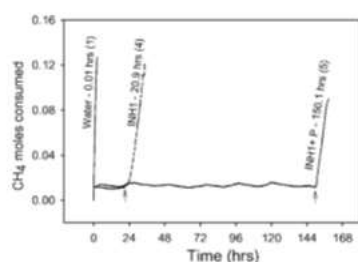**Review Article**

Investigation of Predictive Methods of Gas Hydrate Formation in Natural Gas Transmission Pipelines

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GRAPHICAL ABSTRACT

ABSTRACT

Natural gas hydrate is a solid crystalline compound formed from the composition of water and gas and is part of the clathrate family. Gas hydrate can be formed by pure gas or a gas mixture consisting of two or more components. Gas hydrates are recognized as non-stoichiometric solids. One of the methods or methods that has been most successful in predicting or recognizing hydrate phases in hydrocarbon equilibrium is based on the relative Kvs size of the vapor-solid equilibrium constant. Tables of equilibrium for species or constituents of hydrates known as normal butane are listed in various articles and books. With the discovery of the heaviest constituents of hydrates, their equilibrium constants need to be more accurately predicted in the un-hydrated phase of the hydrocarbon mixtures, especially in the reservoir fluids.

INTRODUCTION

Hydrate is a water network with a set of empty spaces within a short distance. If some of this space is filled by gas molecules, hydrate can be considered as a stable solid. In other words, gas hydrates are complex crystalline molecules that are composed of a mixture of water and suitable gas molecules. Aqueous molecules form unstable networks due to hydrogen bonds, and gas molecules occupy the space between the network slots. When a small amount of grid holes is filled, they crystallize at temperatures even above the freezing point of the gas hydrate molecules [1]. The structure of the hydrated gas will be as follows: Structure I, Structure II and more recently structure H. Recently, various methods have been used to predict the conditions of hydrates, which can be divided into two parts:

1) Experimental methods

2) Methods based on statistical thermodynamics.

Although experimental methods have frequently been replaced by more advanced thermodynamic methods, the need for and use of manual and experimental calculations in the inevitable experimental method still extends to the experimental methods performed through solid-vapor equilibrium constants. He acknowledged that the value of k depends on the constituents [2]. Therefore, it cannot be considered a reliable method

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and has proven to be very useful and accurate estimations for estimating gas hydrate formation conditions, especially for traditional and conventional systems [3].

Investigation of operating conditions of hydrate formation

There are various methods for studying the operating conditions of hydrate formation (temperature and pressure), one of the most common methods is to plot the logarithm of the pressure change in terms of gas temperature. In this case, the curve is a straight line. It is easy to analyze [4].

Temperature: The structure of hydrates is maintained in the water-gas range by molecules soluble in the aqueous phase region. As a result, H_2S and CO_2 accelerate the hydrates formation at high temperatures because they are more soluble in water than most hydrocarbons. Pressure causes the shape of the network to change. In the case of pentane and molecules larger than that, the pressure breaks down the network and prevents the formation of stable hydrates. Hydrates increase like crystals. They form deposits. In fact, high pressure and low temperature in places such as a tube cap on perforated plates and valves cause sedimentation that the maximum force from the variable current can also prevent the hydrates formation in these locations [5]. So high turbulence can easily alter their actual structure. Hydrocarbon liquids help this process through intense washing. These structures are related to the size of the spaces in the network. This space can accommodate methane, ethane, H_2S and CO_2 and other such molecules. That is, the replacement molecule must be of sufficient size to enter the blue groove. There is no molecularly larger molecule than isobutene that could replace the gap. In recent experiments, of course, butanol has been identified as the largest hydrate-forming molecule that could be involved in a network of accumulation of large numbers of small molecules. It is noteworthy that normal butane is not capable of forming stable hydrates but needs the help of another gas to enter the hydrate network and form stable structures. Hydrate is a solid but it differs from the structure of ice. Because it is a crystalline solid. Hydrate is a chemical compound called Clathrate (a solid molecular compound enclosed in a crystalline cavity) that is a term used to designate compounds that may be present in a flat idol species [6].

New methods for molding hydrate gases

A two-step mechanism for hydrate gas production has been proposed:

(1) Perform a semi-chemical reaction to produce alkaline hydrates

(2) Adsorption of small gas molecules from basic alkaline hydrate chain rings.

This new conception is based on previous studies and two equilibriums: Semi-chemical equilibrium reaction in the first phase and physical equilibrium adsorption in the second phase [1, 7]. The results obtained in successive experiments show that the new models are capable of predicting the formation of hydrates for pure gases and a combination of gases. Many of the thermodynamic models available to predict hydrate formation from the various modifications and modifications suggested by the model proposed by Edwards and Plato are available. Scientists have recently suggested that alternating static mechanisms are the basis for the hydrates formation. The basis and purpose of the Vdwp model is based on the relative similarity between hydrate formation and Langmuir absorption [8]. Although the adsorption mechanism is capable of interpreting non-stoichiometric properties and states of hydrates, there are many differences between the two processes. In this section, we will try to describe in some way the actual mechanism of hydrates that resemble the model of hydrates [4, 9].

Proposed mechanism of hydrates formation

A two-step mechanism of hydrate formation is proposed as follows:

Stage One: Stoichiometry of Alkaline Hydrates during a Semi-Chemical Reaction.

Second step: The adsorption of gaseous molecules into a mass of alkaline hydrate chains during a non-stoichiometric process. In the first step, we have assumed that the gas molecules are soluble in water based on the Long and Stevan scheme, which is accomplished by surrounding the guest molecules with several water molecules that surround them. This continuous action, called alkaline hydrates, is carried on one side of the molecules by the gas

molecules, and the other side of the chain remains intact. We have explained this process based on following complex process:

$$H_2o + \lambda_2 G \rightarrow G_{\lambda_2} \cdot H_2o \qquad (1)$$

In this respect G denotes the specific gravity of the gas and λ_2 the number of gas molecules and the number of water molecules in alkaline hydrates. During this stage the intact portion (in the chain) is covered by other alkaline hydrates. In the second step, molecules of small size (Ar, N_2, O_2, CH_4, etc.) that are soluble in water move to the chain loops (the adsorption process). This results from the non-stoichiometric property of the hydrates [6-8, 10]. However, this step will not occur for molecules that are larger in size, such as (ethane, propane, -n-butane and -i-butane), and for those molecules that are capable of being detached from the chain rings. Therefore, the final stoichiometric form of alkaline hydrates will be formed only in the first step. So it can be said that alkaline hydrates are not hypothetical but they are physically present. These were the logical reasons used in Langmuir adsorption theory to explain the saturation of chain rings by gas molecules [11].

Thermodynamic Root Modeling and Evaluation of Pure Hydrate Gas Parameters

Based on the two-step hydrate formation mechanism described above, there are two types of equilibrium in the system. A semi-chemical equilibrium reaction that occurs in the first step and the physical equilibrium absorption that saturates the gas molecules around the chain rings during the second step. For the reaction mentioned in formula (1), if we use chemical equilibrium constants we will have:

$$\mu_B = \mu_w + \lambda_2 \mu_g \qquad (2)$$

In which μ_B chemical potentials of alkaline hydrates, μ_w and μ_g are the standard chemical potentials of water and gas, respectively. After the adsorption of gas molecules into the chains, the chemical potential of alkali hydrates will decrease. μ_B can be displayed as follows:

$$\mu_B = \mu^o{}_B + \lambda_1 \, RT \iota n \, (1-\theta) \qquad (3)$$

Where θ represents the fraction of chain rings encompassed by the gas molecules; $\mu^\circ{}_B$ represents the unsaturated chemical potential of alkali hydrates ($\theta = 0$) and λ_1 denotes the number of chains of small chains per molecule Water contains alkaline hydrates. According to Langmuir's theory θ is calculated as follows.

$$\theta = \frac{Cf}{(1+Cf)} \qquad (4)$$

Where f denotes the specific gas fugacity and C denotes the Langmuir constant. Using general and fundamental thermodynamic equations, the chemical specific potential of gas is calculated as follows. In which $\mu^\circ g$ (T) represents the chemical potential in the ideal gas state, the subtraction equation (2) - (5) follows: And by definition:

$$\mu_g = \mu^\circ{}_g \, (T) + RT \, Lnf \qquad (5)$$

$$\mu^o{}_B + \lambda_1 \, RT \, Ln \, (1-\theta) = \mu_w + \lambda_2 \, [\mu^\circ{}_g \, (T) + RT \, lnf] \qquad (6)$$

Relation (6) can be transformed into the following relation after sorting:

$$f\circ = \exp\left[\frac{\mu_B^o - \mu_w - \lambda_2 \mu_g^o(T)}{\lambda_2 RT} \right] \qquad (7)$$

$$f = f^\circ \, (1-\theta)^\alpha \qquad (8)$$

Where $\alpha = \lambda_1/\lambda_2$ for compound I, $\alpha = \dfrac{1}{3}$ and for compound II, $\alpha = 2$ in the equation shown in (7), f° is not only a function of T, P, and αw of water activity, Refer to Equation (11), but it shows the property of formed alkali hydrates. When $\theta = 0$, equation (8) will be given below. In this case f° accurately represents the fugacity of the gas phase in equilibrium when the alkaline hydrate is unsaturated. ($\theta = 0$). The fraction ($\mu^\circ{}_B - \mu_w$) in Equation (7) can be calculated using multiple thermodynamic equations.

$$f = f^\circ \qquad (9)$$

Where A represents the number of free energy molecules of Helmutz (which is fundamentally related to the energy of the system) and the number of molars of volume change ΔV that can be obtained from the equation (7) can be derived from three factors. The share of each of the components T, P and aw is as follows:

$$\mu_w = A_w + PV_w + RT \ln (a_w) \qquad (10)$$

$$\mu^o{}_B - \mu_w = \Delta A + P\Delta V - RT \ln (a_w) \qquad (11)$$

$$f^\circ = f^\circ (T)\, f^\circ (P)\, f^\circ (a_w) \qquad (12)$$

$$f^\circ(P) = \exp(\frac{\beta P}{T}) \qquad (13)$$

In Equations (12 and 13)

This is where $\beta = \dfrac{\Delta V}{\lambda_2 R}$ the amount of idol can be obtained, β equal to 0.4242 k / bar for compound I and 1.0224 k / bar for compound II, respectively.

$$f^\circ (a_w) = a_w^{\,-1/\lambda_2} \qquad (14)$$

$$f^\circ (T) = A' \exp(\frac{B'}{T - C'}) \qquad (15)$$

$$f^\circ (T) = \exp\left(\frac{D(T - 273.15)}{T}\right) \times A' \exp\left(\frac{B'}{T - C'}\right) \qquad (16)$$

The number λ_2 is equal to 3.23 for compound I and 1.17 for compound II, respectively. In a particular pure composition of a substance, the constants of Antony, A', B', and C' can be obtained in constant and appropriate quantities for the hydrate gas formation, which will be the specific amounts of the same substance. These constant values for intermittent compounds can be obtained by using a two-hydrate compound. Equations (15 and 16) is corrected as follows:

$$C = X \exp(\frac{\gamma}{T - Z}) \qquad (17)$$

The constant D in Equation (17) is 22.5 for compound I and 49.5 for compound II, respectively.

To apply equation (8) in general (θ≠0), θ can be obtained by equation (4). To investigate Langmuir constants, we can integrate two parameters of the Nessel Lenard-Jones peta, which show that the Langmuir constants are very close to the slave numbers. For the application engineer, it is very useful and appropriate to associate the Langmuir C constant with temperature. This can be used to determine the value of Anton's equation:

$$\sum_j O_j = \frac{\sum j\, f_j\, G_j}{1 + \sum j\, F_j\, G_j} \qquad (18)$$

$$\sum_j x_i = 1.0 \qquad (19)$$

$$f_i{}^\circ (T) = \exp\left(\frac{-\sum j\, A_{ij}\, \theta_j}{T}\right) \times \left[A' \exp(\frac{B'}{T - C'})\right] (20)$$

$$(A_{ij} = A_{ji} \dots ,\; A_{ii} = A_{jj}) = 0 \qquad (21)$$

The x, y, and z constants used to determine the Langmuir C constant are calculated from the Lennard-Jones potential functions. The constant values measured for each of these numbers indicate that only loop chains are required to propose the mechanism for the formation of hydrates [12-15].

6. Hydrate formation in gas mixtures

The alkaline hydrate mixture behaves like a mixture of solid solutions with the name alkaline hydrate components. The overall property of the hydrate mixture depends only on the saturation of the gas molecules around the chain rings. In alkaline hydrates whose only difference in volume is summed up and having the same composition, the excess volume and the entropy of the alkaline hydrate mixture should be close to zero [17]. Therefore, it is reasonable to pay attention to the composition of the alkaline hydrate mixture as a true solution. Considering the number of molecules in the solution that affect each other (assuming the solution is ideal), the following equations for the hydrate mixture can be considered:

Where f_i denotes the fugacity of component i calculated by the Patel-Tega state equation. θ_j on the part of the chain rings occupied by the gas component j. x_i indicates the molar fraction of alkali

hydrate i. Determining the type and type of hydrate model based on the Vdw-p convention, which they consider to be due to the calculation of the chemical potential difference between the water and the hydrate network (Δμw), was performed. If we consider the influential factors to determine the hydrate model between the molecules of the ring design, the alkaline group is given by Equation (16) to calculate fi° (T) as follows:

Where Aij is the two-component effective parameter between the components in our solution between the two components i and j [16].

Calculation of Antoine equation constants for a hydrate mixture component

The structure and composition of the hydrate mixture can be different from that of the constituent state in its pure state, the antonine constants A′, B′, C′ in Equations (16) and (22) can be calculated for both compounds I and II. In this case the structure of the hydrate mixture with the gas component in the pure state can be different from the anthracite constants calculated for the two components of the same structure and the mixture of hydrates. The following is an acceptable solution for forming a gas component in a natural gas mixture.

1. To obtain the C_2H_6-C_3H_8 binary system data, it can be used for both C_2H_6 (when it is composed of hydrate II) and C_3H_8 (when mixed) when it is mixed.

2. To obtain the data for the formation of a two-component CH_4-Ar system, one can use the constants for the combination of CH_4 (when the mixture is composed of hydrate compound II) and Ar (when the mixture is formed of compound hydrate I).

3. For H_2S and CO_2, when each of them is mixed with propane, the hydrate compound II will form, and the formation data will be based on the calculated data of compound II antonine constants for H_2S and CO_2 [1،4،7،17].

Calculation results of two-component and multi-component hydrate gases

Comparison of calculated results and values and values of pressure formation in two-component and multi-component systems in gas hydration systems separately. For dual-component systems Ar-N_2, Ar-CH_4, CH_4-H_2S, C_2H_4-C_2H_6, C_2H_6-C_3H_8, all Aijs options will be zero. If for other systems, the Aij crossover

and return parameter is calculated in the system.

Natural hydrate gases: If we consider how the molecules of the mixture work together, we set the value to zero for each pair of Aij that was not available. The mean absolute error of the predictions indicates that the new hydrate models are promising and have a bright future in applied engineering.

Discussed Changing Hydrate Structure: We have known for years that if methane is mixed with a small amount of propane, the hydrate composition will change from I to II. Studies based on new models show that although the percentage of methane in the gas mixture is very high (95%) the volume of alkaline hydrate is very low. This implies that when forming a hydrate mixture, much of it is surrounded by propane, and methane plays only a partial role in this process. From Equation 19 we can see that fi is very sensitive to determine $\sum_j \theta_j$. For propane, the value θ is equal to zero and Fi = f°i. However, for the blend (methane + propane), methane occupies most of the design of the ring chains. This is affected by the presence of propane due to the partial pressure of hydrate formation. For example, when the methane content in the design of the chain ring is 0.8, the partial pressure required for propane to form the hydrate compound II is approximately 0.04 when the pure propane partial pressure is required. However, the propane concentration is low. Based on the analysis above, naming the change in the hydrate composition of methane would be somewhat misleading [5،9،18].

Interaction of molecules with each other

The effect of the Bell molecules on the hydrate phenomenon is examined in the following three categories.

1) Interaction of molecules in solution on alkaline hydrate

2) Interaction between molecules in solution and alkaline hydrate and saturation around the chain rings

3) Interaction on the molecules in solution and their absorption by the chain loops

The effect of the fraction f° (aw) on Equation 13

From Equation 15 we will have f° (aw) = aw$^{-7.67}$ for compound number hydrates (I) and f° (aw) = aw^{-17} for compound number hydrates II. This concept means that the product formation pressure is very sensitive to water activity. A slight decrease in water activity may cause a significant increase in pressure.

For systems that are water soluble and different types of gases soluble.

Therefore $X_w \rightarrow 1.0$, $\gamma w \rightarrow 1.0$ and $\alpha w \approx xw$ therefore equation 15 can be shown as follows.

$$f°(aw) \approx [1-xg]^{-1/\lambda_2} \approx 1+xg /\lambda_2 \qquad (22)$$

Xg represents the total mole fraction of gas species dissolved in the aqueous phase. When f° (aw), xg = 10-13 equals 1.00768 for compound I and 1.017 for compound II, respectively.

On the other hand, for systems containing gases with relatively high solubility in water, such as (H_2S, CO_2) and salt dipole inhibitor, the contribution of f° (aw) will not be partial. The other compounds, the f° (aw) fraction, can easily be exploited by a suitable combination of equilibrium gases based on the equations of state or the available activity coefficients [3.12-7, 19].

11. Hydrate Formation Prediction Method Using Vapor-Solid Balances

One of the methods or methods that has been most successful in predicting or recognizing hydrate phases in hydrocarbon equilibrium is based on the relative Kvs size of the vapor-solid equilibrium constant. Tables of equilibrium for species or constituents of hydrates known as normal butane are listed in various articles and books. With the discovery of the heaviest constituents of hydrates, their equilibrium constants need to be more accurately predicted in the un-hydrated phase of the hydrocarbon mixtures, especially in the reservoir fluids.

Katz *et al.,* at the University of Michigan developed a set of vapor-solid equilibrium constants to predict different states of hydration. The relationships obtained are methane, ethane, propane, isobutene, carbon dioxide and hydrogen sulfide. These are shown in graphs 3 through 5. These curves are for hydrocarbons having a pressure of 4000 Psia. For example, in practice the curve for methane at

pressures above 1000 psia does not work correctly. In this method, the proposed "k" for butane is considered as the one with a low concentration. "K" is freely intended for nitrogen and heavier components because they are hydrated in different states or not at all, such as the dew point calculation method that has been proposed simply as vapor-liquid values with vapor values. - The solid is moved by the graphs of the next pages. This simulation is useful for dealing with higher pressures. It should be noted that in this method manual calculations are relatively tedious and have a high accuracy at pressures above 1000 psia. Trekell and Campbell generalized these simple curves for pressures of 1000 to 6000 psia. Both agree with Katz's relationship. Using gas compounds, a temperature-based scheme for the structure of the hydrate versus pressure-based system can be developed and generalized. This design may come from the lower pressure area or it may be similar to the Katz method. These curves clearly illustrate the concept of each molecule. They show, for example, that the behavior of normal butane is not similar to that of ethane at higher concentrations. At maximum pressure up to 2000 psia. Normal butane to hydrate point slightly increases at psia 3000 pressure and higher pressure lowers hydrate point. This is initially attributed to the deformed network shape, which takes on relatively large holes, which may fit in without molecular arrangement. The following general guidelines are suggested for using this method:

1. Obtain the hydrocarbon residue curve through FEC determination

2. At pressure 1000 psia, table prediction for determination of hydrate formation temperature by algebraic sum

3. Transfer temperature or fat, using dry gas analysis for transverse values and sum of Δt values found from the coordinate source for grapheme methane hydrate. Correction of this temperature for pentane and heavier hydrocarbons will also have satisfactory results if the results are available

4. Repeat the previous steps for 2000 psia pressure and correction for pentane and heavy hydrocarbons

5. Calculate the hydrate temperature at each residual pressure until there is a graph of each until the hydrocarbon dew point pressure or above 13.8

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(MPa) is reached

6. Draw the calculated temperatures and pass the best curve through the points [6-15, 20]

Theoretically, how to eliminate and prevent hydrate formation in gas pipes

Glycol and alcohol may be used to reduce (prevent) the formation of hydrates. This is one of the fundamental phenomena in which the soluble compound may be below the freezing point of the solvent. The appropriate equation is as follows:

$$d = \frac{k_i \times X}{100M - X \times M} \tag{23}$$

d = depression of hydrate point

w = weight percent inhibitor in the liquid water phase

M = mol wt of inhibitor

$K_i = cons\tan t$

The pressures drop (d) should be determined from the hydrate point and reduced by the above linear methods. Ethylene glycol (DEG) is the most commonly used glycol in this work. Because it is a good intermediate between the vapor pressure and the dissolution capacity of the hydrocarbons. This is a suggested value so the fluid flow in the pipeline comprises between 50-60% of the DEG volume. The recent suggestion is about concentration. The solubility will usually be lower than 0.1 to 0.3 gallons of DEG per 100 barrels of hydrocarbon extracted, depending on the aromatic content. Total losses include evaporation, spillage, pump leakage, solubility, and so on, which is usually an average of 1 gallon per 100 barrels of compressed amount transferred from a plant. These diagrams are designed based on the low temperature of the separating units. In a given unit it is possible to operate at temperatures below 50-65 ° F below the hydrate point. The appropriate amount of methanol or glycol to add may be determined by Equation (1). The sequence of calculations is as follows:

1. Determine the hydrate formation temperature of a gas

2. Specifying the lowest expected temperature in the system (in 40°F underground pipes is a good guess if no constant data is available)

3. Calculate the amount of liquid water present at step temperature (2), use the dew point at that temperature, and modifications to the associated water issue.

4. Use the equation to solve w. In equation "d" is the temperature of step (1) minus step (2).

$$W(wt\%) = \frac{Lbs(Lossees)}{Lbs(Losses) + Lbs(Liquid - water)}$$

The following equations are used to calculate the inhibitor losses in the above equation:

DEG = 9.33 1bs / gal
TEG = 9.41 1bs / gal

5. If methanol is used, it should be corrected for lost values in the vapor phase. Chart 12 is used for this purpose. Enter the pressure coordinates at the temperature obtained in step (2). Read the lowest temperature vertically and down to the axis of the low. The divisor of values is available on the axis of the length of the same value as w from equation (1) in step four [1.7.11-15, 21].

13. Calculate Lbs. MeOH / MMScf gas

The total amount of inhibitor injected is equal to the sum of the values obtained from step 5 and step 4. At very low temperatures the injection rate should be such that the glycol water mixture does not freeze.

$$Kvs = \frac{y_8}{x_i^s} \tag{24}$$

The above calculations are if the glycol concentration is high. Check within the indicated ranges. Glycol solubility losses per hydrocarbon will depend on the amount of liquid present. Common wastes range from 1 to 2 gallons per 100 gallons of liquid hydrocarbons. Aromatics or mixtures with sulfur may increase this amount of waste by 2 to 3 times.

$$\sum_{i=1}^{n} x_i^x = \sum_{i=1}^{n} \frac{y_i}{k_{vs}} = 1 \tag{25}$$

Wasting very little volume is often difficult. Because it involves the sum of casualties that come

from a car radiator and the like. Methanol may recycle. However, most efforts are to make the combination more valuable and then simpler. Cost studies indicate that glycol is preferred for continuous injection over methanol. (If applicable) DEG is a poor choice between solubility and evaporation. Under o°F, ethylene glycol may be preferred because it has a better viscosity. It is difficult to separate glycol from hydrocarbons at low temperatures. As described above, the most optimal type of separation is at the highest possible temperature and low pressure [5-9, 22].

14. Prediction of hydrate formation based on thermodynamic closed model

The solid-vapor equilibrium equation is defined on the basis of the molar ratio of a compound in the gas phase to the same ratio in the solid phase, both of which are based on water. When Kvs is the vapor-solid equilibrium ratio, yi is a molar fraction of component i in the water-free vapor phase and X_i^s molar fraction of component i in the hydrate-based phase without water. Calculating temperature and pressure in the form of hydrates from a gas phase is like calculating the dew point for a saturated vapor that we will know by combining:

Whenever n is a combination of hydrate species. Tables for Kvs for Ethane, Methane Propane and isobutene were prepared by Carson and Katz in 1942. CO_2 and H_2S tables have also been developed by Katz and Co-workers (Katz). Robinson and Quirkers also set up a Kvs table for nitrogen and a modified table for isobutene. By using the information Benisson and Campbell found in the methane-butane normal system. Poettman has proposed a Kvs table for normal butane at temperatures and pressures higher than normal butane-hydrate form. This Kvs table can be found in the American Petroleum Research Information Book and the GPA or Fate of Gas Products. Several authors have also extended numerical ratios for the above Kvs tables to facilitate their use in a machine program. It has recently been shown that hydrate mixtures in hydrocarbon fluids are not limited to normal butane and therefore, separation of heavier mixtures such as non-hydrate species is not justified. In fact, compressed oil and gas systems comprise an important consequence of semi-heavy and heavy

hydrocarbon mixtures that are heavier than -n-butane. It has been reported in recent years that only hydrocarbon structures of cyclohexane and cyclo-pentane benzene are available as structure II hydrates and are now generally present in significant concentrations in gas and oil pressurized systems and in a New intensive research has proven that heavy hydrate species of structure II return to the free zone of real fluids. To this end, heavy hydrate species of structure II cannot be ignored and should be considered for more valid statements in the free hydrate region. The development of a practical method developed from Kvs that includes heavy structure hydrate species II requires the creation of tables for these compounds. In view of the above, the method used in forming Kvs tables for heavier hydrate species is very detailed in Structure II. Corresponding equation is also introduced for each combination that will facilitate the use of the Kvs method in a computer program. In addition, the prediction of free hydrate by Kvs method equals the experimental data and thus the thermodynamic closed model is proved with satisfactory results [3.10, 23]

15. Applied Method for Drawing Kvs Tables

The thermodynamic closed model used to form Kvs for each heavy hydrate species is predicted from the boundary phase of the hydrate. An electron-free equation of each phase, the Valder Rama correction through the Patel-Teja equation, is used by a real mixture to calculate the fugacity of each component in all fluid phases. The hydrate phase is regulated by the van der Waals-Plateau solid solution theory and then developed by Parrish and Prausnitz. The Kai model is defined by a spherical nucleus, which is a peta generator of all molecules of the hydrate phase species. In 1963 McKay and Synagogue also provided a detailed and valid explanation of this model. In 1996, Tahiti briefly determined the coefficient of interaction between water and HHF by measuring the composition and predicting solubility. By mutual interaction, the binary parameters are defined as the sudden effects of the molecules. The basic form of all components is the same. For each HHF, three hydrate equilibrium data sets have been developed in four phases: wide, aqueous, liquid hydrocarbon, steam, and hydrates. Two of which are in pairs and one in

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triplicate with methane or nitrogen as auxiliary gases. The hydrate model of the n-kayla keta parameters for HHF has been optimized using methane separation of their experimental data. This model is validated against standalone data and laboratory data sets. The only data used for HHF pairs in the creation of K values is methane or nitrogen in accordance with the Gypsum phase rule. As a result, the components of the various phases and ultimately Kvs will not be a function of the constituents. The method used by the scavenger list for the multiplicative equation is an appropriate process for determining values Kvs. Then the Kvs calculated by the multiplicative equation vanishes against the Kvs determined by the closed-valued model. Finally, the Kvs used in the equation are used to calculate how the two and three HHFs are separated by methane or nitrogen. However, KVs tables should be used simultaneously. Where T is the desired temperature in K and P is the pressure in MPa and consequently they will be compared with the experimental data as well as with the predictions made by the thermodynamic closed model. Explanation of the equation for determining the appropriate Kvs by the closed model of benzene, cyclopentane and cyclohexane has the fundamental effect as explained above. Parameters a to g are constants that must be obtained using the corresponding tables. For Neopentan, the equation will be as follows.

Where T is temperature in Kelvin and P is pressure in MPa.

In reference books such as India's GPS Book, Cyclopentane, Cyclohexane, and Neopentan show relatively high temperatures at different pressures. For example, in these graphs the Kvs calculated from the above equation for benzene are compared with the predictions made by the closed thermodynamic model, which proves the success of the scavenger list method. The current table shows the percentage of mean absolute deviation (% AAD) obtained from Equation 7. In the meantime, the calculated Kvs through the equation or through the closed model proves the viability. In addition, although the HHF methane data used in the determination of Kvs was not satisfactory, it is a satisfactory result that shows the main basis of the table. Where Q_1, Q_2 are the Kvs calculated by the equation or in the closed model

(albeit approximately) and N is the number of points given by the laboratory. The predictions of the hydrate phase bonds are in good agreement with the experimental data, and the maximum error in the prediction of the hydrate pressure layout will not exceed 1 ° C. The observed laboratory data of HHF methane-nitrogen has no use in optimizing parameter models or determining Kvs for HHF. A good agreement between the experimental results and the prediction of pressure separation for the above systems has been shown in the graphs, indicating another successful method of Kvs determination. Tables and equations of solid vapor equilibrium ratios have been developed for four recently discovered Type II hydrates, including benzene, cyclopentane, silco hexane, and neopentane. The equation for each component has 6 constants, which facilitates the use of computer programs [1.8.9-11, 24].
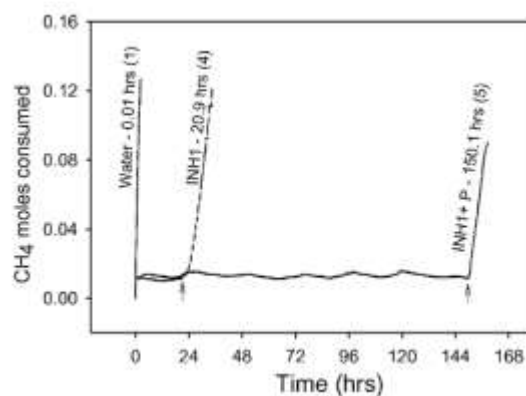

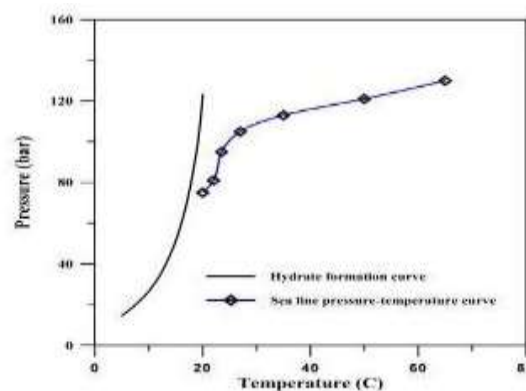**Fig.1.** Influence of PE on delay time of hydrate formation

Fig. 2. Comparison of thermodynamic curve of hydrate formation and temperature curve of pipeline pressure

CONCLUSION

In the industry, one of the thermal, mechanical,

thermodynamic and kinetic methods is commonly used to prevent or eliminate hydrate formation. In thermal methods, they try to keep the gas away from hydrate formation by insulating the pipe, using hot water or oil spin, or by electrically heating the pipe. Using a pig is a mechanical way to relieve hydrate buildup. It can also be changed by adding a third material to the gas mixture fuzzy diagram and eliminating the possibility of hydrates forming at the operating temperature and pressure of the system. Kinetic methods help improve the working conditions of the gas transmission system by increasing the latency or decreasing the growth or adhesion of the hydrate crystals. These methods are usually preferable to thermodynamic methods in which a large amount of additive (more than 25 wt%) is required because of less inhibitory use (less than 1 wt.%). Nowadays, positive aspects of hydrate formation have also been considered. The abundance of hydrated reservoirs in offshore areas has led researchers to view this material as a new

source of energy. It has also introduced high capacity hydrates in gas storage as a new way of storing and transporting natural gas.

Given the above understanding of hydrate formation mechanism and how inhibitory and accelerating substances affect it, it is helpful to select these substances to prevent the formation of hydrates in those which disrupt the process and increase the rate of formation in positive applications. Given the advantages and disadvantages of hydrate formation mentioned in the previous section, hydrate has always been considered a problem that should be avoided, as well as an opportunity to revolutionize the various industries, so Solutions have always been put forward to prevent its creation and to improve the conditions of its formation. Among the different solutions, the use of additives may be the most appropriate.

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