

An examination of the prediction of hydrate formation conditions in sour natural gas

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ABSTRACT

It is the purpose of this paper to briefly review the literature for hydrate formation in mixtures containing hydrogen sulfide. Seven methods for predicting hydrate formation for these systems will be examined. For the set of data examined in this study, which is made up of almost 125 experimental points, the computer methods *CSMHYD* and *EQUI-PHASE Hydrate* are reasonably accurate. The average errors for both *CSMHYD* and *EQUI-PHASE Hydrate* are about 1.5 Fahrenheit degrees (0.8 Celsius degrees). Typically these methods are able to predict the hydrate temperature to within 3 Fahrenheit degrees (1.7 Celsius degrees) 90% of the time.

The hydrate prediction routine in *Hysys*, a general-purpose process simulator, was also quite accurate with an average error of 1.5 Fahrenheit degrees (0.8 Celsius degrees). *Hysys* is able to predict the hydrate temperature to within 3 Fahrenheit degrees (1.7 Celsius degrees) more than 90% of the time. On the other hand, *Prosim*, another general-purpose simulator program, was not as accurate. The average error for *Prosim* was about 2.3 Fahrenheit degrees (1.3 Celsius degrees). It was able to predict the hydrate temperature to within 3 Fahrenheit degrees (1.7 Celsius degrees) only about 65% of the time

The Baillie-Wichert method was specifically designed to handle mixtures containing hydrogen sulfide and is particularly useful for hand calculations. When used within its stated ranges of composition, this method has an average error of 2.0 Fahrenheit degrees (1.1 Celsius degrees). This method predicts the experimental hydrate temperature to within 3 Fahrenheit degrees about 80% of the time.

Finally, the simple K-factor method, also designed for hand calculations, had an average error of 2.7 Fahrenheit degrees (1.5 Celsius degrees). The method predicted the experimental hydrate temperature to within 3 Fahrenheit degrees 60% of the time. The modified K-factor method of Mann et al. (1989) was as accurate as the more rigorous computer models. The average errors for the method of Mann et al. (1989) was 1.5 Fahrenheit degrees (0.8 Celsius degrees) and it predicted the hydrate temperature to within 3 Fahrenheit degrees (1.7 Celsius degrees) about 90% of the time.

While the averages noted above give an overall impression of the accuracy of these methods, the maximum errors reveal the potential for significantly larger errors. Even the computer methods have larger maximum errors, 6.0 Fahrenheit degrees (3.3 Celsius degrees) for *EQUI-PHASE Hydrate*, 7.4 Fahrenheit degrees (4.1 Celsius degrees) for *CSMHYD*., and 6.0 Fahrenheit degrees (3.3 Celsius degrees) for *Hysys*, and 8.0 Fahrenheit degrees (4.4 Celsius degrees) for *Prosim*.

The Baillie-Wichert chart has a maximum error of similar magnitude, 5.8 Fahrenheit degrees (3.2 Celsius degrees). The K-factor has a maximum error of 10.0 Fahrenheit degrees (5.6 Celsius degrees) and for the modified K-factor method of Mann et al. (1989) this was improved to 7.0 Fahrenheit degrees (3.9 Celsius degrees)

INTRODUCTION

Acid gas components, hydrogen sulfide and carbon dioxide, are often found in natural gas. Natural gas with significant quantities of sulfur compounds, and hydrogen sulfide in particular, is called "sour gas". If the natural gas is relatively free of sulfur compounds, then it is referred to as sweet gas. Occasionally the definition of sour gas is blurred because frequently gas that contains carbon dioxide and no sulfur compounds is also referred to as sour gas.

Gas hydrates are solid, ice-like compounds that are notorious for causing problems for producers and processors in the natural gas business. Hydrates differ from ice in two important ways. First, hydrates form at temperatures greater than ice formation temperatures. Second, hydrates are a solid solution. Hydrates only form when water is combined with certain small molecules called "hydrate formers". Among the common components in natural gas, methane, ethane, propane, isobutane, nitrogen, hydrogen sulfide, and carbon dioxide are all hydrate formers.

Of the common components in natural gas, hydrogen sulfide is known to form hydrates at the lowest pressure and they persist to the highest temperatures (Carroll, 2003). In addition, hydrogen sulfide has a significant effect on hydrate formation of a mixture. Based on experience, it is known that sour gas more readily forms a hydrate than does sweet gas.

Conventional wisdom seems to be that hydrate predictions for natural gas containing H₂S are not very accurate. It is the purpose of this paper to put this hypothesis to the test. A database of experimental data was assembled and predictions from seven methods were compared with the measured data.

REVIEW OF EXPERIMENTAL DATA

There is a somewhat surprising lack of data for the hydrate conditions in mixtures of CH₄ and H₂S considering the importance of such data in the construction of hydrate models. A thorough review of the literature revealed that the only such data available are those of Noaker and Katz (1954). Noaker and Katz (1954) examined the hydrate formation conditions for mixtures of hydrogen sulfide and methane. The data represent a combination of experimentally measured compositions and inferred compositions (see original paper for details). Both sets of data were examined here and no distinction is made between the two. The maximum H₂S concentration in the study of Noaker and Katz (1954) was 22 mol%. In their study, the temperature ranged from 38° to 66°F (3.3° to 18.9°C) and the pressure from 150 to 985 psia (1030 to 6800 kPa).

An important experimental investigation of the hydrates in sour gas mixtures is that of Robinson and Hutton (1967). They studied hydrates in ternary mixtures of methane, hydrogen sulfide, and carbon dioxide over a wide range of pressures (up to 2300 psia or 15 900 kPa) and temperatures (up to 76°F or 24.4°C). The hydrogen sulfide content of the gases in the study of Robinson and Hutton (1967) ranged from 5 to 15% and the carbon dioxide from 12 to 22%.

The final set of data examined here is that of Sun et al. (2003) who also measured the hydrate conditions for the ternary mixture of CH₄, CO₂, and H₂S. This set covered a wide range of compositions (CO₂ about 7mol% and H₂S from 5 to 27 mol%), for pressures up to 1260 psia (8700 kPa), and temperatures up to 80°F (26.7°C).

Data Not Included

Schroeter et al. (1982,1983) report some hydrate conditions for mixtures of methane + propane + hydrogen sulfide. At first these data also look like an important contribution to this field. However, these authors did not correct for the solubility of gas in the aqueous phase. Instead they assumed that the gas phase composition was unaffected by the solubility of the various components in the gas. As a part of this work, the solubility effect was recalculated and it is shown that the solubility is not negligible. The hydrogen sulfide concentration in the gas could be half what the authors' claimed. Since they did not

report the actual composition of the gas, these data are dubious. Therefore they were not included in this study. A more detailed discussion of this set of data is included in the appendix. None of the other data sets examined in this study neglected the effect of solubility on the gas mixture composition.

In addition, mixtures that contain non-hydrocarbons other than CO₂ and H₂S (and in particular mixtures that contain nitrogen) were excluded from this study. As well, mixtures that contained non-paraffinic hydrocarbons were not examined.

CALCULATION METHODS

Seven methods for predicting hydrate formation will be examined in this paper:

1. the original K-factor method (hence forward simply referred to as the K-factor method)
2. the chart method of Baillie and Wichert (1987)
3. the K-factor method of Mann et al. (1989)
4. *CSMHYD* from the Colorado School of Mines (release date Aug. 5, 1996)
5. *EQUI-PHASE Hydrate*, (Version 4.0) from the DBR Software Inc.¹
6. *Hysys* (v. 3.2, Build 5029) from AspenTech²
7. *Prosim* (v. 98.3) from Bryan Research & Engineering

The K-factor method was devised by Katz and co-workers in the 1940s (see Carson and Katz, 1942). The K-factor method examined in this paper is that described in Carroll (2003). The charts are presented for pressures between 100 and 4000 psia (700 to 27 600 kPa) for methane, between 100 and 2000 psia (700 to 13 800 kPa) for hydrogen sulfide, and between 250 and 1000 psia (1700 to 6900 kPa) for carbon dioxide. And the correlations based on these charts have the same limits. These pressure limits were not considered in the calculations presented in this study. If necessary, the correlations for the K-factors were extrapolated to higher pressure. Furthermore, Carroll (2003) demonstrated that the K-factor method is surprisingly accurate for predicting the hydrate conditions for the pure components.

Baillie and Wichert (1987) presented a chart method for calculating the hydrate temperature in sour gas mixtures. Their chart has a base temperature estimate calculated from the gravity of the gas and the H₂S concentration and a correction for propane content. The method of Baillie and Wichert (1987) is limited to gases with gravities between 0.6 and 1.0 and mixtures containing less than 50% H₂S, with an H₂S to CO₂ ratio between 10:1 and 1:3. In addition, this method is limited to pressures greater than 100 psia and less than 4000 psia. The method is not strictly for a sweet gas mixture containing CO₂, but may be accurate if the CO₂ is less than about 5 mol% (Wichert, 2003).

Mann et al. (1989) proposed a modified K-factor method. In this method the K-factors are a function of the temperature, pressure and, to a small degree, the composition. However, the major difference between this method and the original K-factor method is that Mann et al. (1989) have two sets of K-factors, one for Type I hydrates and another for Type II (more on hydrate types later). Unlike their predecessor, the new K-factor method is too complicated for hand calculations. The correlation of Mann et al. (1989) used in this study is the version implemented in the software package *Hydrate Plus* from FlowPhase Inc.

The computer methods *CSMHYD* and *EQUI-PHASE Hydrate* as well as the all-purpose simulator packages, *Prosim* and *Hysys*, are based on rigorous thermodynamic models and should not be limited in terms of composition and pressure.

The simple gas gravity method, commonly employed in the natural gas business for predicting hydrates, was not examined in this study. It is well-known that this method is not applicable to mixtures containing either hydrogen sulfide or carbon dioxide.

¹ DB Robinson Software Inc. is now a part of Schlumberger Oilphase-DBR.

² Calculation of the hydrate points for the various mixtures was performed by AspenTech based on pressure and composition data supplied by the author.

Hydrate Types

Hydrates are known to form in at least three crystal structures depending upon the hydrate formers in the mixtures (and in some cases the temperature and the pressure). These hydrate structures are called Type I, Type II, and Type H. Type H is relatively rare and does not occur for the mixtures examined in this study.

Methane, H₂S, and CO₂, the key components in this study, all form Type I hydrates, as do mixtures of these three components. In the natural gas mixtures encountered in industrial practice, propane and butanes are usually present in small but significant amounts. Even a small amount of propane or butane results in the mixture forming a Type II hydrate. So usually, hydrates in natural gas are Type II. Of the seven methods examined in this paper, the method of Mann et al. (1989) and the computer models in *CSMHYD*, *EQUI-PHASE Hydrate*, *Hysys* and *Prosim*, distinguish between the hydrate types, although often the user of the various software packages is unaware of the hydrate type.

DATA ANALYSIS

The seven methods discussed above were used to calculate the hydrate temperatures point-by-point and the summary statistics are presented here.

The deviation, D, is defined as:

$$D = \text{exp}_i - \text{calc}_i \quad (1)$$

where exp is the experimental value and calc is the calculated value for point i. The deviation has units of temperature. The average deviation, AD, is:

$$AD = \frac{1}{NP} \sum_{i=1}^{NP} \text{exp}_i - \text{calc}_i \quad (2)$$

where NP is the number of points. The average deviation has units of temperature. The average absolute deviation, AAD, is:

$$AAD = \frac{1}{NP} \sum_{i=1}^{NP} |\text{exp}_i - \text{calc}_i| \quad (3)$$

which also has units of temperature.

The difference between these two equations is the inclusion of the absolute value in Eqn (3). A small AD and a relatively large AAD indicates that the errors tend to cancel (some are positive and some negative) and indicates less bias in the prediction. If both the AD and AAD are large this indicates a bias in the prediction – a tendency to either over predict (if the AD is negative) or under predict (if the AD is positive) the experimental data.

Results

Each of the calculation methods discussed earlier was used to estimate the hydrate temperatures for each of the data sets. Table 1 shows the errors in predicting the data of Noaker and Katz (1954), Table 2 for Robinson and Hutton (1967), and Table 3 for Sun et al. (2003). Finally, Table 4 shows the predictions for the complete set of data (i.e. the three sets of experimental data combined).

Table 1 Errors in Predicting the Hydrate Temperatures from the Data of Noaker and Katz (1954)

| | Number of Points | Average Deviation (°F) | Ave. Absol. Deviation (°F) | Maximum Deviation (°F) | % Deviat. Larger than 3 Fahr. | % Deviat. Larger than 5 Fahr. |
|-----------------|------------------|------------------------|----------------------------|------------------------|-------------------------------|-------------------------------|
| K-factor | 29 | +0.2 | 0.8 | 2.6 | 0 | 0 |
| Baillie-Wichert | 11 | -1.5 | 1.7 | 3.2 | 9 | 0 |
| Mann et al. | 29 | -0.3 | 1.3 | 3.9 | 7 | 0 |
| CSMHYD | 29 | -0.3 | 1.2 | 3.6 | 7 | 0 |
| EQUI-PHASE | 25 | -1.0 | 1.6 | 5.1 | 8 | 4 |
| Hysys | 25 | -1.1 | 1.6 | 5.1 | 8 | 4 |
| Prosim | 25 | +1.6 | 1.9 | 4.4 | 20 | 0 |

Table 2 Errors in Predicting the Hydrate Temperatures from the Data of Robinson and Hutton (1967)

| | Number of Points | Average Deviation (°F) | Ave. Absol. Deviation (°F) | Maximum Deviation (°F) | % Deviat. Larger than 3 Fahr. | % Deviat. Larger than 5 Fahr. |
|-----------------|------------------|------------------------|----------------------------|------------------------|-------------------------------|-------------------------------|
| K-factor | 36 | +4.3 | 4.3 | 9.8 | 83 | 28 |
| Baillie-Wichert | 29 | +0.6 | 1.3 | 5.6 | 7 | 3 |
| Mann et al. | 36 | +1.6 | 1.8 | 7.0 | 8 | 3 |
| CSMHYD | 36 | +1.5 | 1.7 | 7.4 | 11 | 3 |
| EQUI-PHASE | 37 | +1.2 | 1.3 | 6.0 | 5 | 3 |
| Hysys | 37 | +1.2 | 1.3 | 6.0 | 8 | 3 |
| Prosim | 36 | +3.1 | 3.2 | 6.3 | 62 | 5 |

Table 3 Errors in Predicting the Hydrate Temperatures from the Data of Sun et al. (2003)

| | Number of Points | Average Deviation (°F) | Ave. Absol. Deviation (°F) | Maximum Deviation (°F) | % Deviat. Larger than 3 Fahr. | % Deviat. Larger than 5 Fahr. |
|-----------------|------------------|------------------------|----------------------------|------------------------|-------------------------------|-------------------------------|
| K-factor | 58 | +2.2 | 2.7 | 10.9 | 33 | 18 |
| Baillie-Wichert | 59 | -1.1 | 2.4 | 5.8 | 27 | 3 |
| Mann et al. | 58 | +0.2 | 1.5 | 7.0 | 10 | 5 |
| CSMHYD | 58 | +0.6 | 1.5 | 6.4 | 14 | 9 |
| EQUI-PHASE | 58 | -0.5 | 1.6 | 4.5 | 9 | 0 |
| Hysys | 59 | -0.6 | 1.6 | 4.5 | 9 | 0 |
| Prosim | 59 | +2.1 | 2.1 | 8.0 | 29 | 10 |

Table 4 Errors in Predicting the Hydrate Temperatures from the Overall Data Set

| | Number of Points | Average Deviation (°F) | Ave. Absol. Deviation (°F) | Maximum Deviation (°F) | % Deviat. Larger than 3 Fahr. | % Deviat. Larger than 5 Fahr. |
|-----------------|------------------|------------------------|----------------------------|------------------------|-------------------------------|-------------------------------|
| K-factor | 123 | +2.3 | 2.7 | 10.9 | 40 | 16 |
| Baillie-Wichert | 99 | -0.6 | 2.0 | 5.8 | 19 | 3 |
| Mann et al. | 123 | +0.5 | 1.5 | 7.0 | 9 | 3 |
| CSMHYD | 123 | +0.7 | 1.5 | 7.4 | 11 | 5 |
| EQUI-PHASE | 124 | -0.1 | 1.5 | 6.0 | 7 | 2 |
| Hysys | 125 | -0.1 | 1.5 | 6.0 | 8 | 2 |
| Prosim | 124 | +2.2 | 2.3 | 8.0 | 36 | 7 |

In addition to the errors given above, listed in these tables are the percentages of the calculations that are within 3 or 5 Fahrenheit degrees (1.7 or 2.8 Celsius degrees) of the experimental temperature. It is typical in engineering design to add a safety factor of 5 Fahrenheit degrees so these statistics give an estimate of how safe this margin is for sour gas mixtures.

Figures 1 through 7 are parity plots for the various prediction methods, each of the seven methods is shown on a separate plot. These graphs are plots of the predicted hydrate temperature as a function of the experimental hydrate temperature. If the prediction method were a perfect fit of the experimental data then all of the points would lie on the $x = y$ line. Also plotted on each graph are error bands that deviate from the $x = y$ line by 3 Fahrenheit degrees (1.7 Celsius degrees).

By and large, the parity plots do not reveal much more than the error tables presented earlier. However, the plots for the K-factor method and *Prosim* demonstrate that these methods tend to under-predict the hydrate temperature. On these plots the vast majority of the points are to the right and below the $x = y$ line.

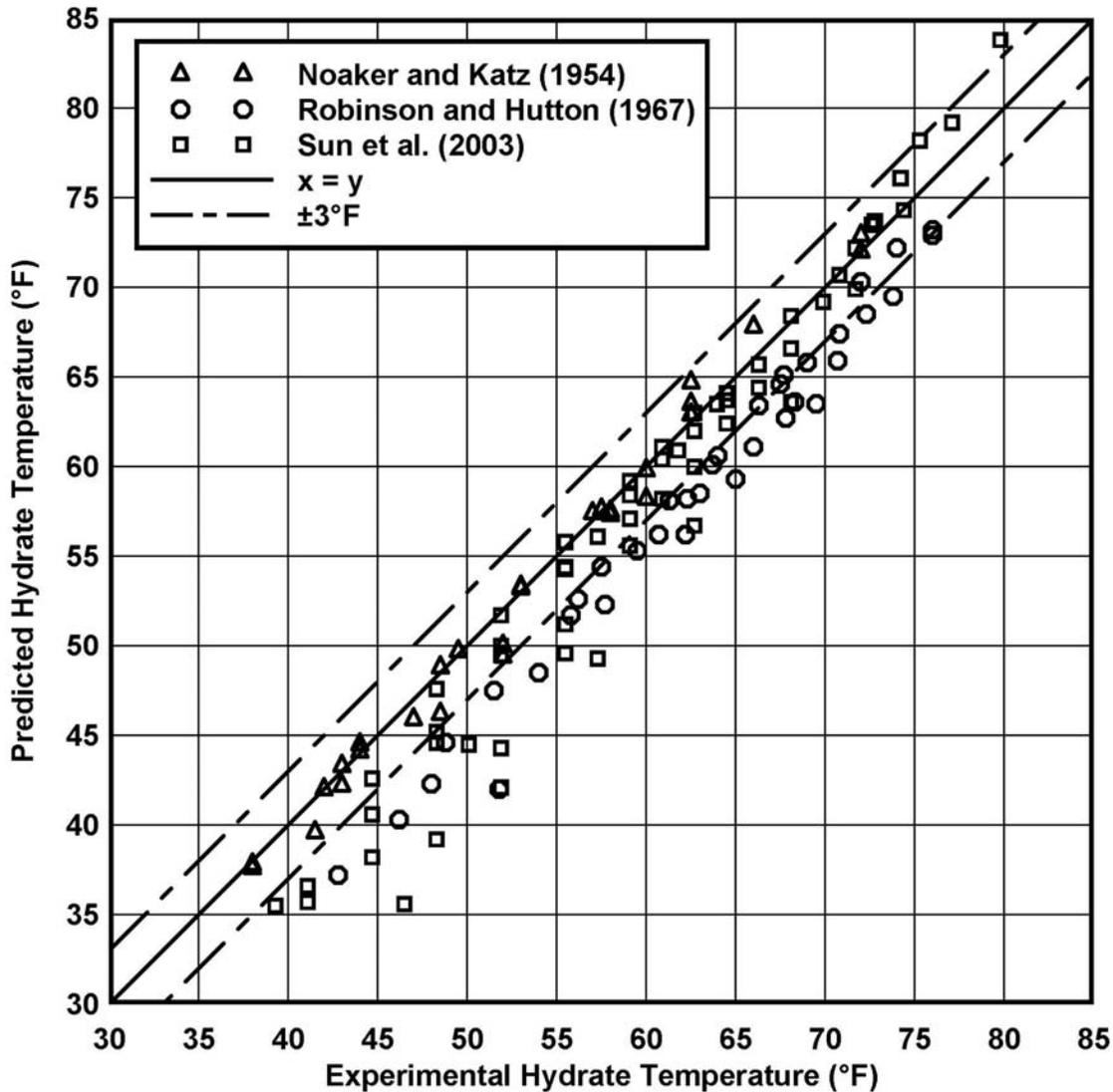
In addition, the plots reveal one thing that the error tables cannot. The plots show that regardless of the method, the larger errors occur at the lowest temperatures. With the exception of the K-factor method and *Prosim*, there are very few points for temperatures greater than 55°F that are outside the $\pm 3^\circ\text{F}$ bands. However at lower temperatures, each method has several points outside the $\pm 3^\circ\text{F}$ bands.

DISCUSSION

The observation that Robinson and Hutton (1967) made based on their data, that the K-factor method is not very accurate for sour gas mixtures is also the conclusion of this study. The K-factor method tends to under-predict the hydrate temperature and errors much larger than 3 Fahrenheit degrees are quite common. However, if errors as large as 5 Fahrenheit degrees are tolerable, than this method is satisfactory, but 16% of the time this method under predicts the hydrate temperature by more than 5 Fahrenheit degrees.

At first it may seem a little surprising that the K-factor method is so accurate for predicting the hydrate temperatures given by the data of Noaker and Katz (1954). However, there is a simple explanation for this observation. These were the data used to produce the K-factor chart for hydrogen sulfide. In fact, the K-factor chart produced in the paper of Noaker and Katz (1954) was reproduced virtually unchanged in the *GPSA Engineering Data Book* (1998) and hence in Carroll (2003) and other similar reference books. So, for this set of data, the K-factor method is more of a correlation than a prediction. For the other sets of data, the K-factor method is the poorest method.

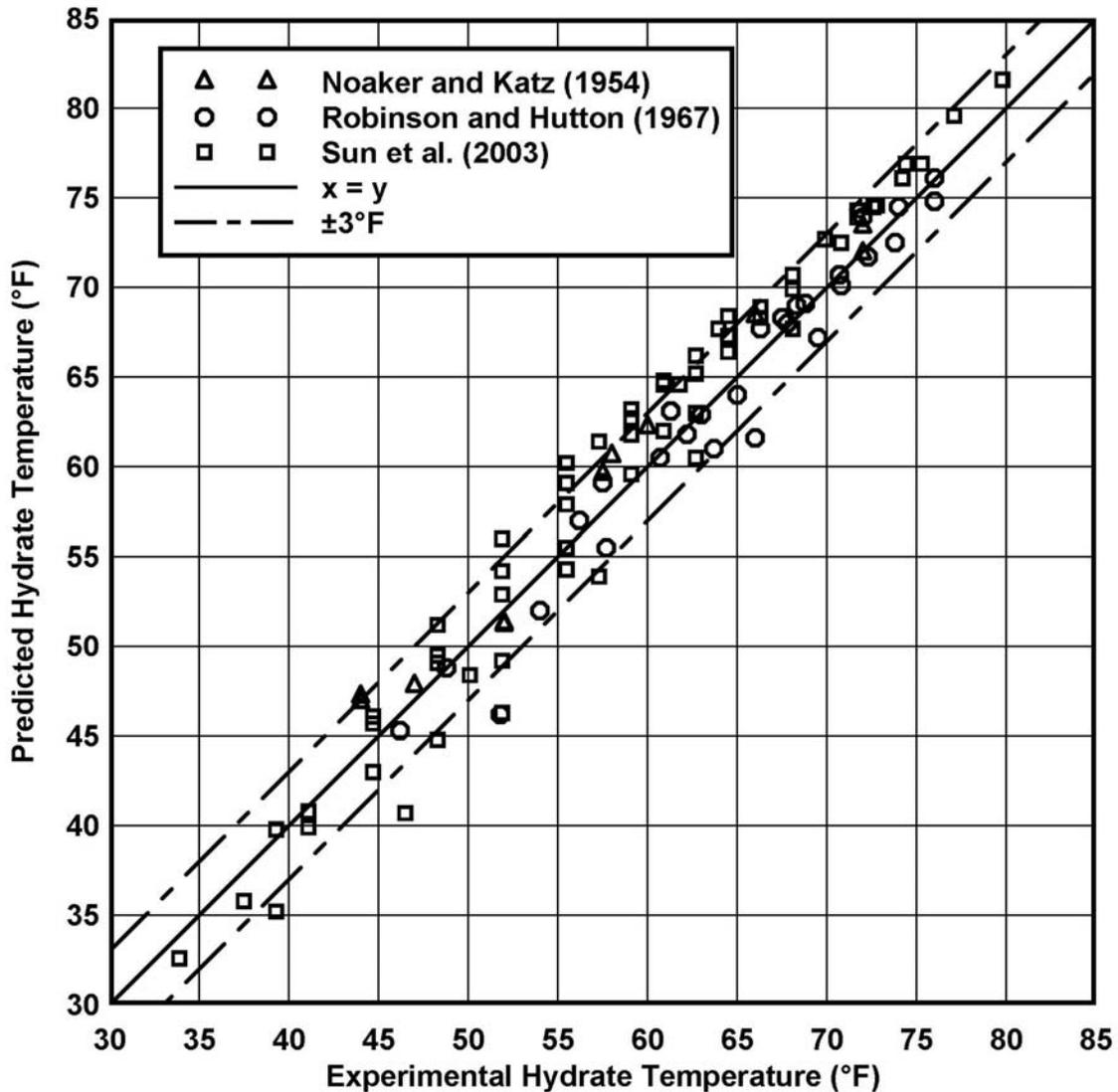
Fig.1 Parity Plot for the Predictions Using the K-factor Method



Extending the K-factor method to account for more effects as implemented by Mann et al. (1989) significantly improves the predictions. The average error for this method is about half that of the original K-factor method. In addition, the method of Mann et al. (1989) predicts the hydrate temperature to within 3 Fahrenheit degrees more than 90% of the time.

The Baillie and Wichert (1987) method is surprisingly accurate for a relatively simple method. Based on this test, the chart predicts the hydrate temperature to within 3 Fahrenheit degrees about 80% of the time. Of the available methods designed for hand calculations, this is the preferred method for sour gas systems. However, additional investigation, not presented in this study, show that the chart should be used with caution for mixtures that contain carbon dioxide and *no* hydrogen sulfide. The chart is designed for mixtures of CO₂ and H₂S and when present in combination with H₂S the CO₂ concentration can be quite large. However, in the absence of H₂S the CO₂ concentration should probably be limited to less than 5%.

Fig. 2 Parity Plot for the Predictions Using the Baillie-Wichert Chart

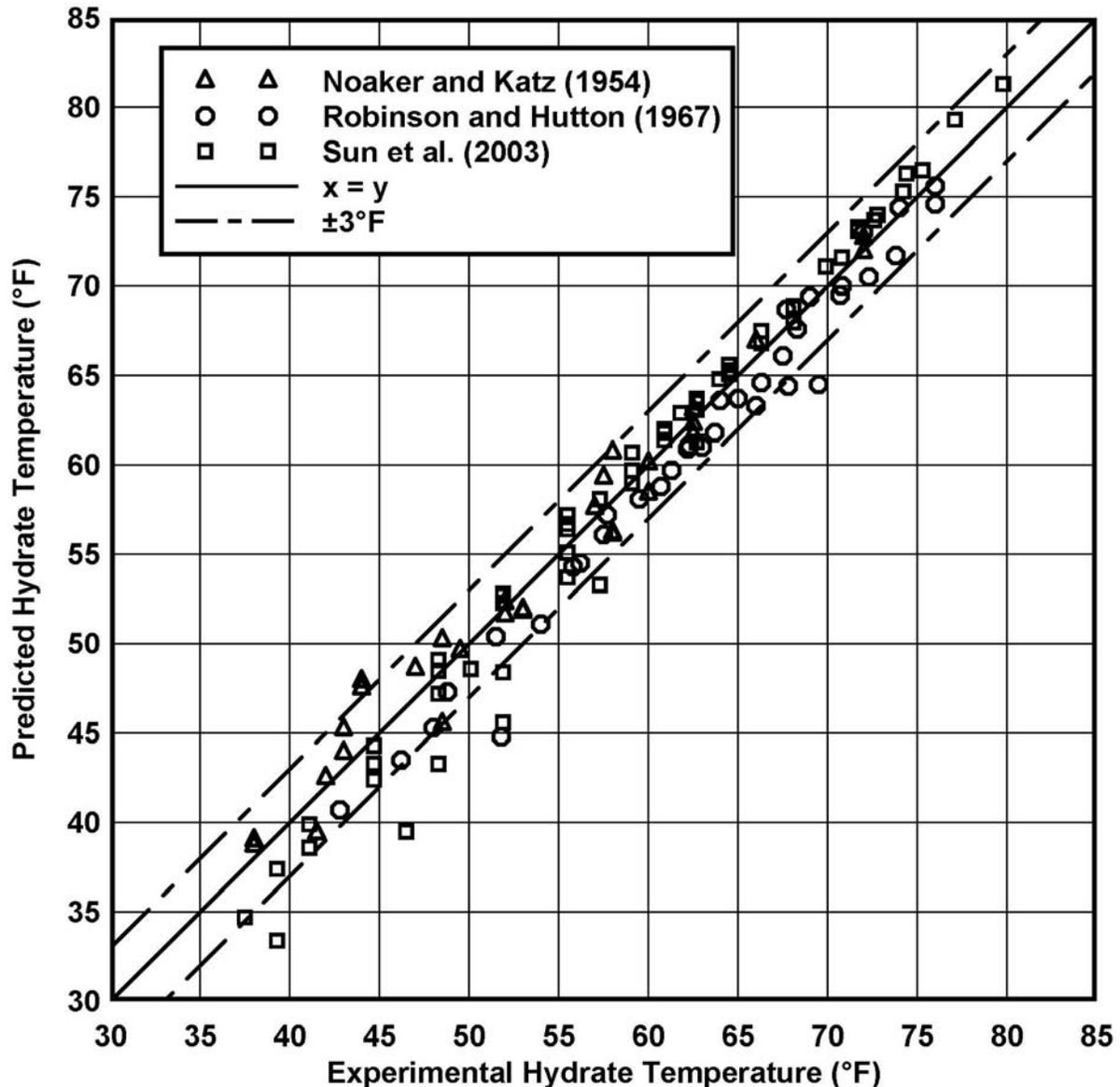


Clearly, and not surprisingly, *CSMHYD*, *EQUI-PHASE Hydrate*, and *Hysys* are the most accurate of the methods examined. However, the hydrate predictions built into *Prosim* are not quite as accurate. The errors with *Prosim* are significantly larger than those from the other computer methods, and, as demonstrated by the parity plots, *Prosim* consistently under predicts the hydrate temperatures for these mixtures.

Water Content

All of the experimental data were measured in the presence of free water and all of the predictions presented here assume that there is plenty of water. It is well-known that dehydrating a gas can reduce the hydrate formation temperature. This effect is not considered in this study. Furthermore, there are no experimental data available for water-reduced sour gas system for comparison.

Fig. 3 Parity Plot for the Predictions Using the Method of Mann et al. (1989)

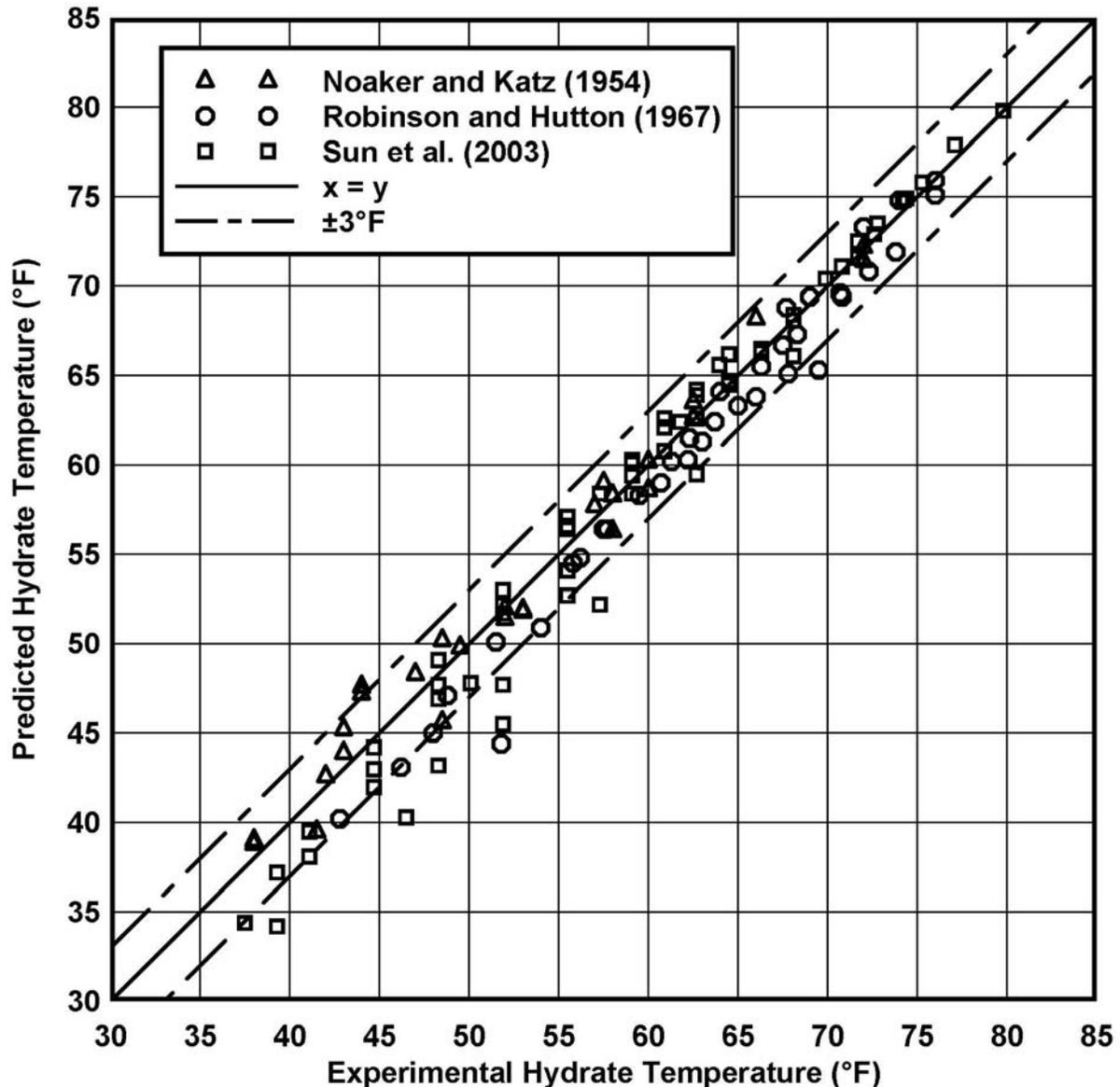


CONCLUSIONS

As presented in this study, some of the common methods for predicting the hydrate conditions are reasonably accurate for mixtures containing H_2S and CO_2 . When used within their respective ranges of applicability, the average errors in the predicted hydrate pressures are less than 3 Fahrenheit degrees (1.7 Celsius degrees). However, errors in the predicted temperature as large as 11 Fahrenheit degrees (6.1 Celsius degrees) may be encountered when using simple methods and 8 Fahrenheit degrees (4.4 Celsius degrees) for the complex methods. Therefore the user of these methods is advised to use some caution applying them.

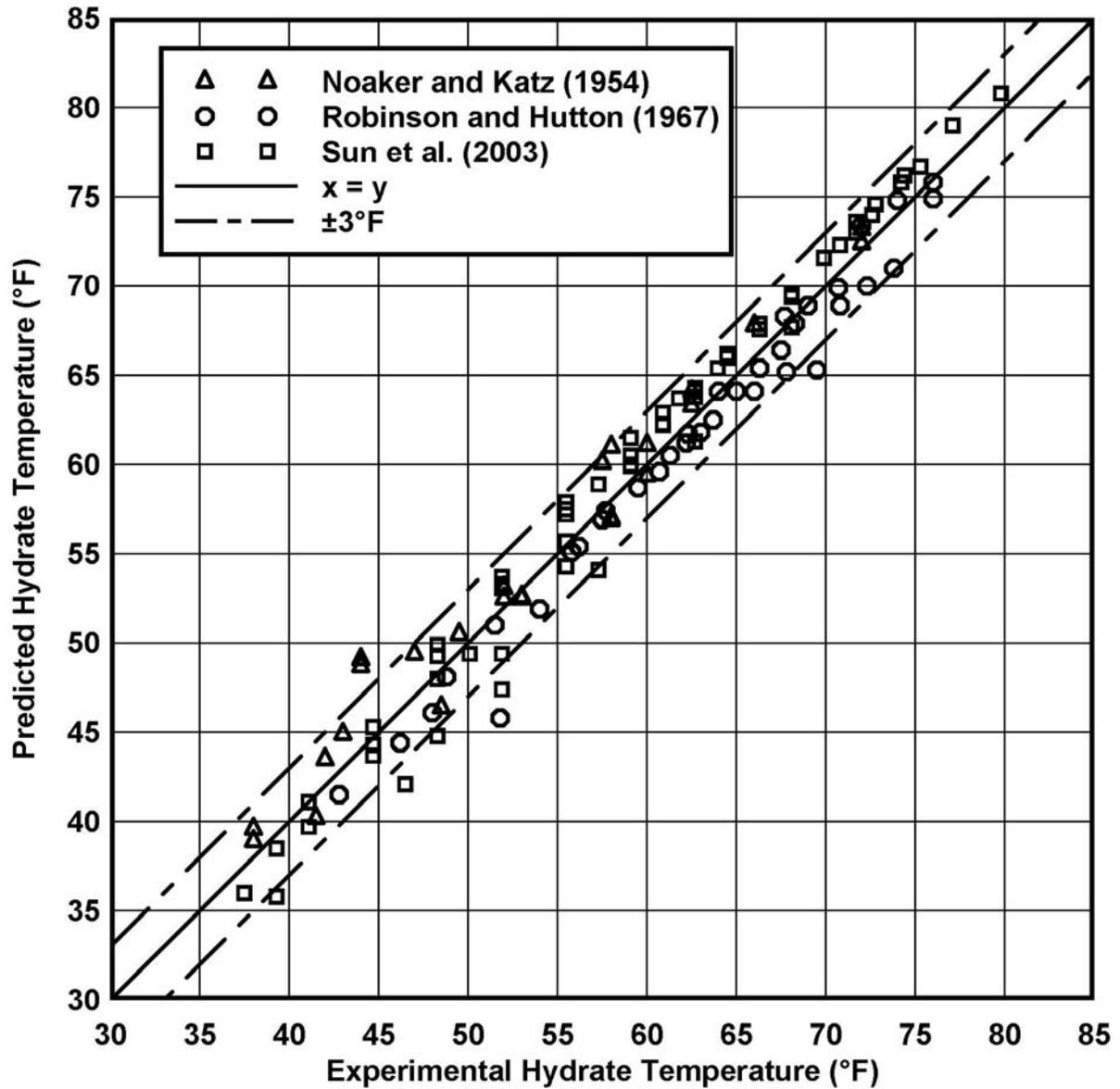
It is a little difficult to extrapolate these results to acid gas mixtures (i.e. those containing 90% or more hydrogen sulfide and carbon dioxide). However, the design engineer should use these methods with caution when calculating the hydrate formation conditions with acid gases.

Fig. 4 Parity Plot for the Predictions Using CSMHYD



This study was somewhat hampered by the lack of available data in the literature. There is a need for a thorough and accurate set of data for the hydrate formation conditions for the binary mixture $\text{H}_2\text{S} + \text{CH}_4$. Also, for those dealing with acid gas, a set of data for the binary $\text{H}_2\text{S} + \text{CO}_2$ would be useful for building and testing models. Also a set of data for a mixture similar to those found in industrial practice (i.e. those containing ethane, propane, n-butane and isobutane; and even heavier hydrocarbons, as well as methane, H_2S , and CO_2) would be very valuable for testing the models.

Fig. 5 Parity Plot for the Predictions Using EQUI-PHASE Hydrate



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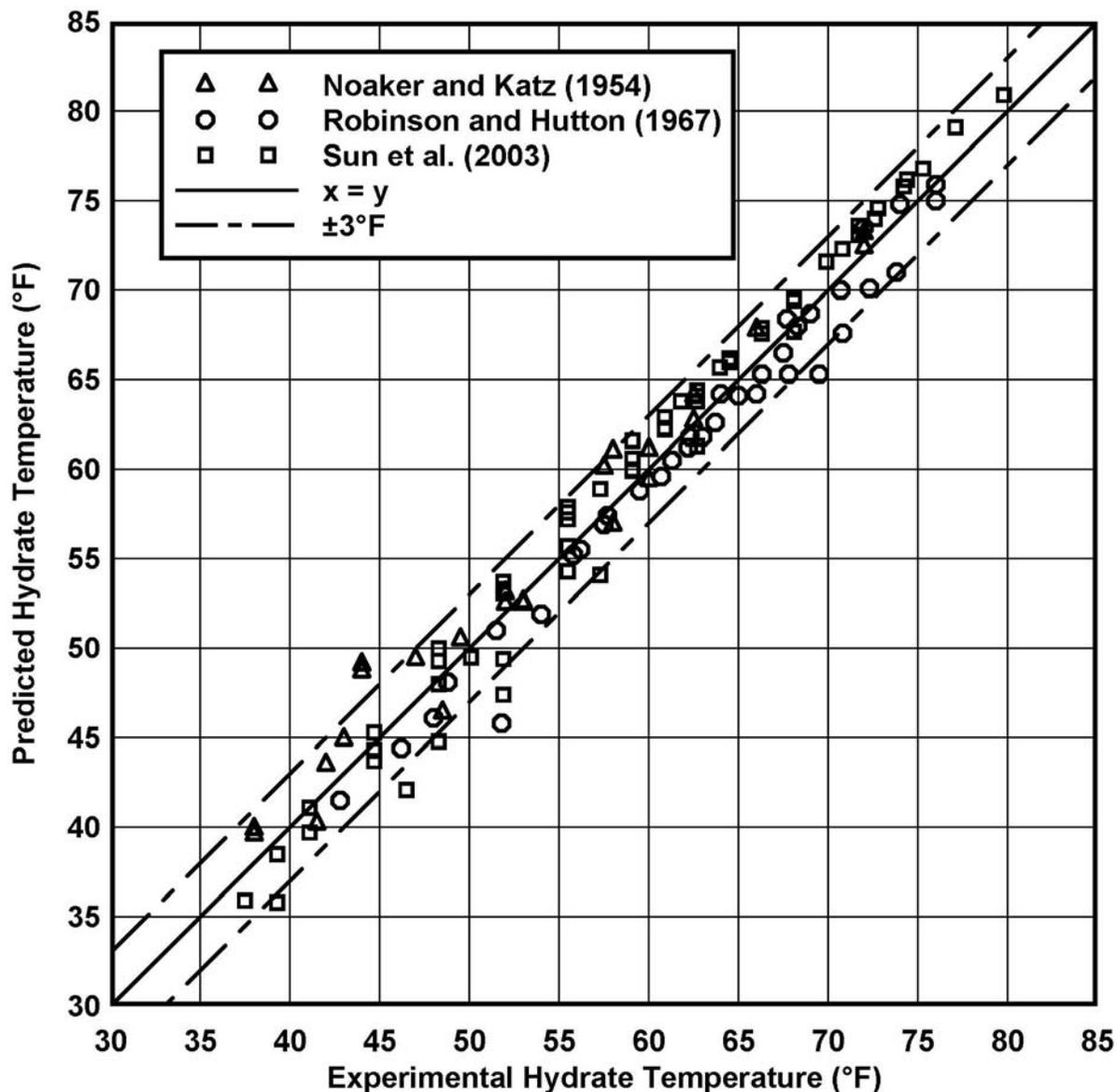
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Fig. 6 Parity Plot for the Predictions Using Hysys



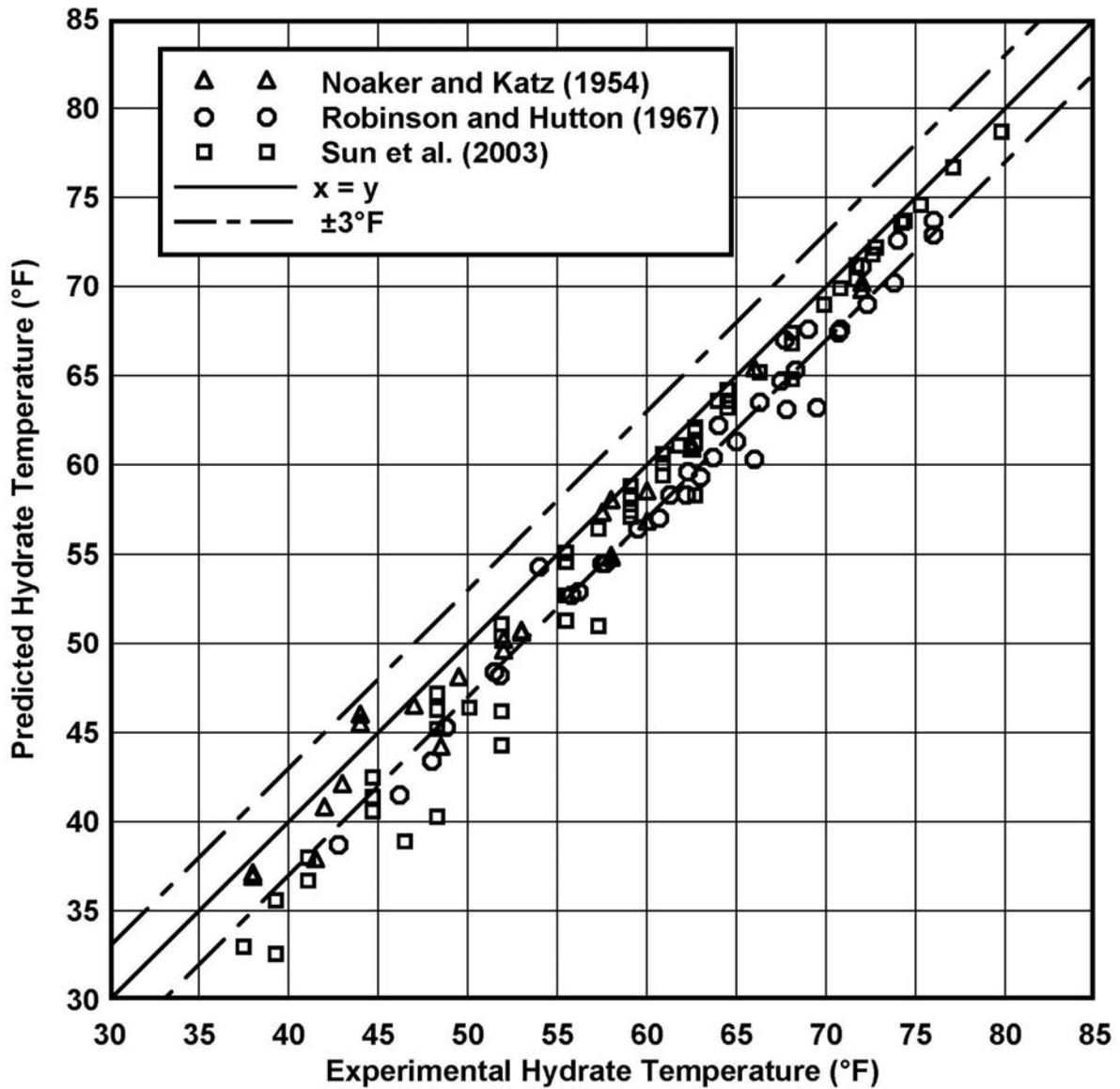
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Fig. 7 Parity Plot for the Predictions Using Prosim



Schroeter, J.P., R. Kobayashi, and H.A. Hildebrand, "Hydrate Decomposition Conditions in the System H_2S -Methane-Propane", *Ind. Eng. Chem. Fundam.*, **22**, 361-364, (1983).

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APPENDIX Discussion of the Data of Schroeter et al. (1982,1983)

The data of Schroeter et al. (1982,1983) appear to be an important contribution to the study of sour gas hydrates. However, it is unclear whether or not the data are of high quality. The reason for this skepticism is outlined in this appendix.

In the experiments of Schroeter et al. (1982,1983), they charged the cell once with a gas of known composition. They claim that “calculations reveal that the differential solubility of H₂S in water – as compared to that of methane and propane – should change the H₂S concentration in the gas phase by no more than approximately 0.2%.” Even the simplest details of this calculation are not reported (for example Henry’s constants or the name of the software used). The calculations presented here shows that this may not be the case.

Furthermore they claim that “later experimental determination of the H₂S gas phase concentration was consistent with this calculation.” Unfortunately, they do not report the measured compositions. Nor do they state for how many mixtures they actually measured the composition. If they actually measured the composition of the gas phase, why weren’t these values reported? Regardless of their contention that the composition is unchanged by the solubility, the measured compositions should have been reported because they are more accurate.

Thought Experiment

A simple calculation “experiment” was performed to test the theory that the differential solubility is negligible. No claim is made that this thought experiment follows the actual experiment, but it presents a possible scenario.

According to the experimental description provided, the cell has a volume of 135 cm³. To conduct an experimental run, they state that approximately 25 cm³ of water was placed in the cell. This is approximately equal to 1.39 mole of water (or 1390 mmol), using a density of 1.00 g/cm³ for water and a molar mass of 18.015 g/mol.

This leaves 110 cm³ of cell volume that is occupied by the gas. *AQUALibrium* from FlowPhase Inc. was used to calculate the density of the gas at the temperature and pressure of the experimental run. Using this density, the volume of the gas, and the reported feed composition of the gas, the number of moles of each component in the gas phase was calculated. These calculations are summarized in Table A1. The unusual combination of °C and psia was used in the original report and will be retained here as well.

The total moles of each of the four components (water plus gas) were used in a flash calculation, which was performed using *AQUALibrium*, to obtain the equilibrium composition. The resultant compositions of the gas phase are summarized in Table A2.

As can be seen from Table A2, according to this thought experiment the composition of the gas is significantly different from the values presented in Schroeter et al. (1982,1983) – and the change in H₂S concentration is significantly larger than 0.2%.

Hydrate Prediction

As an additional test of this theory, the hydrate pressure will be predicted using *EQUI-PHASE Hydrate* with both the original compositions and those recalculated as outlined above. The results of these calculations are presented in Table A3.

With the original composition the hydrate pressure is always under-predicted and the average error is about 18%. This error is a little higher than expected based on the other sets of data examined in this study.

Table A1 Calculated Density and Moles of Gas in the Cell for the Experiments of Schroeter et. al (1982)

| Temp (°C) | Press (psia) | Gas Density (kg/m ³) | Moles of Gas (mmol) | H ₂ S (mol%) | CH ₄ (mol%) | C ₃ H ₈ (mol%) | H ₂ S (mmol) | CH ₄ (mmol) | C ₃ H ₈ (mmol) |
|-----------|--------------|----------------------------------|---------------------|-------------------------|------------------------|--------------------------------------|-------------------------|------------------------|--------------------------------------|
| 2.8 | 81.4 | 4.678 | 27.36 | 4.174 | 88.654 | 7.172 | 1.14 | 24.25 | 1.96 |
| 4.6 | 102.4 | 5.869 | 34.32 | 4.174 | 88.654 | 7.172 | 1.43 | 30.43 | 2.46 |
| 11.0 | 205.8 | 11.73 | 68.60 | 4.174 | 88.654 | 7.172 | 2.86 | 60.81 | 4.92 |
| 14.2 | 293.5 | 16.78 | 98.13 | 4.174 | 88.654 | 7.172 | 4.10 | 86.99 | 7.04 |
| 18.0 | 488.3 | 29.39 | 171.87 | 4.174 | 88.654 | 7.172 | 7.17 | 152.37 | 12.33 |
| 2.7 | 49.2 | 3.017 | 16.45 | 11.975 | 81.009 | 7.016 | 1.97 | 13.33 | 1.16 |
| 10.4 | 118.5 | 7.169 | 39.10 | 11.975 | 81.009 | 7.016 | 4.68 | 31.67 | 2.75 |
| 19.5 | 408.0 | 25.24 | 137.65 | 11.975 | 81.009 | 7.016 | 16.48 | 111.51 | 9.70 |
| 7.2 | 53.4 | 3.826 | 17.67 | 31.710 | 60.888 | 7.402 | 5.60 | 10.76 | 1.31 |
| 13.1 | 99.5 | 7.071 | 32.65 | 31.710 | 60.888 | 7.402 | 10.35 | 19.88 | 2.42 |
| 19.1 | 209.5 | 15.02 | 69.36 | 31.710 | 60.888 | 7.402 | 21.99 | 42.23 | 5.13 |
| 24.3 | 370.5 | 27.24 | 125.79 | 31.710 | 60.888 | 7.402 | 39.89 | 76.59 | 9.31 |
| 27.8 | 620.0 | 48.30 | 223.05 | 31.710 | 60.888 | 7.402 | 70.73 | 135.81 | 16.51 |

Table A2 Recalculated Composition of the Gas in Equilibrium with an Aqueous Liquid

| Temp (°C) | Press (psia) | Vapor Composition as Calculated | | | | Vapor Comp. - Water-Free | | |
|-----------|--------------|---------------------------------|------------------------|--------------------------------------|-------------------------|--------------------------|------------------------|--------------------------------------|
| | | H ₂ S (mol%) | CH ₄ (mol%) | C ₃ H ₈ (mol%) | H ₂ O (mol%) | H ₂ S (mol%) | CH ₄ (mol%) | C ₃ H ₈ (mol%) |
| 2.8 | 81.4 | 2.17 | 90.43 | 7.27 | 0.14 | 2.17 | 90.55 | 7.28 |
| 4.6 | 102.4 | 2.23 | 90.37 | 7.27 | 0.12 | 2.23 | 90.49 | 7.28 |
| 11.0 | 205.8 | 2.45 | 90.17 | 7.28 | 0.10 | 2.45 | 90.26 | 7.29 |
| 14.2 | 293.5 | 2.57 | 90.06 | 7.29 | 0.09 | 2.57 | 90.13 | 7.30 |
| 18.0 | 488.3 | 2.75 | 89.90 | 7.28 | 0.07 | 2.75 | 89.96 | 7.29 |
| 2.7 | 49.2 | 6.30 | 86.04 | 7.44 | 0.22 | 6.31 | 86.23 | 7.46 |
| 10.4 | 118.5 | 7.04 | 85.41 | 7.40 | 0.16 | 7.05 | 85.54 | 7.41 |
| 19.5 | 408.0 | 7.98 | 84.57 | 7.36 | 0.09 | 7.99 | 84.65 | 7.37 |
| 7.2 | 53.4 | 18.84 | 72.14 | 8.74 | 0.28 | 18.89 | 72.34 | 8.76 |
| 13.1 | 99.5 | 20.30 | 70.86 | 8.61 | 0.23 | 20.35 | 71.02 | 8.63 |
| 19.1 | 209.5 | 21.81 | 69.57 | 8.45 | 0.17 | 21.85 | 69.69 | 8.46 |
| 24.3 | 370.5 | 23.14 | 68.39 | 8.32 | 0.14 | 23.17 | 68.49 | 8.33 |
| 27.8 | 620.0 | 24.67 | 67.05 | 8.17 | 0.11 | 24.70 | 67.12 | 8.18 |

Table A3 Hydrate Pressures for the Schroeter et al. (1982) Mixtures Calculated Using *EQUI-PHASE Hydrate*

| Temperature (°C) | Experimental Pressure (psia) | Calculated Pressure (psia) | |
|---------------------|------------------------------------|----------------------------|-----------------------------|
| | | Original Composition | Recalculated Composition |
| 2.8 | 81.4 | 68.8 | 84.0 |
| 4.6 | 102.4 | 85.4 | 103.9 |
| 11.0 | 205.8 | 182.0 | 217.8 |
| 14.2 | 293.5 | 266.9 | 317.0 |
| 18.0 | 488.3 | 429.9 | 505.8 |
| 2.7 | 49.2 | 43.3 | 56.8 |
| 10.4 | 118.5 | 104.6 | 133.6 |
| 19.5 | 408.0 | 301.0 | 372.7 |
| 7.2 | 53.4 | 41.4 | 52.4 |
| 13.1 | 99.5 | 79.3 | 97.8 |
| 19.1 | 209.5 | 154.4 | 185.9 |
| 24.3 | 370.5 | 283.7 | 335.7 |
| 27.8 | 620.0 | 448.9 | 520.5 |

On the other hand, using the recalculated compositions, the hydrate pressure prediction is dramatically improved. The average error is only -0.1% and the absolute average error is 7.6% , about half the error as was obtained using the original compositions. Furthermore, the small error indicates that there is no tendency to over- or under-predict the hydrate pressure.

Similar results were obtained when the hydrate was predicted using the *CSMHYD* software package. That is, if the original compositions are used then the hydrate pressure is under predicted. These results are summarized in Table A4. When the recalculated values are used then better estimates of the hydrate pressure are obtained.

Conclusion

The results presented here do not represent conclusive proof, but they provide strong evidence that something is amiss with the set of data presented by Schroeter et al. (1982,1983). It appears as though the compositions reported may not be the actual compositions in the equilibrium cell.

Based on the reasoning presented here, it was concluded that this set of data is not of high quality and therefore was not included in the data sets examined in the main portion of this report.

In addition, it is not recommended that the original compositions be replaced with the recalculated ones. The best conclusion is simply that the original compositions are probably in error and thus the hydrate data are dubious.

Table A4 Hydrate Pressures for the Schroeter et al. (1982) Mixtures Calculated Using CSMHYD

| Temperature (°C) | Experimental Pressure (psia) | Calculated Pressure (psia) | |
|---------------------|------------------------------------|----------------------------|-----------------------------|
| | | Original Composition | Recalculated Composition |
| 2.8 | 81.4 | 67.5 | 82.0 |
| 4.6 | 102.4 | 83.3 | 100.7 |
| 11.0 | 205.8 | 173.9 | 206.5 |
| 14.2 | 293.5 | 251.6 | 296.0 |
| 18.0 | 488.3 | 396.0 | 460.0 |
| 2.7 | 49.2 | 42.5 | 55.9 |
| 10.4 | 118.5 | 101.0 | 128.6 |
| 19.5 | 408.0 | 282.0 | 346.1 |
| 7.2 | 53.4 | 39.9 | 50.9 |
| 13.1 | 99.5 | 75.7 | 93.8 |
| 19.1 | 209.5 | 145.0 | 175.2 |
| 24.3 | 370.5 | 260.1 | 308.1 |
| 27.8 | 620.0 | DNC | 459.9 |

DNC – did not converge