

Correlations for Predicting Vapour – Solid Equilibrium Constants

By

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Abstract

The reliability of prediction models in determining hydrate forming temperatures adequately is of paramount importance. Most correlations have been found to vary significantly from experimental hydrate forming temperature data. This study is focused on developing correlations for predicting vapour solid constants for methane, ethane, propane, iso – butane, normal – butane, carbon IV oxide and hydrogen sulphide by extracting over 2000 data points from the GPSA chart. The correlations developed in this study were used to develop a computer program for predicting natural gas hydrate formation temperatures for mitigating the challenges posed by natural gas hydrate formation in process installations. The correlations gave correlation coefficients between 0.9 and 0.99. The computer model developed gave an average relative error of -3.73%, coefficient of correlation of 0.94 and a standard deviation of 5.9%.

1. Introduction

In hydrocarbon production, the most occurring phases are the hydrocarbon liquid and gas phase with water as an additional phase in the liquid. When variables describing change in the entire system (temperature, pressure, and compositions) remain constant with time and position, the phases can co-exist in equilibrium. A good acquaintance of the conditions under which these phases can be present is a matter of great significant practical importance in designing surface facilities, pipelines, and development of compositional models¹

The produced hydrocarbon fluid moves from surface production facilities through any of the transportation modes to refineries, end users, etc. One major difficulty in the use of Natural Gas is its transportation and storage. Also, the transportation of Natural Gas plays an important role in the Oil/Gas industry and as such, it must be done with much effectiveness since it is a vital commercial activity that takes place on daily basis. Of all Natural Gas transportation modes, pipelines have been adjured the most cost effective, efficient and safest way of transporting Natural Gas, but if not handled with great care, could lead to liquidation which occur as a result of poor management. Pipeline transportation entails construction of long distance, large diameter steel pipelines to move the Natural Gas to domestic, commercial, and industrial users many miles away from the field.

At specific conditions especially at high pressures and low temperatures, we expect the formation of Natural Gas Hydrates whenever there is a system of Natural Gas and water co-existing. The Natural Gas Hydrates are a serious problem in the Natural Gas production and transportation through pipelines because they plug pipelines and process equipments and in some cases, cause

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¹ Tarek Ahmed (2001); “Reservoir Engineering Hand Book”, 2nd Ed; Gulf Publishing Company, United States

bursting. This is as a result of not knowing the interactions between the hydrocarbon phases involved (Natural Gas and Water). Since there is the tendency of the hydrocarbon fluid to flash vaporize as a result of turbulence, sharp bends, etc in the pipeline; a good understanding of the Vapor-Solid interactions is of significant importance to take proactive steps against formation of Natural Gas Hydrates in the pipelines.

Natural Gas Hydrate are solid crystalline compounds (CLATHRATE) formed by the combination of Natural Gas and Water under pressure at relatively low temperatures. The Clathrate formation phenomenon involves a host and guest association and this occurs when water molecules form cage-like configuration around smaller guest molecules. The water is the mainframe of the configuration while the empty spaces are occupied by hydrocarbon molecules. Also the crystals of Natural Gas Hydrates look like ice or wet snow in appearance and do not have ice's solid structure because they are less dense, but also exhibit properties that are commonly related with chemical compounds.

The most common guest molecules are methane, ethane, propane, iso-butane, normal butane, nitrogen, carbon dioxide, and hydrogen sulphide. They have often been found responsible for operating difficulties at wellheads, pipelines, and other processing equipments during flow of Natural Gas and it becomes necessary to define and also avoid conditions that help promote the formation of hydrates. The chemical formulas of some Natural Gas Hydrates are:

1. Methane Hydrate ($\text{CH}_4 \cdot 7\text{H}_2\text{O}$)
2. Ethane Hydrate ($\text{C}_2\text{H}_6 \cdot 8\text{H}_2\text{O}$)
3. Propane Hydrate ($\text{C}_3\text{H}_8 \cdot 18\text{H}_2\text{O}$)
4. CO_2 Hydrates ($\text{CO}_2 \cdot 7\text{H}_2\text{O}$)

1.1. Conditions Necessary for Natural Gas Hydrate Formation

Some conditions that promote Natural Gas Hydrate formation are:

- I. Presence of liquid water
- II. Low temperature
- III. High pressure
- IV. Composition of Natural Gas
- V. High velocity or agitation
- VI. Presence of seed crystals of hydrate
- VII. Presence of highly soluble gas in water, such as H_2S or CO_2

1.2. Measures Taken to Prevent Natural Gas Hydrate Formation in Pipelines

Some measures that can be taken to prevent Natural Gas Hydrate formation in pipelines are:

- I. Applying heat

- II. Insulating
- III. Addition of inhibitors into gas streams to decrease freezing point.

Transportation through pipelines has met many challenges like bursting, plugging, corrosion, liquid holdup, etc. Most of these problems or challenges are as a result of inadequate knowledge of the interactions between the molecules/phases and Natural Gas Hydrate formation conditions. In addition, most of the computations (including software) required for adequately predicting hydrate forming pressures and temperatures are iterative, rigorous and time consuming. In general, most of the software are expensive and not easy to get locally. This study therefore seeks to develop a cost effective, user friendly software for predicting hydrate forming temperatures, made from correlations developed from GPSA² chart.

1.3. Methods for Predicting Natural Gas Hydrate Formation

Various methods exist for adequately predicting hydrate forming conditions. In addition to software, the three (3) most used methods are:

1. Gas Gravity Method

This method involves the use of the gas-gravity plot developed by Katz³. The plot relates the gas gravity of the gas stream to the hydrate formation temperature with pressure. This method is suitable for sweet gas mixtures. The Katz gravity chart was generated from limited amount of experimental data and gives accurate results up to 65°F. However, they recommended that the Baillie and Wichert method is better than this method, when applied to sweet gas mixtures since there is the inclusion of a correction factor for propane⁴

2. Empirical Correlations

These methods consist of the use of empirical correlations in predicting hydrate forming temperatures and pressures. Some of the widely used correlations include:

- I. Sloan⁵ developed a correlation to predict hydrate formation temperature for sweet natural gas. His correlation is of the form:

$$T^{\circ}F = -16.5 - \frac{6.83}{\gamma_g^2} + 13.8 \ln P \tag{1}$$

- II. Hammerschmidt⁶ developed a hydrate formation temperature correlation given by:

$$T^{\circ}F = 8.9P^{0.285} \tag{2}$$

² GPSA Engineering Data Book, 11th Edition, Gas Processors Suppliers Association; Tulsa, OK; 1998

³ Katz D.I “Handbook of Natural Gas Engineering”; McGraw Hill, New York, 1959

⁴ Carroll J. J “Natural Gas Hydrate”; A Guide for Engineers”. Gulf Professional Publishing, Houston, TX, 2003

⁵ Sloan E. D: Clathrate Hydrates of Natural Gases: 2nd Edition, CRC Press 2007.

⁶ Hammerschmidt, E.G; American Gas Association Monthly. 8: 278, 1936

III. Motiee⁷ used regression method to determine six coefficients that would correlate temperature, pressure and specific gravity. His correlation is of the form:

$$T = b_1 + b_2 \log(P) + b_3 (\log(P))^2 + b_4 \gamma_g + b_5 \gamma_g^2 + b_6 \gamma_g \log(P) \quad (3)$$

IV. Berge⁸ correlation

$$\text{For } 0.555 \leq \gamma_g < 0.58$$

$$T = -96.03 + 25.37 \ln P - 0.64 (\ln P)^2 + (\gamma_g - 0.555) / 0.025 \times \left[80.61 \times P + 1.16 \times \frac{10^4}{(P+596.16)} - 96.03 + 25.37 \times \ln P - 0.64 \times (\ln P)^2 \right] \quad (4)$$

Where P=Pressure (psi), T=temperature (°F) and γ_g = Specific gravity of gas stream

3. K-Factor Method:

The K-factor method makes use of the Vapor-Solid-Equilibrium constants developed by Carson and Katz. This method is based on the fact that Natural Gas Hydrates are solids and the vapor-solid equilibrium constant is gotten experimentally. The Natural Gas Hydrate constants are predicted from an empirical equation of the form:

$$K_{vs,i} = y_i / x_i \quad (5)$$

Where y_i is the mole fraction of the i^{th} hydrocarbon component in the gas phase considered on a water-free basis and x_i is the mole fraction of the same component in the solid phase on a water-free basis. Equation (6) usually needs to satisfy;

$$\sum_{i=0}^n \frac{y_i}{x_i} = 1 \quad (6)$$

Usually this method is iterative and gives reasonable results for sweet natural gases and has been proven to be appropriate up to about 1000psia. The inclusion of non-hydrocarbon gases such as CO₂, N₂ and H₂S may cause inaccurate results and the equilibrium constants taken as infinity.

2. Study Objectives

The objectives of this study are to develop:

1. Correlations to predict K-solid values for different gas hydrate forming molecules
2. A cost-effective computer model that can predict gas hydrate formation temperature using the K-solid method.

⁷ Motiee, M; Estimate Possibility of Hydrates: Hydrocarbon Processing. 98; 1991

⁸ Berge, B.K; Hydrate Prediction on a microcomputer; Paper SPE 15306 presented at the symposium on Petroleum Industry Applications of Microcomputers; 1986

3. Methodology

The method adopted for this study was the development of novel correlations for Vapor-Solid-Equilibrium (K-solids) constants for methane, ethane, propane, Iso-butane, Normal Butane, Carbon(IV)Oxide and Hydrogen Sulfide, and a computer program (software using a modern high level computer programming language, VISUAL STUDIO 2010) to predict Natural Gas Hydrate formation Temperature using the developed K- solid correlations).

The study made use of Two Thousand and Twenty-Five (2,025) data sets (points) extracted from vapor-solid equilibrium charts by GPSA. Comparative statistical error analysis was carried out to check the performance and accuracy of the computer program developed using experimental values from literature and results from HYDRATE PLUS software.

Table 1: Temperature and Pressure Limits Used in This Study

| COMPONENTS | PRESSURE (psia) | TEMPERATURE (°F) |
|------------------|-----------------|------------------|
| METHANE | 100 to 4,000 | 32 to 81 |
| ETHANE | 100 to 4,000 | 32 to 81 |
| PROPANE | 100 to 4,000 | 32 to 76 |
| ISO-BUTANE | 50 to 2,000 | 32 to 72 |
| NORMAL-BUTANE | 200 to 1,500 | 32 to 50 |
| CARBON(IV)OXIDE | 250 to 1,000 | 32 to 60 |
| HYDROGEN SULFIDE | 100 to 2,000 | 32 to 95 |

3.1. Statistical Analysis

The following statistical parameters were used to check the performance of the new correlations. The criteria used were:

- i. Percentage mean relative error
- ii. Percentage mean absolute relative error
- iii. Standard deviation and
- iv. Correlation coefficient.

3.1.1. *Percentage Mean Relative Error:*

This is given as:

$$\% \text{ MRE} = \frac{\sum_{i=1,2,\dots}^n E_i}{n} \quad (7)$$

$$E_i = \left[\frac{X_{mea} - X_{mo}}{X_{mea}} \right] \times 100\%. \quad i = 1, 2, \dots, n \quad (8)$$

Where;

E_i = Relative Error of each element (%)
 X_{mea} = measured data
 X_{mo} = Result from model

3.1.2. Percentage Mean Absolute Relative Error:

This is given as:

$$\% \text{ MARE} = \frac{\sum_{i=1,2,\dots}^n |E_i|}{n} \quad (9)$$

3.1.3. Standard Deviation:

$$\% \text{ SD} = \sqrt{\sum_{i=1,2,\dots,n}^n \left[\left(E_i - \left(\frac{\bar{X} - (X)_{mo}}{(X)_{meas}} \right)_i \right)^2 \right] / n - 1} \quad (10)$$

And

$$\bar{X} = \frac{\sum_{i=1,2,\dots}^n (E_{mea})_i}{n} \quad (11)$$

3.1.4. Correlation Coefficient (r):

This statistical parameter describes the level of the association between the measured data and values gotten from model. The correlation coefficient of zero indicates no relationship between the measured and the model's values, a close value to 1.0 indicates a perfect positive relationship.

4. Results and Discussion

From the data points obtained from the k – solid chart (GPSA), the following correlations were developed.

METHANE

$$K_s = T_1 + T_2 \frac{\log(P)}{\log(T)} + T_3 \frac{\log(P)^2}{\log(T)} + T_4 \frac{\log(P)}{\log(T)^2} + T_5 \frac{\log(P)^3}{\log(T)} + T_6 \frac{\log(P)}{\log(T)^3} + T_7 \frac{\log(P)^4}{\log(T)} + T_8 \frac{\log(P)}{\log(T)^4} \quad (12)$$

ETHANE

$$K_s = T_1 + T_2 \frac{\log(P)}{\log(T)} + T_3 \frac{\log(P)^2}{\log(T)} + T_4 \frac{\log(P)}{\log(T)^2} + T_5 \frac{\log(P)^3}{\log(T)} + T_6 \frac{\log(P)}{\log(T)^3} + T_7 \log\left(\frac{P}{T}\right) \quad (13)$$

PROPANE

$$K_s = T_1 + T_2 \frac{\log(P)}{\log(T)} + T_3 \frac{\log(P)^2}{\log(T)} + T_4 \frac{\log(P)}{\log(T)^2} + T_5 \frac{\log(P)^3}{\log(T)} + T_6 \frac{\log(P)}{\log(T)^3} + T_7 \frac{\log(P)^4}{\log(T)} + T_8 \frac{\log(P)}{\log(T)^4} + T_9 \log\left(\frac{P}{T}\right) \quad (14)$$

I-BUTANE

$$K_s = T_1 + T_2 \frac{\log(P)}{\log(T)} + T_3 \frac{\log(P)^2}{\log(T)} + T_4 \frac{\log(P)}{\log(T)^2} + T_5 \frac{\log(P)^3}{\log(T)} + T_6 \frac{\log(P)}{\log(T)^3} + T_7 \log\left(\frac{P}{T}\right) \quad (15)$$

N-BUTANE

$$K_s = T_1 + T_2 \frac{\log(P)}{\log(T)} + T_3 \frac{\log(P)^2}{\log(T)} + T_4 \frac{\log(P)}{\log(T)^2} + T_5 \frac{\log(P)^3}{\log(T)} + T_6 \frac{\log(P)}{\log(T)^3} \quad (16)$$

CO₂

$$K_s = T_1 + T_2 \frac{\log(P)}{\log(T)} + T_3 \frac{\log(P)^2}{\log(T)} + T_4 \frac{\log(P)}{\log(T)^2} + T_5 \frac{\log(P)^3}{\log(T)} + T_6 \frac{\log(P)}{\log(T)^3} + T_7 \frac{\log(P)^4}{\log(T)} + T_8 \frac{\log(P)}{\log(T)^4} + T_9 \log\left(\frac{P}{T}\right) \quad (17)$$

H₂S

$$K_s = T_1 + T_2 \frac{\log(P)}{\log(T)} + T_3 \frac{\log(P)^2}{\log(T)} + T_4 \frac{\log(P)}{\log(T)^2} + T_5 \frac{\log(P)^3}{\log(T)} + T_6 \frac{\log(P)}{\log(T)^3} + T_7 \frac{\log(P)^4}{\log(T)} + T_8 \frac{\log(P)}{\log(T)^4} \quad (18)$$

Table 2: Coefficients of Correlations

| COEFF. | METHANE | ETHANE | PROPANE | I-BUTANE | N-BUTANE | CO ₂ | H ₂ S |
|----------------|--------------|--------------|--------------|--------------|--------------|-----------------|------------------|
| T ₁ | 3.878243745 | -6.474176398 | 24.87738815 | -10.08529882 | 3.781851659 | 72.17670437 | 11.67536118 |
| T ₂ | -2.279609736 | 36.93088692 | -48.0392788 | 22.42760365 | 4.314007627 | -74.54144954 | -19.68079767 |
| T ₃ | -10.11135939 | 2.60191673 | 21.72338125 | 3.166107635 | 0.641032781 | 10.32955337 | 12.49673999 |
| T ₄ | 54.46030321 | -97.76261314 | -16.62223252 | -50.28213272 | -27.96968833 | -100.7522738 | -27.92148496 |
| T ₅ | 2.482571231 | -0.121875811 | -4.466018832 | -0.237337512 | 0.002729381 | 11.84531229 | -2.985773325 |
| T ₆ | -63.39337156 | 74.26035832 | 11.831553 | 39.0077784 | 23.53793642 | 56.45146339 | 36.27797084 |
| T ₇ | -0.185023423 | -10.97041924 | 0.350627232 | -10.8349819 | | -2.215382105 | 0.278342391 |
| T ₈ | 17.42692589 | | 22.67028875 | | | 90.60195809 | -5.692814554 |
| T ₉ | | | 0.769148194 | | | -30.47461873 | |

4.1 Cross Plots of Model vs Measured K- Values

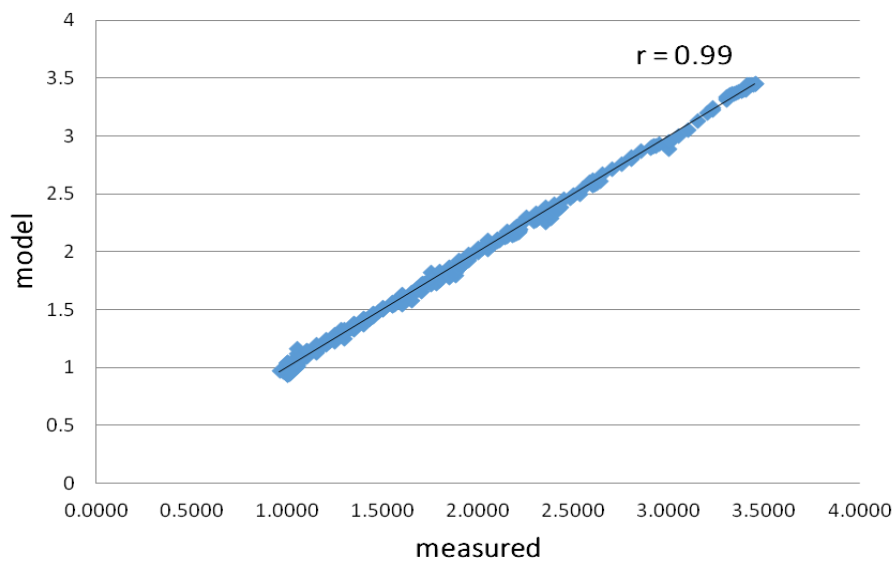


Fig 1: Plot of model against measured K- Value data for Methane

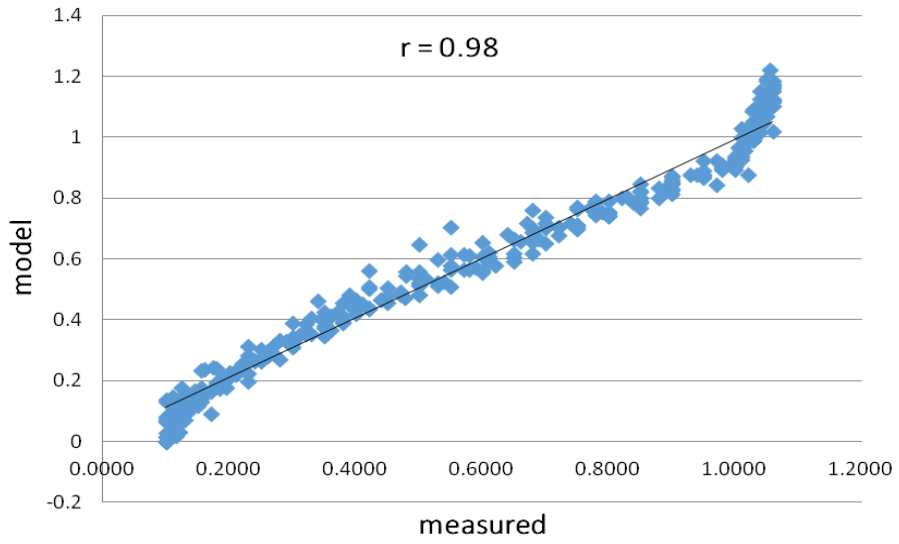


Fig 2: Plot of model against measured K- Value data for Ethane

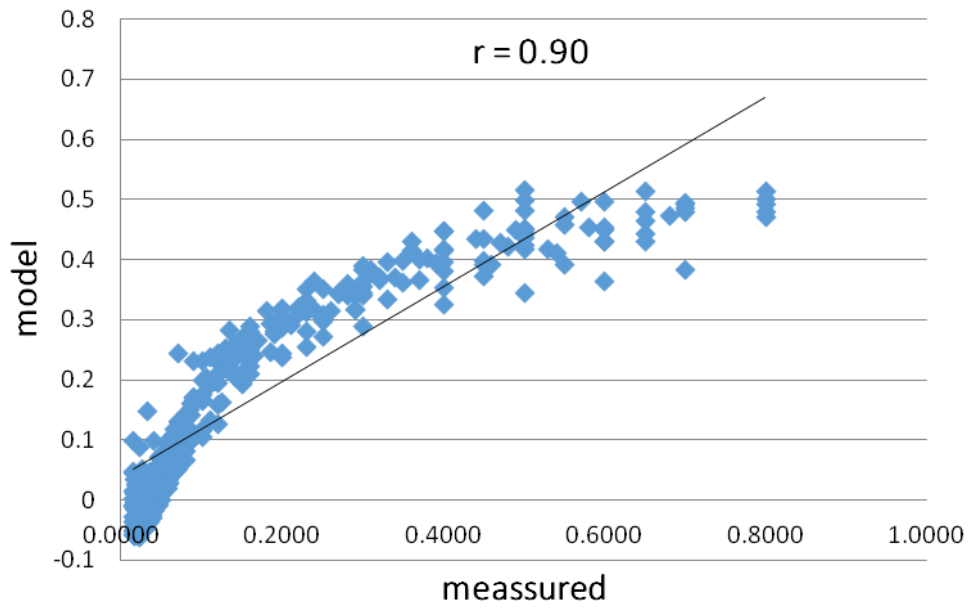


Fig 3: Plot of model against measured K- Value data for Propane

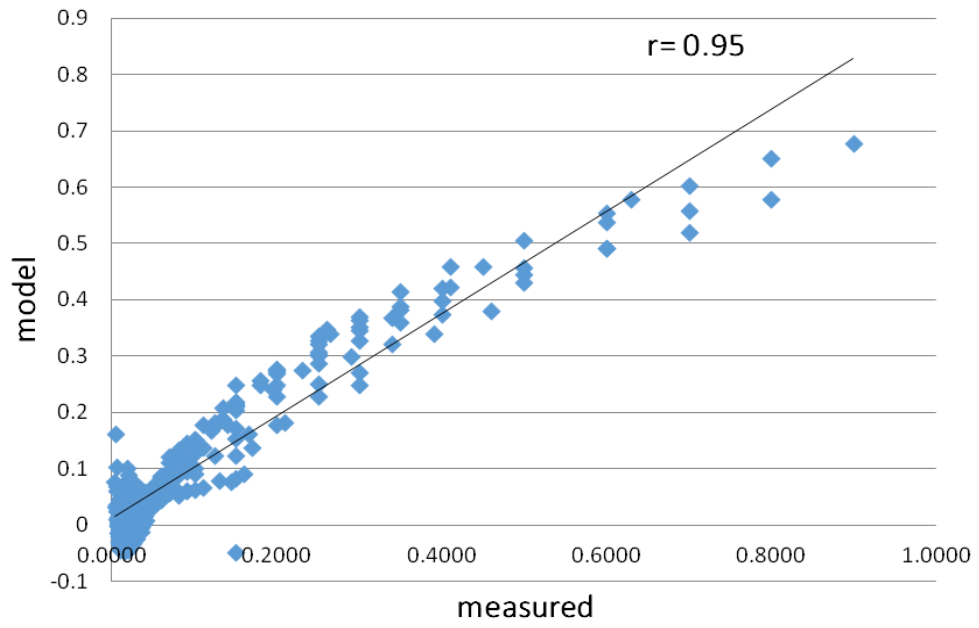


Fig 4: Plot of model against measured K- Value data for Iso-Butane

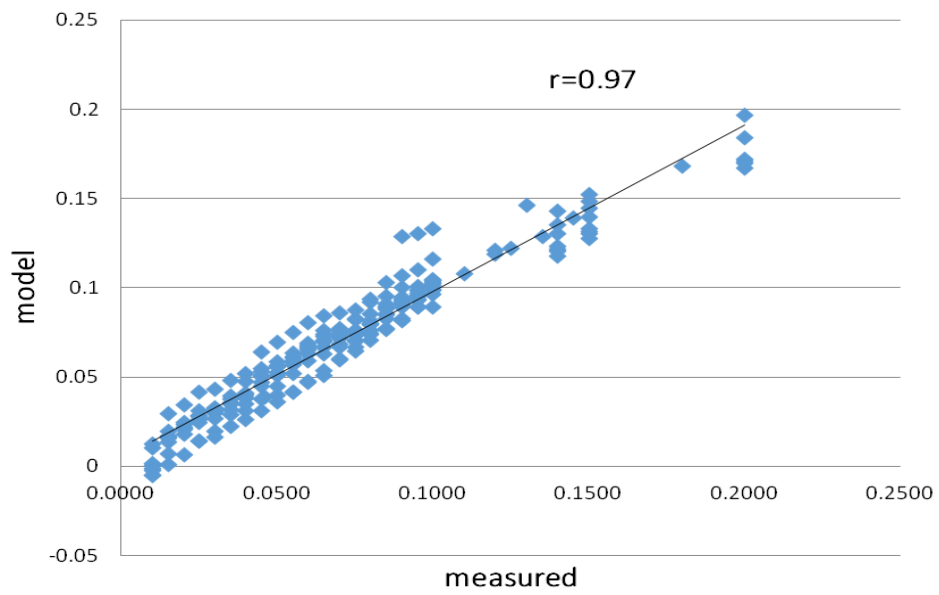


Fig 5: Plot of model against measured K- Value data for n-Butane

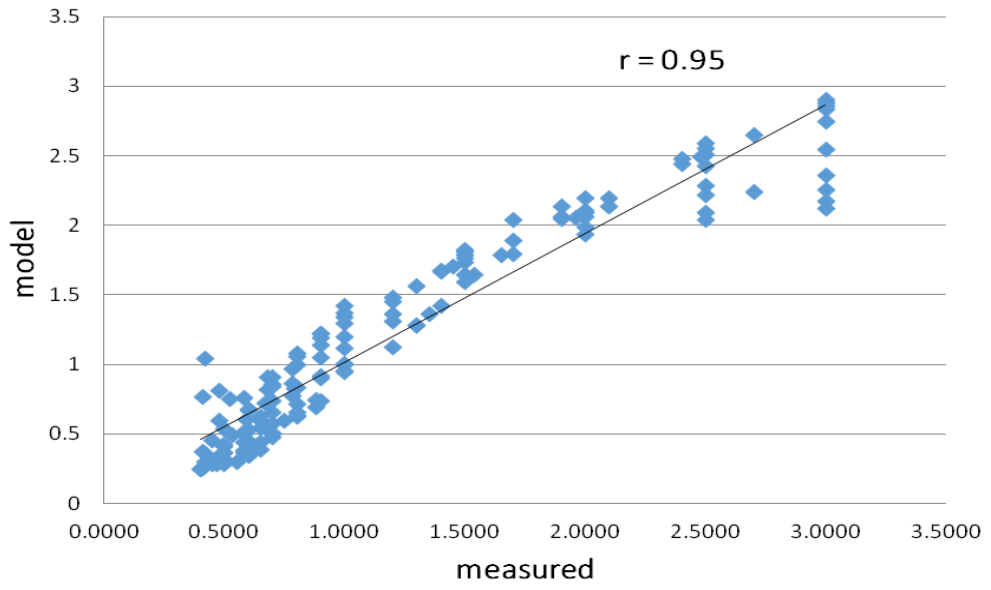


Fig 6: Plot of model against measured K- Value data for Carbon (IV) Oxide

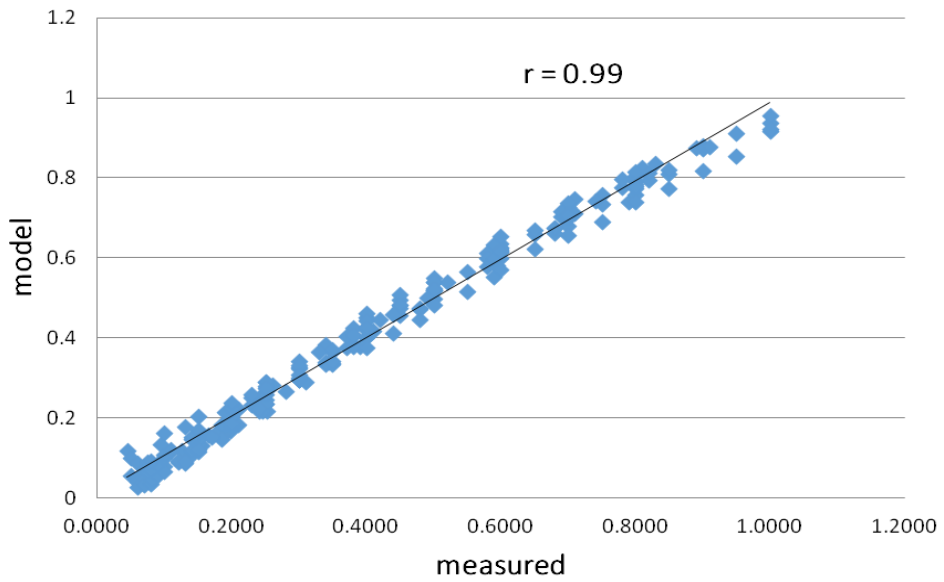


Fig 7: Plot of model against measured K- Value data for Hydrogen Sulfide

Table 3: Comparative Analysis of HYD-TEMP, HYDRATE PLUS and EXPERIMENTAL Values.

| S/n | Specific gravity | Pressure (Psia) | TEMPERATURE (°F) | | | ERROR, PERCENT | |
|-----|------------------|-----------------|--------------------------|----------|--------------|----------------|--------------|
| | | | Experimental Temperature | HYD-TEMP | HYDRATE PLUS | HYD-TEMP | HYDRATE PLUS |
| 1 | 0.555 | 458 | 35 | 35.70 | 36.01 | -2.0 | -2.9 |
| 2 | 0.555 | 600 | 40 | 41.00 | 40.90 | -2.5 | -2.3 |
| 3 | 0.555 | 800 | 45 | 46.20 | 45.80 | -2.7 | -1.8 |
| 4 | 0.6 | 250 | 40 | 44.60 | 42.80 | -11.5 | -7.0 |
| 5 | 0.6 | 480 | 50 | 50.80 | 52.50 | -1.6 | -5.0 |
| 6 | 0.6 | 980 | 60 | 58.70 | 61.50 | 2.2 | -2.5 |
| 7 | 0.6 | 2625 | 70 | 75.80 | 70.84 | -8.3 | -1.2 |
| 8 | 0.65 | 110 | 30 | 36.00 | 34.60 | -20.0 | -15.3 |
| 9 | 0.65 | 390 | 50 | 51.60 | 52.90 | -3.2 | -5.8 |
| 10 | 0.65 | 2050 | 70 | 74.40 | 71.50 | -6.3 | -2.1 |
| 11 | 0.7 | 120 | 35 | 40.70 | 41.50 | 16.3 | -18.6 |
| 12 | 0.7 | 340 | 50 | 53.70 | 56.50 | -7.4 | -13.0 |
| 13 | 0.7 | 690 | 60 | 63.60 | 65.30 | -6.0 | -8.8 |
| 14 | 0.7 | 3400 | 75 | 59.60 | 77.20 | 20.5 | -2.9 |
| 15 | 0.8 | 280 | 50 | 51.40 | 49.90 | -2.8 | 0.2 |
| 16 | 0.8 | 1700 | 70 | 70.00 | 69.80 | 0.0 | -0.3 |
| 17 | 0.9 | 110 | 40 | 41.40 | 43.80 | -3.5 | -9.5 |
| 18 | 0.9 | 230 | 50 | 51.20 | 54.90 | -2.4 | -9.8 |
| 19 | 0.9 | 2600 | 75 | 67.80 | 75.40 | 9.6 | -0.5 |
| 20 | 1 | 195 | 50 | 53.90 | 52.60 | -7.8 | -5.2 |
| 21 | 1 | 440 | 60 | 63.90 | 64.60 | -6.5 | -7.7 |
| | | | Er | | | -3.73 | -5.78 |
| | | | Ea | | | 6.81 | 5.83 |
| | | | SD | | | 9.2 | 8 |
| | | | r | | | 0.94 | 0.99 |

From Table 3, the HYD-TEMP software compared well with the experimental data⁹ and HYDRATE PLUS software; with an average error of -3.73% and a standard deviation of 9.2.

⁹ Ahmed, K and Fattah, A (2004): Evaluation of Empirical Correlations for Natural Gas Hydrate Predictions. King Saud University, Saudi Arabia.

This is an indication that the correlations developed in this study for vapor – solid equilibrium constants can be used for hydrate temperature predictions with reasonable accuracy.

5. Conclusions and Recommendations

1. A new vapor-solid-equilibrium constants predictive model has been developed using the GPSA charts.
2. The correlations were used to develop a software (HYD-TEMP) for predicting Natural Gas Hydrate Formation Temperature based on K-solid method. When compared with experimental data, the results from HYD-TEMP software had an average absolute error of -3.73%, a standard deviation of 9.2 and a correlation coefficient of 0.94. While that of HYDRATE PLUS gave an average absolute error of -5.78%, standard deviation of 8 and a correlation coefficient of 0.99.
3. The HYD-TEMP software, can be used in the Petroleum and Gas industry with reasonable accuracy.
4. More experimental data are needed to improve performances of iso-butane, CO₂ and propane.