods are not accurate for estimating the water content of acid gases, which includes carbon dioxide.

Fig. 2 Data from Olds et al. (1942) for the Water Content of Methane (solid lines smoothing of Olds et al., broken lines Simple Model)
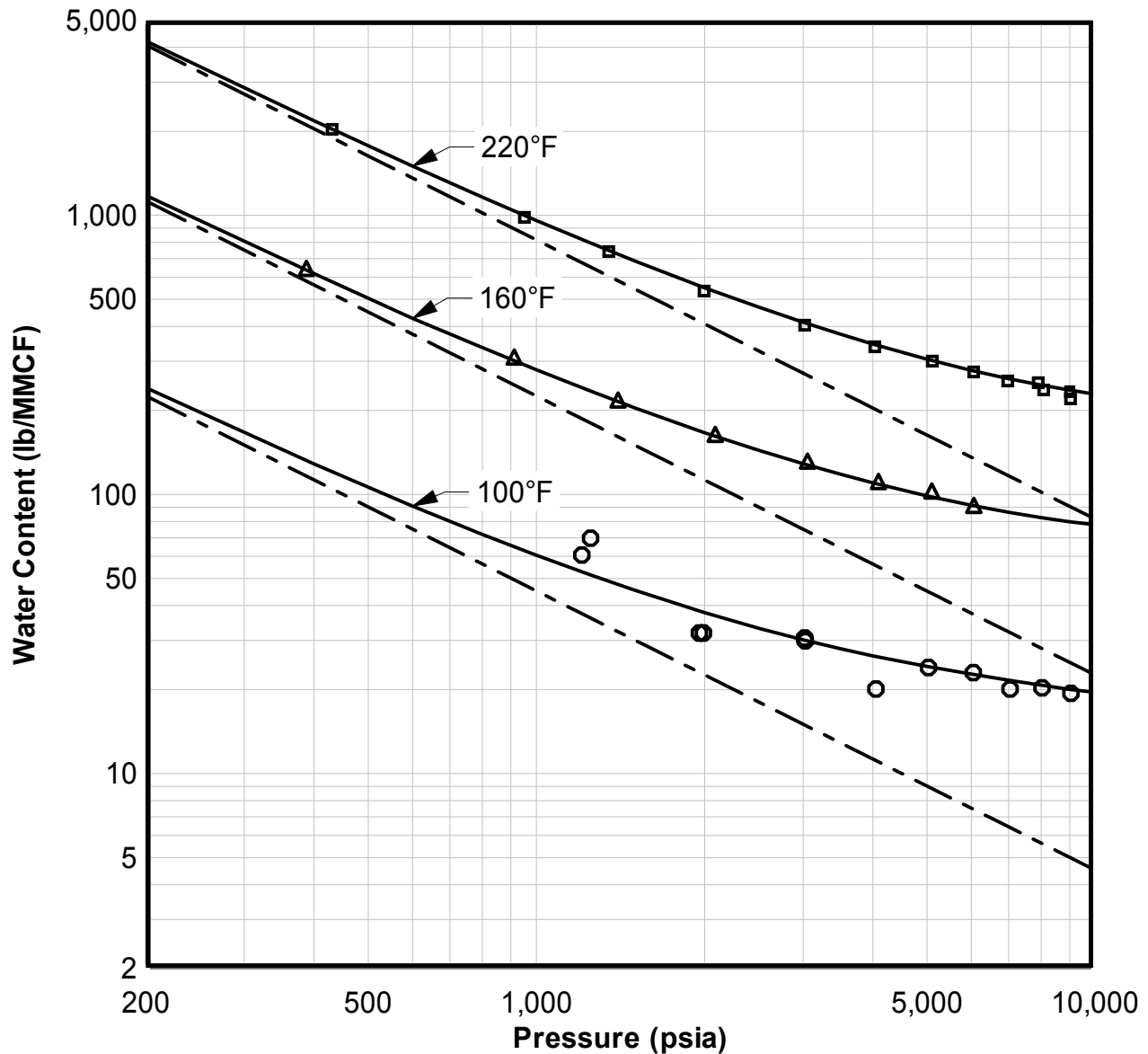
Table II summaries the errors for the various methods for predicting the water content of cabon dioxide.

Of the four methods examined, AQUAlibrium is clearly the best. AQUAlibrium predicts the correct qualitative behavior – only AQUAlibrium exhibits the minimum in the water content. And it is reasonably accurate with an AE of -3.4% and AAE of only 5.3% over the region of interest. Such errors are comparable to those for the much simpler methane calculations.

However, at low pressures (less than about 200 psia) the three simpler methods are useful to make order of magnitude estimates. In this region the Ideal Model, McKetta-Wehe chart and the Bukacek equation predict the water content to within about 10%.

Table II – Comparison of the Models for Estimating the Water Content of Carbon Dioxide

Source of Data	Ideal		McKetta		Bukacek		AQUAlibrium	
	AE	AAE	AE	AAE	AE	AAE	AE	AAE
Wiebe and Gaddy [6][1]	67.5	73.7	57.9	63.2	58.0	65.2	-6.10	7.02
Wiebe and Gaddy [6][2]	75.0	75.0	64.0	64.6	65.2	64.7	-2.11	3.08
Gillespie et al. [5]	31.2	31.2	28.1	28.1	22.8	22.8	-8.01	9.36
Coan and King [7]	19.5	19.5	16.1	16.1	11.2	11.2	-2.22	3.78
King et al. [8]	88.7	88.7	81.5	81.5	81.4	81.4	2.05	2.43
Müller et al. [9]	-4.67	5.35	-2.94	5.48	-7.70	7.70	-11.16	11.16
Zawisza and Malesinska [10]	10.49	10.49	12.87	12.87	8.77	8.77	7.59	7.59
overall[1]	41.6	41.6	36.9	37.0	33.5	34.4	-3.39	5.34
overall[2]	43.3	41.6	38.2	37.0	35.1	34.0	-2.24	4.22

1 – all of the points
2 – possibly anomalous point not included (see text for discussion of this point)

Fig. 3 shows the water content of CO_2 at 122° and 167°F. On this plot are shown the data points from three sources and the predictions from AQUAlibrium. At 122°F the model is an excellent fit of the experimental data from both Wiebe and Gaddy and Coan and King.

However, at 167°F there appears to be some significant disagreement. The data point of Wiebe and Gaddy (1941) at about 350 psia is clearly in error. It is almost one half the value from the other two sets of experimental data at approximately the same pressure. The error in the AQUAlibrium prediction of this point is about 70%. Therefore in Table II, the summary of the errors, errors are also calculated if this point is not included. When this single point is removed from the analysis the AAE for AQUAlibrium improves to only 3.1%.

In addition from Fig. 3 the minima in the water content are clear. At 122°F the minimum is at about 1000 psia, whereas at 167°F the minimum is at about 1500 psia.
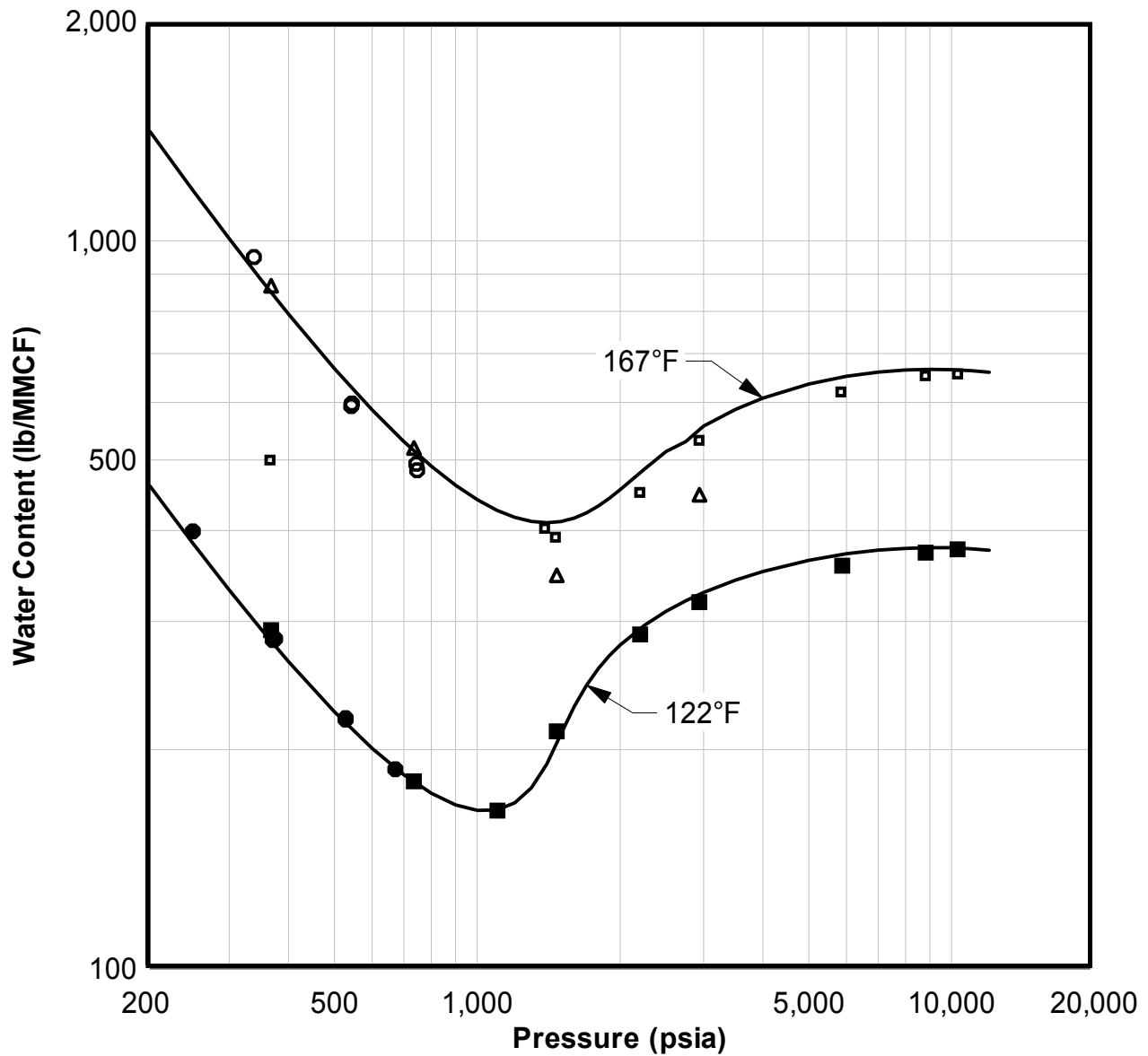
Hydrogen Sulfide
H_2S is the most complex of the pure components studied in this paper. In addition to exhibiting a minimum in the water content, a non-aqueous liquid is encountered in the range of pressure and temperature examined in this study.

Table III lists the errors from four models. The errors are separated into the predicted water content of the gas, the water content of the liquid, and then the combined, overall error.

At low pressures, less than 50 psia even the simple models are accurate as reflected by the errors for the data from Wright and Maass. At these low pressures all methods predict the experimental data to within a few percent. For moderate pressures, up to 200 psia, the simple models are still not too bad, errors less than about 20%. As the pressure continue to increase, and as the phase changes from vapor to liquid, the errors for the simple models become very large – up to 90%.

**Fig. 3   Water Content of Carbon Dioxide at 122°F and 167°F
(Data points: squares - Weibe and Gaddy, circles - Coan and
King, and triangles - Gillespie et al. Curves from AQUAlibrium)**

As was mentioned earlier, it is well known that the simple methods are not accurate for estimating the water content of hydrogen sulfide. This work confirms that observation.

Table III – Comparison of the Models for Estimating the Water Content of Hydrogen Sulfide

Source of Data	phase	Ideal		McKetta		Bukacek		AQUAlib.	
		AE	AAE	AE	AAE	AE	AAE	AE	AAE
Selleck et al. [1]	both	49.1	49.1	44.1	44.1	43.0	43.0	2.57	10.41
	gas	28.7	28.7	23.6	23.6	22.3	22.3	6.45	9.45
	liquid	90.5	90.5	87.0	87.0	86.9	86.9	-8.69	10.05
Wright and Maass [4]	gas	-0.50	0.50	-1.50	1.64	-1.54	1.54	-1.23	1.29
Gillespie et al. [5]	both	65.9	65.9	62.8	62.8	61.2	61.2	-4.34	7.48
	gas	21.8	21.8	20.0	20.0	15.5	15.5	3.67	4.88
	liquid	89.2	89.2	85.3	85.3	85.3	85.3	-8.56	8.85
overall	both	43.0	43.3	39.8	40.6	38.8	39.6	-1.22	6.84
	gas	16.0	16.4	13.2	14.4	11.7	12.9	2.92	5.35
	liquid	89.5	89.5	85.8	85.8	85.7	85.71	-8.59	9.18

Of the methods discussed in this work, only AQUAlibrium is designed to handle both gas and non-aqueous liquid phases. Therefore it is no surprise that overall it is the best model of the four. Overall the average errors are respectable, less than 3%. The AAE is significantly large, about 10%, which is more due to the scatter in the experimental data. For the vapor region the AAE is 6.5% and for liquids it is only 9.5%, both quite respectable.

As was discussed earlier in this paper, Selleck et al. presented smoothed values based on their experimental data. The AE for their smoothed data is 2.0% and the AAE is 6.0% for all of the data. In the vapor region, the AE is 1.9% and the AAE is 10.0% and for the liquid region the AE is 2.8% and the AAE is 10.5%. These errors are comparable to those from AQUAlibrium; thus it is fair to conclude that the model used in AQUAlibrium is as accurate as the smoothing of Selleck et al. (1952).

Fig. 4 shows two isotherms for the water content of hydrogen sulfide. This plot shows the experimental data of Gillespie et al. and the predictions from AQUAlibrium and from the Ideal Model. From this graph it is clear that AQUAlibrium is an excellent qualitative model of the experimental data. The vertical broken lines indicate the three-phase point.

The Ideal Model, the sloping broken lines, is good in the low-pressure limit but at high pressure it is grossly in error, but for the high-pressure gas the Ideal Model exhibits significant deviations. Furthermore, the Ideal Model cannot predict the phase change and the effect of that change on the water content.

Among the other interesting observations that can be made from Fig. 4 is that the water content of liquid H_2S at 100°F is indeed only a weak function of the pressure. Both the experimental data of Gillespie et al. and the calculation from AQUAlibrium exhibit this behavior. This is contrary to the smoothed data from Selleck et al.

**Fig. 4 Water Content of Hydrogen Sulfide at 100 and 200°F
(Data from Gillespie at al., 1984, solid curves from AQUAlibrium,
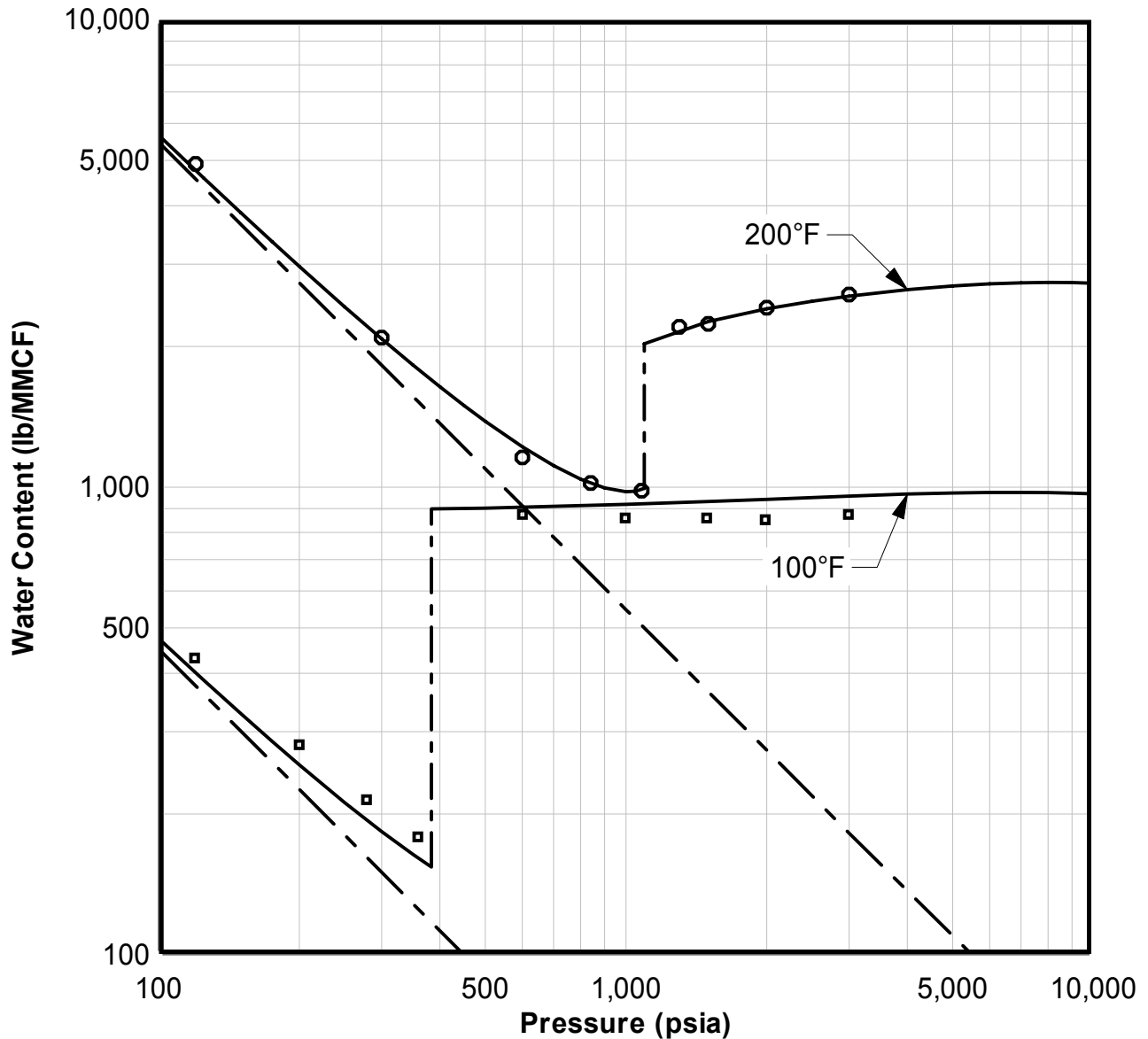and sloping broken cruves from Ideal Model)**

Fig. 5 shows two more isotherms for the water content of hydrogen sulfide (120° and 220°F) showing the raw data of Selleck et al. and the calculation from AQUAlibrium. It is useful for the reader to compare this figure to Fig. 1. It is important to reiterate that at 220°F Selleck et al. did not believe a three-phase point existed; a point that was later found by Carroll and Mather. In spite of the misinterpretation of Selleck et al., for this isotherm it is fair to conclude that AQUAlibrium is an accurate fit of the raw data.

Fig. 5 Water Content Hydrogen Sulfide at 120° and 220°F
(Data from Selleck et al., 1952, curves from AQUAlibrium)
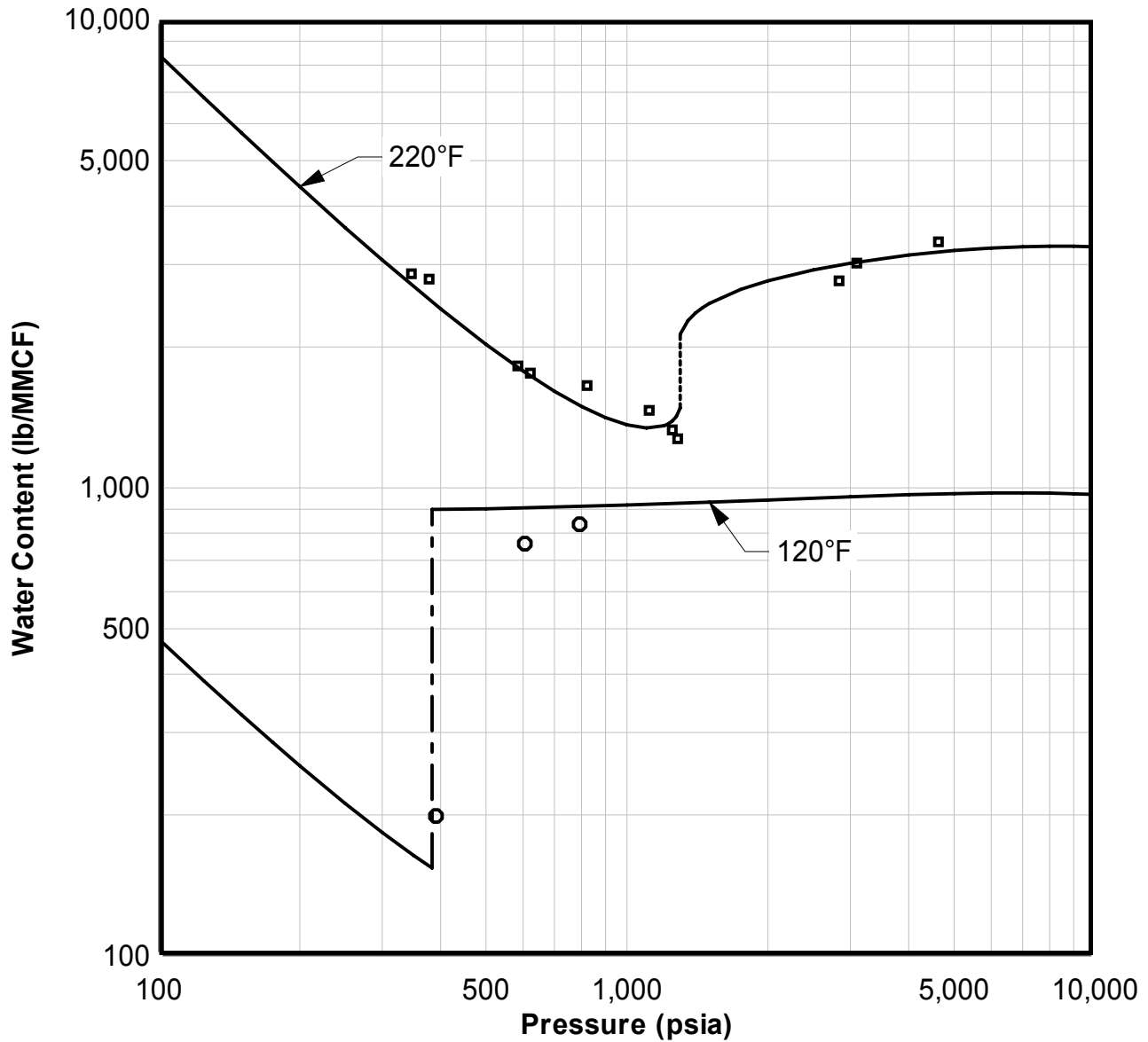
Also, AQUAlibrium does not show the strong pressure dependence of the water content of liquid H_2S at 120°F. It is useful for the reader to compare the water content at 120°F, with that at 100°F (Fig. 4). AQUAlibrium is probably a better interpretation of the raw data than is the smoothing of Selleck et al.

CONCLUSIONS

The Ideal Model for estimating the water content of gas should only be use at low pressure, less than 50 psia. However, for the low-pressure region it can be used for acid gases as well as sweet gas. At pressure up to 200 psia the Ideal Model will have errors of up to 25% and thus should only be used for order of magnitude estimates only. At higher pressure the method should not be used.

However, this demonstrates that the Ideal Model does provide the correct limiting behavior, even for acid gases. Thus, any advanced model should also exhibit this limiting behavior.

As demonstrated in this paper, the methods of McKetta-Wehe and Bukacek are accurate for sweet gases throughout the range of pressure and temperature examined in this study. However, these methods are only accurate for low-pressure estimates when dealing with acid gas. These methods cannot handle the minimum in the water content observed in both H_2S and CO_2 and they cannot handle the water content of the liquid, such as was demonstrated for H_2S.

AQUAlibrium is accurate for all three scenarios – sweet gas, acid gas (including the minima in the water content), and liquefied gases. Unlike the other models, AQUAlibrium was specifically designed to handle all three of these regions.

It is important to note that other software packages are available for predicting the water content of sweet gas, sour gas, and acid gas. The users of these programs should verify for themselves that the predictions are sufficiently accurate for their purposes.

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APPENDIX A – Definition of Error Estimates Used in this Paper

The average error, AE, expressed as a percentage, is defined as:

$$AE = \frac{1}{NP} \sum_{i=1}^{NP} \frac{value(i) - estimate(i)}{value(i)} \times 100\%$$

(A-1)

where "value" is the value used to construct the model, "estimate" is the estimated value at the same conditions, and NP is the number of points. The average error can have either a positive or negative values, but regardless of the model, however the better the fit the closer this value is to zero.

The absolute average error, AAE, is defined as:

$$AAE = \frac{1}{NP} \sum_{i=1}^{NP} \frac{|value(i) - estimate(i)|}{value(i)} \times 100\%$$

(A-2)

The difference between these two is that in the average error positive and negative errors tend to cancel each other, which makes the model look better than it actually is. The average absolute error can only have a positive value, because of the absolute value function. It is a better indication of the "goodness of fit" than is the average error. A small AE and a relatively large AAE usually indicates a systematic deviation between the function (values) and the predictions (estimates).

There are other methods for estimating the error of a model, but these are sufficient for our purposes.

THE WATER CONTENT OF ACID GAS AND SOUR GAS FROM 100° TO 220°F AND PRESSURES TO 10,000 PSIA. PART 2 – MIXTURES

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ABSTRACT

The water content of the pure components is an interesting application and an important prerequisite. However, it is almost always mixtures that are encountered in industrial practice. Thus, it is important to review the available data for mixtures and examine the accuracy of the methods for predicting the water content of sour gas.

This paper, the second in the series, includes a discussion of the available experimental data and comparison of a few available models. It will also include some discussion of the water content of the non-aqueous liquid phase, which may also be encountered in these mixtures. As with the previous paper, this paper will be limited to temperatures from 100° to 220°F and for pressures up to 10,000 psia.

Only limited data are available in the literature for the water content of sour gas mixtures. The new data of Ng et al. [1] will be reviewed. These data are an extensive new set of data covering a wide range of temperature and pressures and are for several compositions. However, other data will be examined as well.

THE WATER CONTENT OF ACID GAS AND SOUR GAS FROM 100° TO 220°F AND PRESSURES TO 10,000 PSIA PART 2 – MIXTURES

INTRODUCTION

As was discussed in the previous paper it is important for engineers to be able to accurately predict the water content of natural gas. The water content of sour gas, acid gas, and liquefied gases pose an additional problem.

LITERATURE REVIEW

There are only limited data available for the water content of mixture of the components that compose natural gas. This is especially true for sour gas mixtures. This makes such data quite valuable.

Lukacs [2] measured the water content for a few mixtures of methane and hydrogen sulfide at 160°F at pressures up to 1400 psia. He also presented data for the water content of pure methane and those data were examined in the first paper in this series. The errors in the water content for the data of Lukacs [2] were obtained by performing repeated measurements. For the sour gas mixtures, their water content mixtures are accurate to within ±3.5%, with a maximum error of 8%

Another interesting investigation was performed by Huang et al. [3]. They studied two mixtures of methane + carbon dioxide + hydrogen sulfide + water and their study included vapor-aqueous liquid, aqueous liquid-non-aqueous liquid and vapor-liquid-liquid equilibria. However only their water content data will be considered here.

The measurements of Huang et al. are at three temperatures: 100°, 225°, and 350°F. Although the last two isotherms are outside the range of interest in this study, the second one is only slightly so. Thus the 225°F isotherm will be included in this analysis. Their data were for pressure from 700 to 2500 psia. For the water composition they state that the measurements of the water concentration are accurate to ±0.2 mol%, which is equivalent to ±95 lb/MMCF. This is a very large error for some of the measurement. The measured water contents for the first mixture at 100°F are only approximately 90 lb/MMCF. Perhaps this is a misprint and the errors are ±0.02 mol%, which would make the largest errors on the order of ±10%. On the other hand several of the composition in this paper do not sum to unity. The error in the sum is as large as 0.32 mol%. In other measurements such an error may not be significant but for these water content measurements this is quite large. For the calculations presented the compositions were first calculated on a water-free basis and the renormalized. The stated experimental water mole fractions were converted to lb/MMCF without renormalizing.

Song and Kobayashi [4] reported some water content data for a mixture of CO_2 (94.69 mol%) and methane (5.31 mol%). Although almost all of their data are outside the range of temperature of interest in this work, this is interesting set of data, which demonstrate the effect of a relatively small amount of methane on the water content of CO_2.

Recently Ng et al. [1] published a set of VLE data for sour gas mixtures at 120° and 200°F and pressures from 200 to 10,000 psia. Because of the range of temperature and pressure covered by these experiments, they are a significant contribution to the literature. In addition to presenting water content information, these data also include measurements of the solubility of gas mixtures in water and the densities of the equilibrium phases. However, in this paper only their water content data will be examined. Finally, a detailed discussion of the errors with these data is presented later in this paper.

CALCULATING THE WATER CONTENT

Methods for calculating the water content of natural gas were presented in the previous paper and therefore will not be repeated here. Most of those methods were specifically designed for sweet gas systems. The reader is referred to the first paper for the details of those methods. Some of those methods will be used for predicting the water content of the mixtures examined in this paper.

In addition there are some methods that are specifically designed for estimating the water content of sour gas mixtures. They will be reviewed briefly in the sections that follow.

Maddox Correction

Maddox [5] developed a method for estimating the water content of sour natural gas. His method assumes that the water content of sour gas is the sum of three terms: 1. a sweet gas contribution, 2. a contribution from CO_2, and 3. a contribution form H_2S.

The water content of the gas is calculated as a mole fraction weighted average of the three contributions.

$$w = y_{HC}w_{HC} + y_{CO_2}w_{CO_2} + y_{H_2S}w_{H_2S} \tag{1}$$

where w is the water content, y is the mole fraction, the subscript HC refers to hydrocarbon, CO_2 is carbon dioxide and H_2S is hydrogen sulfide. Charts are provided to estimate the contributions for CO_2 and H_2S. The chart for CO_2 is for temperatures between 80° and 160°F and the chart for H_2S is for 80° and 280°F. Both charts are for pressures from 100 to 3000 psia.

To use this method, one finds the water content of sweet gas, typically from the McKetta-Wehe chart then the corrections for the acid gases are obtained from their respective charts.

Although these charts have the appearance of being useful for calculating the water content of pure H_2S and pure CO_2 the author advises that they should not be used for this purpose.

In the appendix of this paper the charts are converted into mathematical expressions that can then be used for computer calculations. Finally a computer program was written that combined the sweet gas estimate from Bukacek (see Part 1 of this series of papers) and the correlations of the Maddox correction.

Robinson et al. Charts

Robinson et al. [6] used an equation of state method to calculate the water content of sour natural gases. Using their equation of state model they generate a series of charts; one chart for 300, 1000, 2000, 300, 6000, and 10,000 psia. The temperature range for the charts is 50° to 350°F, although it is slightly narrower at some pressures. A third parameter on the chart is the H_2S equivalent and is calculated as follows:

$$y_{H_2S}^{equiv} = y_{H_2S} + 0.75\,y_{CO_2} \tag{2}$$

The charts are applicable for H_2S equivalent up to 40 mole %.

These charts remain popular, but they require multiple interpolations, which makes them a little difficult to use. This method will not be examined in detail in this paper.

Wichert Correction

Wichert and Wichert [7] proposed a relatively simple correction based on the equivalent H_2S content of the gas. The equivalent H_2S content used in this correlation is that defined by Eqn. (2).

They presented a single chart where given the temperature pressure and equivalent H_2S one could obtain a correction factor, F_{corr}. Correction factors range from 0.95 to 5.0. The correction factors tend to increase with increasing H_2S equivalent and increasing pressure, and decrease with increasing temperature.

The water content of the sour gas is calculated as follows:

$$w = F_{corr} w_{M-W}$$ (3)

where w is the water content of the sour gas, F_{corr} the a correction factor, and w_{M-W} is the water content of sweet gas from the McKetta-Wehe chart. F_{corr} is dimensionless so the two water content terms simply have the same units, typically lb/MMCF, in order to be dimensionally consistent.

This method is limited to an H_2S equivalent of 55 mol% and is applicable for temperatures from 50° to 350°F and pressure from 200 to 10,000 psia.

This method is much simpler to use than the charts of Robinson et al. [6] since it does not require the interpolations of the earlier method.

AQUAlibrium

AQUAlibrium was introduced in Part 1 of this series of papers. It will be used in this paper for estimating the water content of mixtures. One advantage of AQUAlibrium over the simpler methods is that AQUAlibrium is applicable for calculating the water content of both the gas and the non-aqueous liquid phases. The simple methods cannot be used to predict the water content of a non-aqueous liquid.

All of the calculations presented in this paper were performed using AQUAlibrium Version 2.0i.

<center>WATER CONTENT OF MIXTURES</center>

Fig. 1 shows the water content of methane, carbon dioxide, and hydrogen sulfide at 120°F. The curves were calculated using AQUAlibrium and the accuracy of this method for these components was demonstrated in the first paper in this series. This figure shows the diversity of behavior that occurs.

At low pressure the water content is essentially the same for all three substances. At these low pressures the water content is a function of the temperature and pressure and is accurately predicted using the ideal model. As the pressure increases the phase behavior for the three substances is significantly different.

The water content of methane, as an example of sweet gas, continually decreases as the pressure increases. This is reflected in the McKetta-Wehe chart for estimating the water content of sweet gas, which was demonstrated to be highly accurate for estimating the water content of methane.

On the other hand, the water content of carbon dioxide exhibits a minimum. This is characteristic of acid gases and very sour gas mixtures.

Finally hydrogen sulfide liquefies. For this reason the water content of hydrogen sulfide exhibits a discontinuity. Carbon dioxide behaves similarly, but at lower temperature. The temperatures at which a CO_2-rich liquid forms is outside the range of interest here.

It is logical to assume that the behavior of the mixtures would have characteristics of the three pure components. Sour gas mixtures that contain only a small amount of CO_2 and H_2S would behave in

Fig. 1 Water Content of Three Gases at 120°F
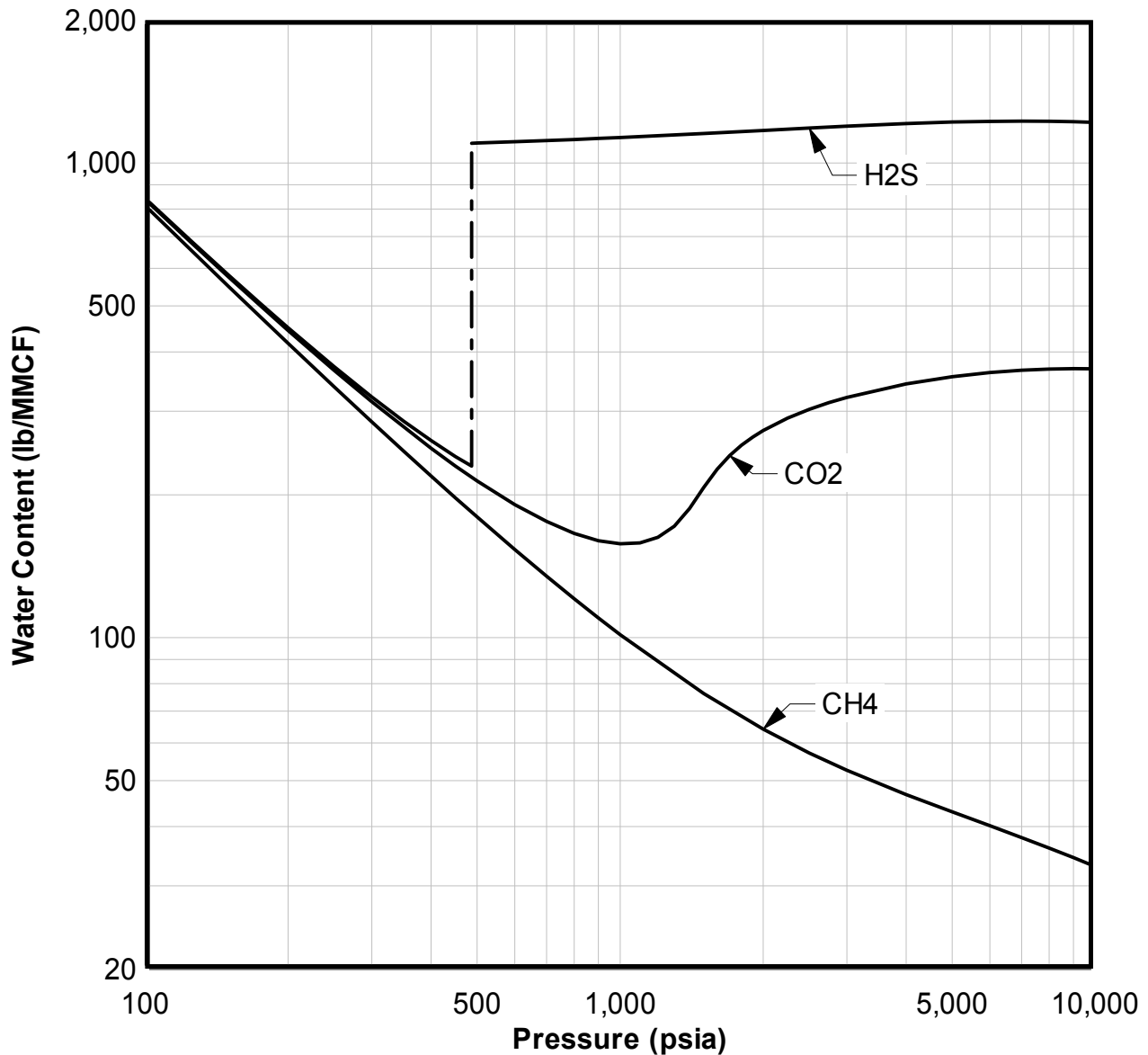
a manner similar to pure methane. That is, the water content of these gases would be a continually decreasing function of the pressure. Very sour mixtures would behave more like pure CO_2 in as much as they would have a minimum in the water content, but they would not form a second liquid. Finally, mixtures rich in H_2S would behave in a fashion similar to pure H_2S. These mixtures would liquefy if the pressure and temperature are in the correct range.

COMPARISON WITH DATA

Table I shows the data from Lukacs [2] and predictions from AQUAlibrium, the Wichert correlation, and the Bukacek-Maddox method. For comparison purposes, the McKetta-Wehe chart predictions are also included. For this set of data the AE for AQUAlibrium is less than 0.7% and the

AAE is 2.1%. The Wichert correlation is an excellent prediction of this set of data with an AE of only -0.7% and an AAE of 2.8%. The Bukacek-Maddox method consistently overpredicted the water content on average by about 11%.

Table I – Comparison with the Data of Lukacs [2]

Temp °F	Pressure psia	H₂S Conc. mol%	Water Content, lb/MMCF				
			exper.	McKetta	AQUA.	Wichert	B-M
159.8	1395	16.0	226	220	235	231	260
160.0	1010	17.0	292	280	294	294	322
160.0	611	19.0	442	410	435	418	467
160.0	358	21.0	712	700	692	707	723
160.0	1392	27.5	247	220	255	264	297
160.0	925	29.0	328	300	329	330	375

• B-M is the combined Bukacek-Maddox method discussed in the text and appendix.

Another interesting set of data was extracted from the GPSA Engineering Data Book [8]. The original source of these data is a little unclear, although some of the data are from Lukacs [2] and thus are a repeat from the previous table. The table from the GPSA Data Book is repeated here as Table II, but predictions from AQUAlibrium and the Bukackek-Maddox method are also included.

Next consider the data of Huang et al. [3]. The Wichert correlation can only be used to predict the first mixture. For the second mixture the H₂S equivalent is outside the range of their correlation. The Bukacek-Maddox method can only be used for a few points as well. Because the mixtures contain CO_2 the Bukacek-Maddox method is limited to 160°F. AQUAlibrium can be used to predict the water content for all points, including the liquid-liquid points.

Table III summarizes the errors for the predicted water content of the Huang et al. [3] mixtures using several methods described earlier. The Wichert correlation is highly accurate, but it is only applicable to about half of the data. AQUAlibrium is also a good prediction of these values, but only for the water content of the vapor. The errors for the two points for the water content of the liquid, the errors from AQUAlibrium are about 30%. The Bukacek-Maddox method is surprisingly poor at predicting these data.

Table II – Fig. 20-12 from the *GPSA Engineering Data Book* with AQUAlibrium and the
Bukacek-Maddox Method Added for Comparison

Mixture	Tem °F	Pres psia	Water Content, lb/MMCF				
			Exper.	Eq 20-1	Fig. 20-10 & 20-11	AQUA-librium	B-M
11% CO_2/89% C_1	100	2000	40.6	42	39.2	42	39.4
11% CO_2/89% C_1	160	1000	286	277	287	284	287
20% CO_2/80% C_1	100	2000	40.6	43	44.1	46.0	40.7
20% CO_2/80% C_1	160	1000	282	278	287	293	295
8% H_2S/92% C_1	130	1500	111	105	112	105	113
27.5% H_2S/72.5% C_1	160	1367	247	258	273	258	300
17% H_2S/83% C_1	160	1000	292	278	290	296	325
60% CO_2/10% H_2S/30% C_1	100	1100	81	72	NA	82	75
10% CO_2/81% H_2S/9% C_1	100	1900	442	72	NA	556	120
5.31% C_1/94.69% CO_2	77	1500	109.2	38	NA	126.3	27.2
5.31% C_1/94.69% CO_2	122	2000	164.6	105	NA	235.6	100

Note: • Eq. 20-1 and Fig. 20-10 and 20-11 refer to the *GPSA Engineering Data Book*, where Eq. 20-1
   is the method of Maddox and Fig. 20-10 and 20-11 are the figures of Robinson et al.
   • B-M is the combined Bukacek-Maddox method discussed in the text and appendix.

Table III – Comparison of the Various Methods for Predicting the Water Content of the Data of
Huang et al. [3]

Method	Points	AE (%)	AAE (%)	MaxE (%)
McKetta-Wehe	12	46.3	46.3	91.9
Bukacek	12	46.8	46.8	92.0
Bukacek-Maddox	6	39.1	39.4	72.9
Wichert	7	-0.2	3.9	7.4
AQUAlibrium – all points	12	-10.2	10.4	31.1
AQUAlibrium – vapor only	10	-6.5	6.9	17.6

Data of Ng et al.

The new data from Ng et al. [1] are an important set and deserve special treatment. Most of these data are for the quinary system: water, methane, propane, hydrogen sulfide, and carbon dioxide. There are some data for an eight-component mixture as well.

In the analysis of the water content of the gas, the mole fraction water in the measured composition was removed and then the composition was normalized to obtain the water-free composition. The mole fraction water in the gas was then converted to a lb/MMCF equivalent.

In addition, two mixtures deserve special considerations. These mixtures are those designated 5HC-95AC2 and 5HC-95AC3 by the authors and are very rich in the acid gas components. The first mixture has an estimated critical temperature of approximately 120°F. Therefore the 120°F data points are nearly at the critical temperature. The critical region is typically difficult for performing equilibrium calculations. Thus these points present a significant challenge. The second mixture has an estimated critical temperature of approximately 160°F. Therefore, the three high pressure points for the this mixture at 120°F are liquid-liquid equilibrium points.

The 200 psia Isobar

From the analysis of the pure component data it was concluded that to within about 10% the water content at 200 psia is independent of the component. This assumption was extrapolated to mixtures based on this observation and based on the current models for water content. For example the Wichert correlation indicates that at 200 psia the water content of a sour gas at 200 psia for sour gas is within 5% of the value for sweet gas.

First consider the data at 200°F and 200 psia. Ng et al. [1] measured 9 points at these conditions. The average water content for these points is 2930 lb/MMCF and the range of experimental water content is less than 10%. As a function of H_2S equivalent the experimental points show a maximum water content at approximately 60 mol%, although such a conclusion may not be justified from the data. These data reinforce the observation stated earlier regarding low pressure water content.

Fig. 2 shows the experimental water content at 200°F and 200 psia as a function of H_2S equivalent. Shown on this plot is the prediction from the Wichert correlation. Note at these conditions the Wichert correlation predicts that the water content decreases with increasing H_2S equivalent. It also appears that the McKetta-Wehe point for sweet gas is a little low at these conditions, but a close review of the chart indicates that the water content at 200°F and 200 psia is 2600 lb/MMCF.

Also shown on this plot is the Bukacek-Maddox correlation, which was constructed assuming that the H_2S equivalent was equal to the H_2S mole fraction. This method predicts the experimental data of Ng et al. [1] at 200°F and 200 psia to within better than 10%. It is worth noting that these conditions are outside the range for the CO_2 contribution for the Maddox correction, so this correlation probably should not have been used for this example.

In addition predictions from AQUAlibrium are also presented. The curve labeled AQUAlibrium (simplified) on Fig. 2 was constructed based on mixtures of methane + hydrogen sulfide. The points labeled AQUAlibrium (actual) are the values calculated using the experimental compositions. At these conditions the simplified and actual are approximately coincident.

Furthermore, It is clear from this plot that this prediction from AQUAlibrium and the Bukacek-Maddox method are essentially equivalent.

However, from all of this it is fair to conclude that this reinforces the observation regarding the composition effect at 200 psia. That is, to within ±10% the water content is independent of the composition at 200 psia.

Fig. 2 Water Content of Sour Gas at 200°F and 200 psia
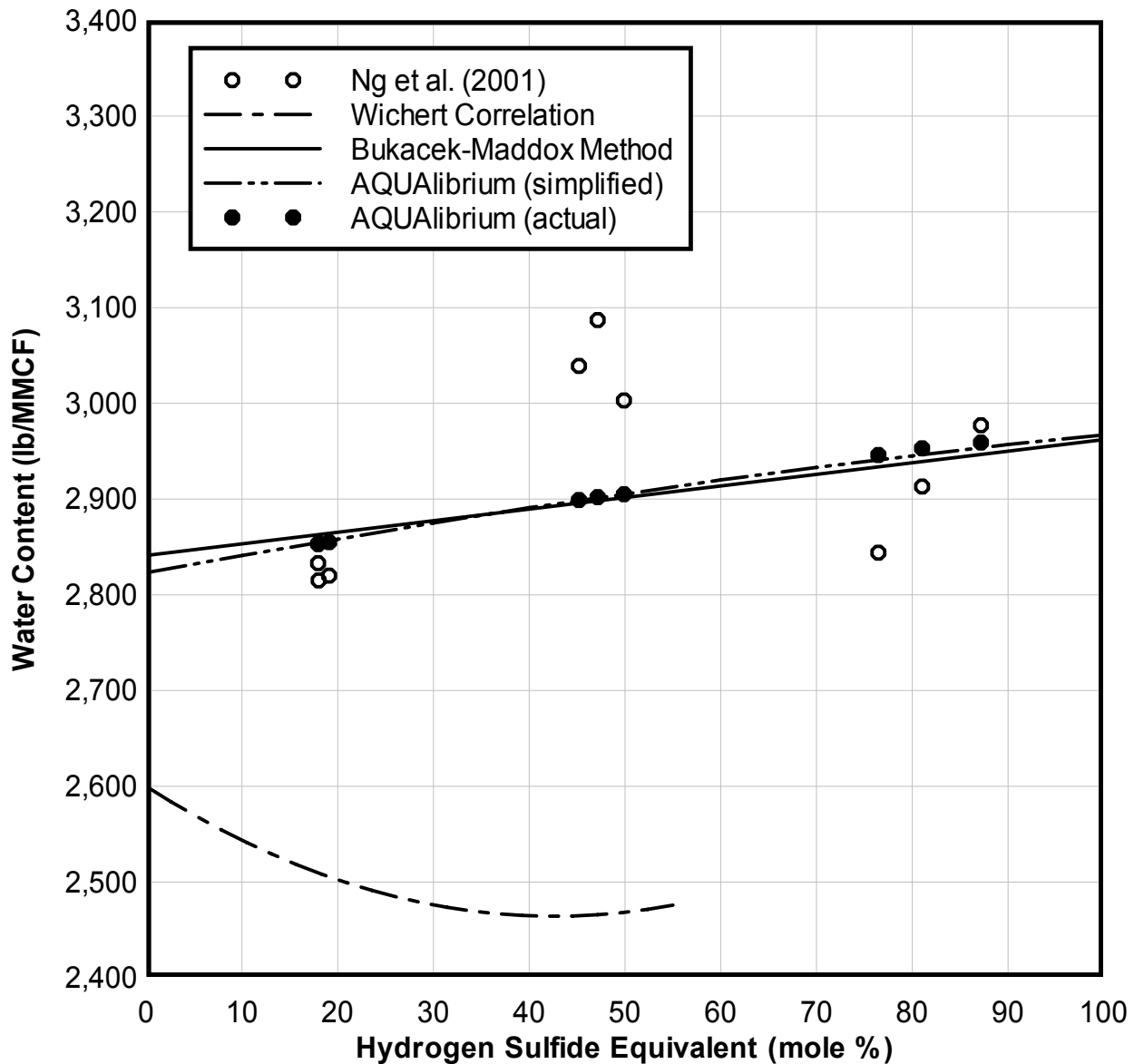
On the other hand, the data of Ng et al. [1] at 120°F and 200 psia exhibit some unusual behavior. At these conditions they measured 11 points. The average water content at these conditions is 500 lb/MMCF but the range is from 388 to 620 lb/MMCF – much greater than 10%.

Fig. 3 shows the water content at 120°F and 200 psia as a function of the H_2S equivalent. As with the previous figure, the predictions from the Wichert correlation and the Bukacek-Maddox method are also plotted. Again, with the Maddox correction the H_2S equivalent is assumed to be equal to the H_2S mole fraction. As with the previous figure the plot labeled AQUAlibrium is based on mixtures of hydrogen sulfide and methane.

Fig. 3 Water Content of Sour Gas at 120°F and 200 psia
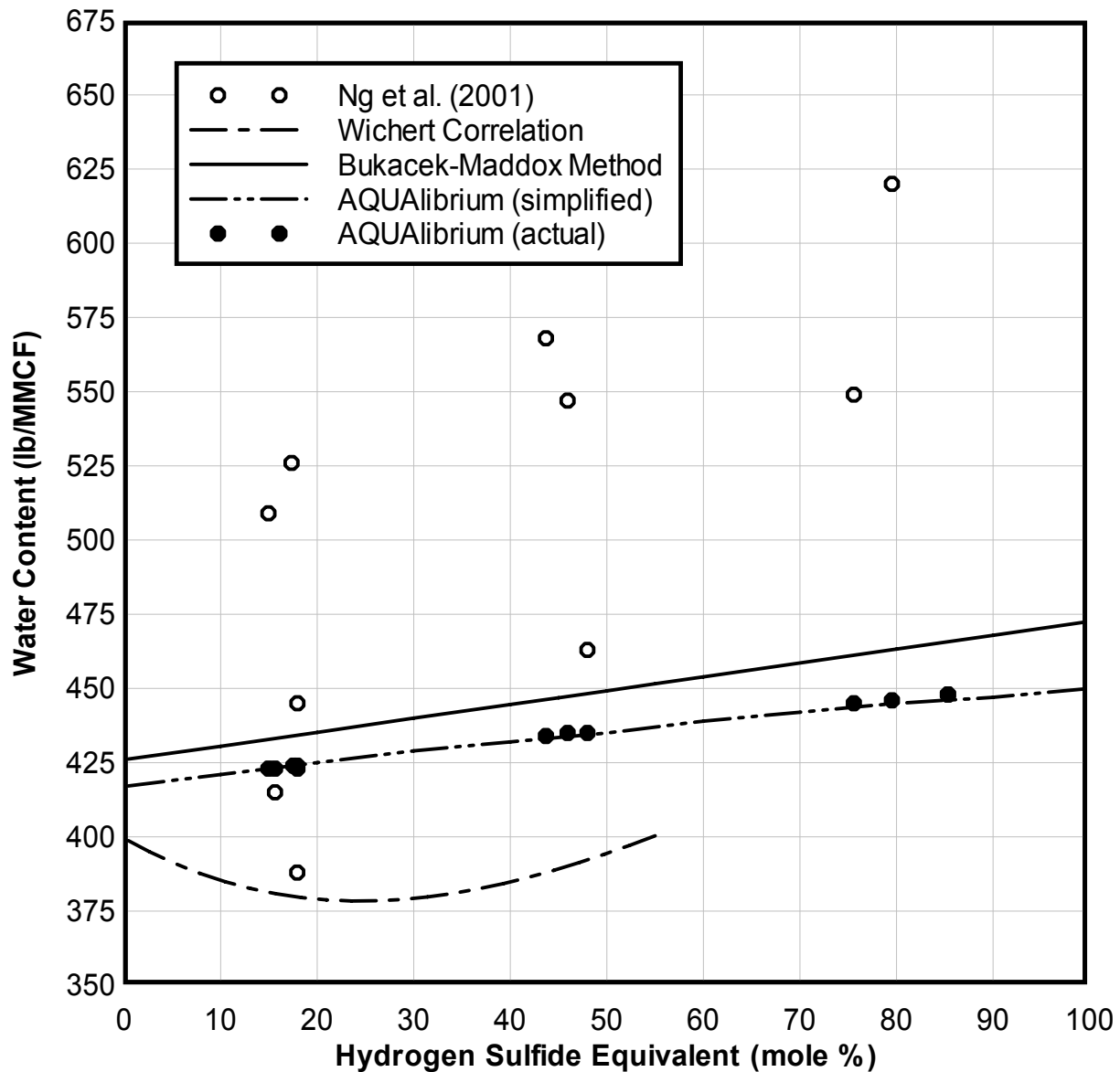
The predictions for 120°F are similar to those for 200°F but the data are significantly different. In addition, the behavior of the data seems a little unusual. It is difficult to criticize the experimental data, but either there is an error in this subset of their data or the phenomena is unusual. This subset of data deviates from the observations up to this point.

The Complete Set of Data

Now we will examine the entire set of data. To begin with the limitations of some of the correlations should be noted. The Wichert correlation is valid only for H_2S equivalent up to 55 mol%. This only covers 71% of the data of Ng et al. [1]. Because of the CO_2 content, the Maddox correlation is limited to 160°F and pressures up to 3000 psia. Therefore this method can be compared with only 31% of the data of Ng et al. [1]. These correlations will only be compared with the data in their

specified ranges. AQUAlibrium is not limited by pressures, temperature, or composition and thus will be compared with all of the data.

The errors for the various methods are listed in Table IV. However, this information does not completely reveal the details of the various prediction methods. Therefore these predictions should be examined in more detail.

Fig. 4 shows a plot of predicted value versus experimental value using the McKetta-Wehe chart. Most engineers working in the natural gas business know that the McKetta-Wehe chart is not applicable to sour gas mixtures. This is clearly demonstrated in this figure. The McKetta-Wehe method consistently predicts water content that is significantly less than the experimental values. On average the prediction is in error by about 40%.

Table IV – Comparison of the Various Methods for Predicting the Water Content of the Data of Ng et al. {1}

Method	Points	AE (%)	AAE (%)	MaxE (%)
Simple	83	55.5	55.5	98.3
McKetta-Wehe	83	41.7	41.9	94.5
Bukacek	83	40.1	40.6	94.5
Bukacek-Maddox	26	16.7	21.2	73.6
Wichert	59	11.6	15.2	44.5
AQUAlibrium	83	2.9	10.2	37.7

Fig. 5 shows the predictions based on the Bukacek-Maddox method, as described in this paper. Because the Bukacek-Maddox method is limited to 160°F for mixtures containing CO_2, only the values at 120°F are presented. For most of the points the error is in the range of ±20%, as indicated by the broken lines on the plot. However there are five points that are designated as "Rogue Points" on the figure because they exhibit very large errors. Two of these points are for the mixture 5HC-95AC2, which are in the near critical region, and one is for the mixture 5HC-95AC3, which is a liquid-liquid point. Many of the other points for these special mixtures are outside the range of the Bukacek-Maddox method. The other two rogue points are simply poor predictions.

The predictions from the Wichert correlation are shown in Fig. 6. By and large this correlation predicts the experimental data to within ±20%, with the exception of about 15 points (about one quarter of the predictions). In addition, the Wichert correlation tends to predict lower water content than the measured values. None of the points for the two special mixtures are included in this analysis. All of the points for the special mixtures are too rich in acid gas and are outside the range of the Wichert correlation.

Finally, Fig. 7 shows the predictions from AQUAlibrium. For AQUAlibrium all of the experimental points are examined, including all of the points for the two special mixtures. In general AQUAlibrium predicts the experimental values to within ±20%. Less than 15% of the values are outside this range of error. In addition, there is no bias in the AQUAlibrium predictions. That is AQUAlibrium does not tend to overpredict or underpredict the experimental values.

Fig. 4 Water Content of the Ng et al. (2001) Mixtures Versus the Predictions Using McKetta-Wehe Chart
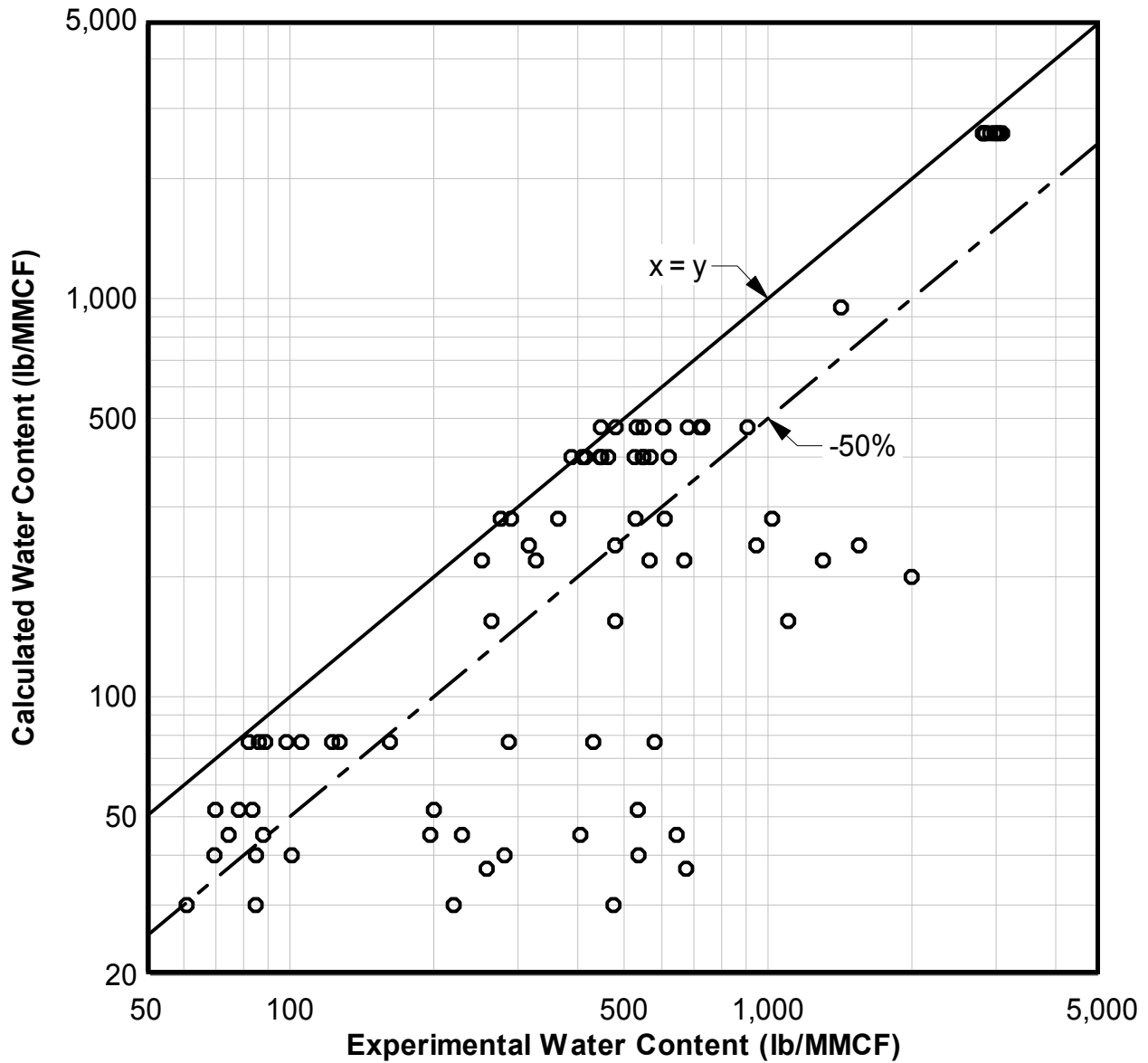
Additional Comments

In the examination of the pure component data large scatter was observed in the experimental data. It is probably fair to conclude that there is some error in the experimental data of Ng et al. [1]. They state that the error in the water content is only 25 ppm, which in the worst case is an error of only ±0.4%. A better estimate of the error is probably ±10%. Thus some of the error observed is at least partially attributable to the experimental data.

The detailed analysis of the low-pressure data, and in particular at 120°F, also indicates that perhaps the error in the data of Ng et al. [1] is larger than 25 ppm. However, there appears to be no reason to question these experimental data based on the information provided in their report.

Fig. 5 Water Content of the Ng et al. (2001) Mixtures Versus the Predictions Using the Bukacek-Maddox Method
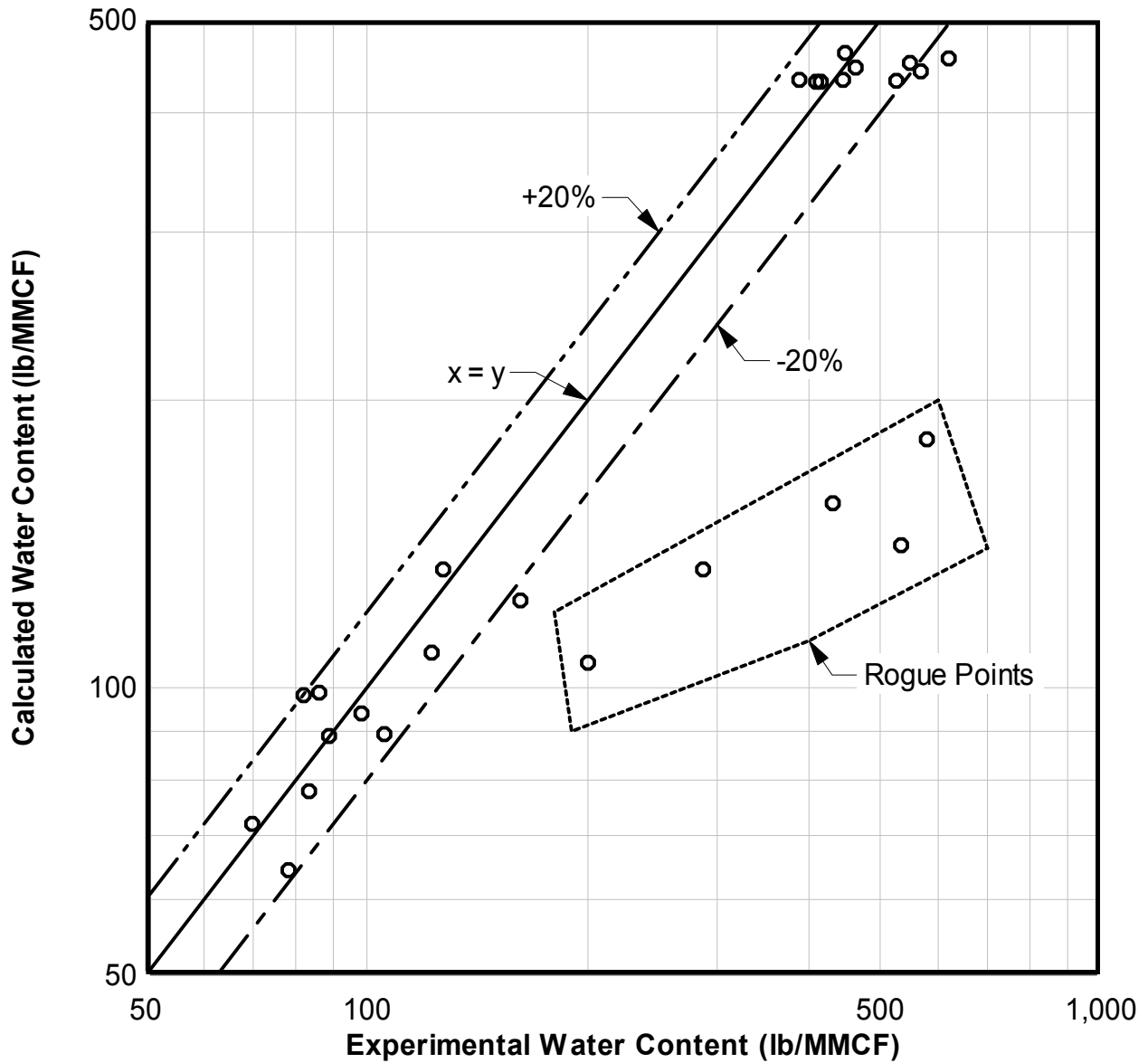

CONCLUSIONS

A few methods available in the open literature were compared to the available experimental data. In general it is fair to conclude that these methods are not highly accurate, errors of 20% are typical, but larger errors can be expected. On the other hand, for some data sets the errors are much smaller than this.

Fig. 6 Water Content of the Ng et al. (2001) Mixtures Versus the Predictions Using the Wichert Correlation
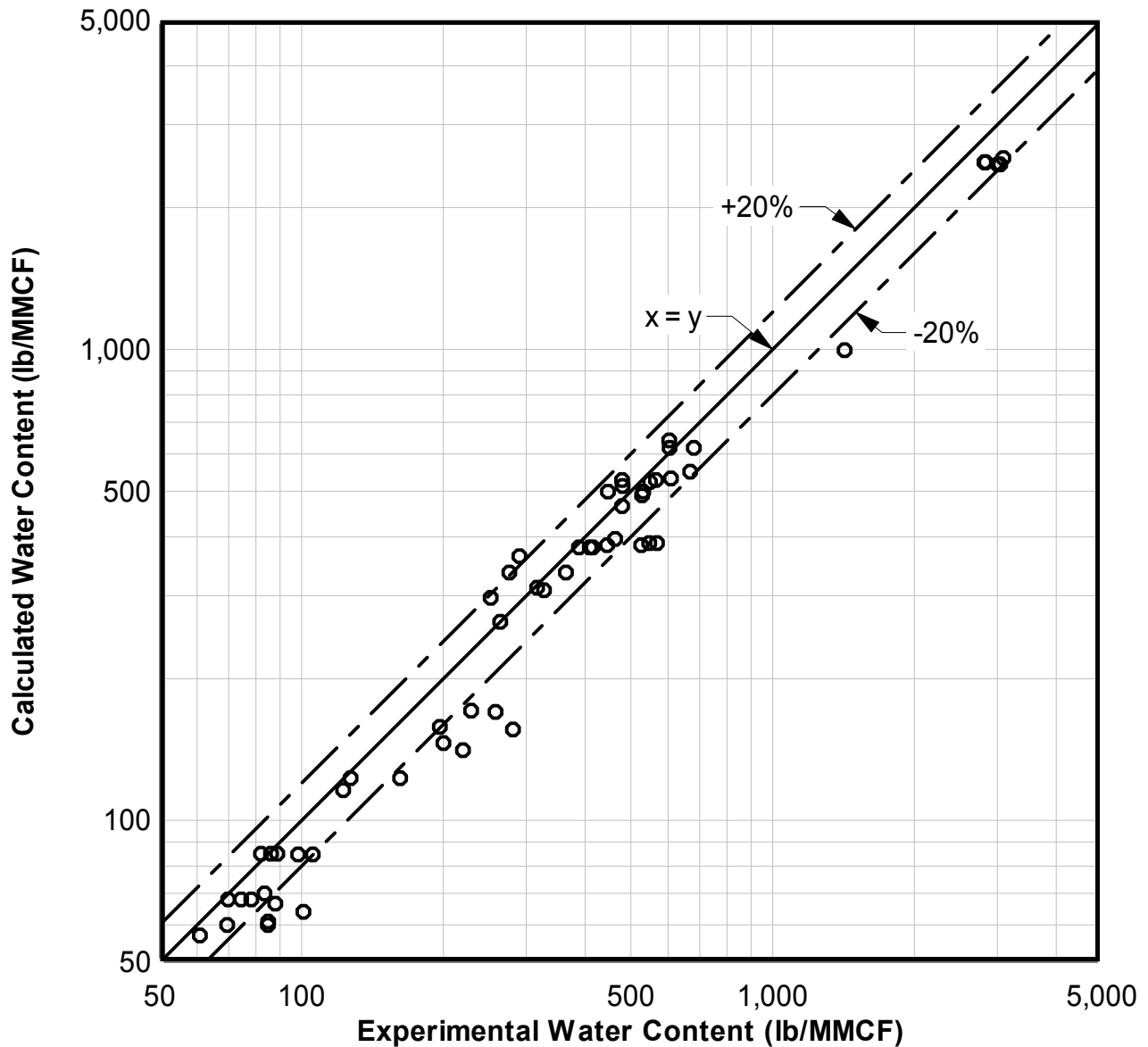
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Fig. 7 Water Content of the Ng et al. (2001) Mixtures Versus the Preditions Using AQUAlibrium
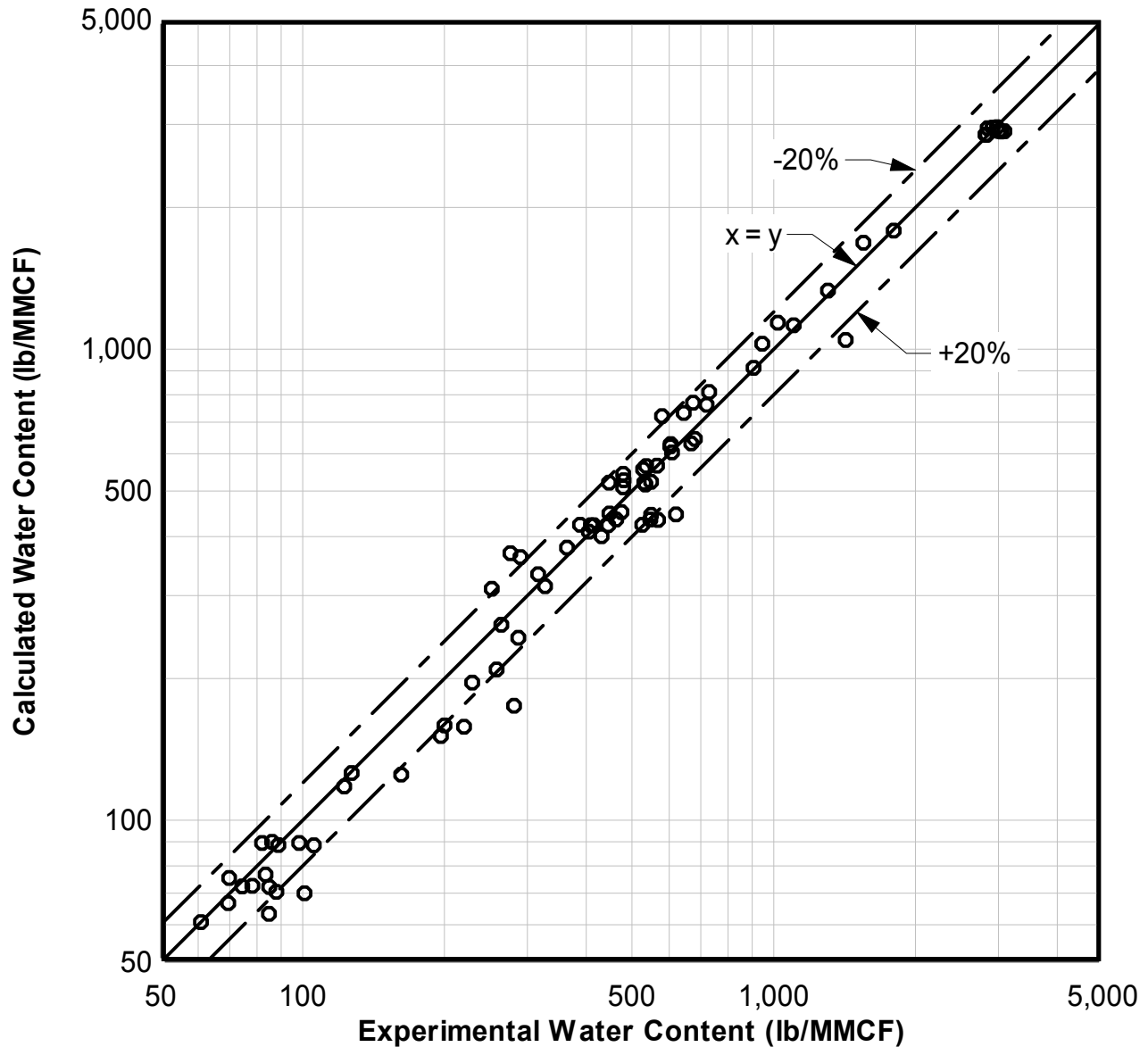
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APPENDIX – Correlation of the Maddox Charts

The Maddox charts for the contribution of hydrogen sulfide and carbon dioxide to the water content of sour gas are sufficiently easy to use for hand calculations. However, a mathematical expression is required for computer computations.

An attempt was made to correlate the correction factors as a function of both the pressure and the temperature, without much success. Therefore the water content was correlated as a function of the pressure only using the following relation:

$$log\, w = a_0 + a_1\, log\, P + a_2\, (log\, P)^2 \qquad\qquad (A1)$$

where w is the water content in lb/MMCF, P is the total pressure in psia, and a set of coefficients a_0, a_1, and a_2, was obtained for each isotherm. The coefficients are listed in Table IA. Note this equation uses common logarithms. Although these equations are not a perfect fit of the curves, they are probably as accurate as errors associated with reading the charts.

In the computer program the water content contribution is calculated along an isotherm and them linear interpolation is used to obtain the value at the desired temperature.

The correction factor from Maddox is combined with the sweet contribution of Bukacek to construct a simple computer program for calculating the water content of sour gas.

Table IA – Correlation Coefficients for Calculating the Maddox Correction
for the Water Content of Sour Natural Gas

Temperature (°F)	a_0	a_1	a_2
Carbon Dioxide			
80	6.0901	-2.5396	0.3427
100	6.1870	-2.3779	0.3103
130	6.1925	-2.0280	0.2400
160	6.1850	-1.8492	0.2139
Hydrogen Sulfide			
80	5.1847	-1.9772	0.3004
100	5.4896	-2.0210	0.3046
130	6.1694	-2.2342	0.3319
160	6.8834	-2.4731	0.3646
220	7.9773	-2.8597	0.4232
280	9.2783	-3.3723	0.4897