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Investigating Thermodynamic Mechanism of Gas Hydrate Formation in Natural Gas Transmission Pipelines

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Abstract

Natural gas hydrate is a solid crystalline compound formed by combining water and belongs to Klatryts's family. Guest gas molecules are trapped in water lattice cavities created by hydrogen bonds between water molecules. Based on Long and Quam's model, hydrate formation at low temperatures and high pressures can be explained. As temperature decreases, the kinetic energy of the molecules of liquid phase decrease and the number of hydrogen bonds between water molecules increases. The formation of these bonds increases the number of molecular aggregations on the surface. As the number of cavities increase, the conditions for hydrate formation become more favorable and the chance of gas molecules being suddenly trapped in one of these cavities increases. Similarly, as the pressure increases, the number of gas molecules per unit of water surface increases, the probability of gas molecules being trapped in one of these cavities increases, which in turn increases the risk of hydrate formation. Based on tests of Leatherhaus et.al, it can be concluded that inhibitors such as salt can slow or stop the process of hydrate formation by reducing the number of cavities on the surface or like PV cap by blocking the cavities.

Keywords: Hydrate, Liquid Phase, Hydrogen Bond, Inhibitor

Introduction:

The proposed mechanism of hydrate formation:

A two-stage mechanism of hydrate formation is proposed as follows:
The first stage: the formation of stoichiometric alkaline hydrates in a semi-chemical reaction.
The second stage: absorption of gas molecules in a mass of alkaline hydrates chains in a non-stoichiometric process.
In the first stage, based on Stevan and Long model, it has been assumed that gas molecules are dissolved in water. This is done by surrounding guest molecules by several water molecules. This is done continuously. Gas molecules occupy alkaline side of these molecules, and the other side of the chain remains intact. This process is described by the complex process below:

$H_2o + \lambda_2 G \rightarrow G_{\lambda 2} . H_2o$ (1)

Where, G is the weight of gas, and λ2 is the number of gas molecules and the number of water molecules in the alkaline hydrates. During this stage, the untouched part (of the chain) is covered by other alkaline hydrates. In the second phase, small molecules like (Ar, N2, O2, CH4, etc.) that are dissolved in water move to chain rings (absorption process). This is the result of non-stoichiometric property of hydrates.
At this stage, this can not occur for molecules that have a larger size, like (ethane, propane, -n -i butane and butane), as well as for those molecules that have the ability to separate from the chain rings. Therefore, the final form of stoichiometric of alkaline hydrates is only formed at the first step. So it can be said that alkaline hydrates are not hypothetical but these molecules are physically available. These are the logical reasons being used in Langmuir theory to explain the saturation of chain rings used by gas molecules.

Thermodynamic root of the model and investigation of parameters of pure gas hydrates:

Based on the two-stage mechanism of hydrate formation, which was explained earlier, there are two types of equilibrium in the system. A semi-chemical equilibrium reaction occurred in the first stage, and physical equilibrium absorption saturating gas molecules around the chain rings during the second stage. In the reaction in formula (1), if chemical equilibrium constants are used, we will have:

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

Where, μ_B is chemical potential of alkaline hydrates, μ_w and μ_g are respectively standard chemical potential of gas and water. After absorption of gas molecules in chain rings, chemical potential of alkaline hydrates decreases. μ_B is shown as:

(3) $\mu_B = \mu^o_B + \lambda_1 RT\imath n (1-\theta)$

Where, θ is a fraction of chain rings surrounded by gas molecules, μ°_B is unsaturated chemical potential of alkaline hydrates (= 0), and λ1 indicates the number of small chain rings on water molecule in alkaline hydrates. Based on the theory of Langmuir, θ is calculated as follows:

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

Where, f is the fugacity for gas and C is Langmuir' sconstant. Using the general and fundamental thermodynamics relationships, special chemical potential of gas is calculated as follows:

(5) $\mu_g = \mu^\circ_g (T) + RT \ Lnf$

Where, $\mu^\circ_g(T)$represents the chemical potential of the ideal gas. The result of subtracting the equations (2) - (5) in as follows:

(6) $\mu^o_B + \lambda_1 RT \ Ln (1-\theta) = \mu_w + \lambda_2 [\mu^o_g (T) + RT \ lnf]$

And,

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

Equation 6 can be turned to:

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

Where, $\alpha=\lambda_1/\lambda 2$, and $\alpha = \frac{1}{3}$ and $\alpha = 2$ for compounds I and II, respectively. In equation (7), f° is not only a function of the T, P and αw of water activity, see equation (11), but also it represents a property of the formed alkaline hydrate. When $\theta = 0$, equation (8) will be as follows:

(9) $f = f^\circ$

Here, f° exactly represents gas phase fugacity in equilibrium , when the alkaline hydrates is unsaturated (θ= O). $(\mu^o_B - \mu_w)$ in equation (7) can be calculated using various thermodynamic relations.

(11) $\mu_w = A_w + PV_w + RT \ lnaw$

(12) $\mu^o_B - \mu_w = \Delta A + P\Delta V - RT \ lna_w$

Where, A represents the number of Helmholtz free energy moles (which is essentially related to the energy of system) and the number of moles of volume change ΔV, the constant value of which can be obtained. equation (7) can be considered the result of three factors . Therefore, T, P and aw are represented as:

(13) $f^\circ = f^\circ (T) \ f^\circ (P) \ f^\circ (aw)$

And in equation 13:

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

Where, $\beta = \frac{\Delta V}{\lambda_2 R}$

β is equal to 0.4242 k/bar and 1.0224 k/bar for compound I and II, respectively.

(15) $f^\circ (aw) = aw^{-1/\lambda 2}$

The number of λ2 is equal to 3.23 and 1.17 for compound I and II, respectively.

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

In a specific, pure composition made up of one material, Antoine constants of A′, B′ and C′ can be calculated in suitable size and constant value of gas hydrates formation. These constant values for alternative compounds can be obtained by measuring a two-hydrate composition. The values that have a downward trend can be observed for specific gases in the relevant table. If hydrates are formed by cooling, the constants listed in the table will remain unchanged but the equation (16) is corrected as follows:

$$f^{\circ}(T) = \exp\left(\frac{D(T-273.15)}{T}\right) \times A' \exp\left(\frac{B'}{T-C'}\right) \quad (17)$$

Where, D in equation 17 is equal to 22.5 and 49.5 for compositions Iand II, respectively.

Generally, for applying equation (8), (θ≠o), θ can be obtained through equation (4). To investigate the Langmuir constants, integration of two parameters of Lennard-Jones potential can be used and the obtained values indicate that Langmuir constants are very close to Sloan numbers. For a practical engineer, it is very useful and appropriate to relate C Langmuir constant with the temperature. In this case, to determine the value, Antoine equation is used:

$$C = X \exp\left(\frac{\gamma}{T-Z}\right) \quad (18)$$

Constants X, y, Z which are used to determine Langmuir constant C, are calculated by Lennard-Jones potential functions.

The results of the calculations of binary and multicomponent gas hydrates:

The comparison of the results and the calculated values in binary and multicomponent systems are available separately in gas hydrate systems. For binary systems Ar-N2, Ar-CH4, CH4-H2S, C2H4-C2H6, C2H6-C3H8, Aijs is equal to zero while in other systems, cross and return parameters of Aij is calculated.

Natural gas hydrates:

If the effects of the molecules of the compound are taken into consideration, for each pair of Aij without value and amount, the value of zero is considered.

Debatable issues in changing hydrate structure:

It has been known for long that if methane is combined with a small amount of propane, hydrate structure changes from I to II. Studies based on new models show that although the amount of methane in gas mixture can be very high (95%), the volume of its alkaline hydrate is very low. This means that when hydrate mixture is being formed, much of it is surrounded by propane and methane is only a mediator. Through Equation 19, one can find out that fi is very critical to determine $\sum_j \theta_j$. For propane, θ is equal to zero and $F_i=f^{\circ}_I$ although for the composition and the mixture (methane + propane), methane has mostly occupied the area around ring chains. This is because hydrate formation pressure is slightly decreased because of the presence of propane. For example, when mole fraction of methane around the ring chain is 0.8, the partial pressure that propane requires for the formation of hydrates II is approximately 0.04 percent of the partial pressure required by pure propane is needed in this case. No matter how low the concentration of propane in this action is.

The effect of f° (aw) part in Equation 13:

By equation 15, f° (aw) = $aw^{-7.67}$ and f°(aw) = aw^{-17} for hydrate compound I and II, respectively. This means product formation pressure is very sensitive to water activity as a slight decrease in water activity may significantly increase the pressure. For systems consisting of water and different types of gas with low solubility capability, $X_w \rightarrow 1.0$, $\gamma_w \rightarrow 1.0$, and $\alpha_w \approx x_{w..}$ therefore, equation 15 can be shown as follows:

(23) $$f°(aw) \approx [1\text{-}xg]^{-1/\lambda 2} \approx 1+xg\ /\lambda_2$$

Where, xg is the total mole fraction of gas types having been dissolved in the aqueous phase. When xg = 10^{-13}, f°(aw) is equal to 1.00768 and 1.017 for compound I and II, respectively.
On the other hand, for systems containing gases with relatively high dissolvability in water, such as (H2S, Co2) as well as bipolar salt inhibitors, the portion of f°(aw) will not be partial.

How to remove and prevent hydrates forming in pipelines in theory:

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

1 ($$d = \frac{k_i \times X}{100M - X \times M}$$

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 ethylene glycol (DEG) is the most commonly used glycol for this purpose since it is soluble in carbohydrates. It is a suggested amount. Therefore, liquid flow in pipeline comprises between 50-60% volume percent of DEG. The recent suggestion is about concentration. The solubility is usually less than 0.1 to 0.3 gallons DEG per 100 barrels of extracted hydrocarbons, which depends on the amount of aromatic. Total losses include evaporation, loss, leakage of the pump, solubility, and so on and it is usually 1 gallon per 100 barrels of the compressed amount transferred from a plant. These figures are planned based on low temperature of separator units. In a specific unit, there is possibility of activity at a temperature 50-65°F lower than hydrate point. The appropriate amount ofmethanol or glycol may by determined using equation (1). The order of calculation would be as follows:

1. Determining the temperature of hydrate formation from a gas
2. Determining the lowest temperature expected in the system (in the underground pipe 40F is a good estimation if constant data is not available)
3. Calculating the amount of liquid water present at stage 2, using water dew point at that temperature
4. Using the equation to calculate w. In the equation, "d" is the temperature at stage 1 minus the temperature at stage 2.

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

to calculate the wastes of inhibitor in the equation above, the following constants are used:

DEG = 9.33 1bs / gal
TEG = 9.41 1bs / gal
5- If methanol is used, correction is needed for the amount wasted in the vapor phase. Figure 12 is used for this purpose. The coordinates of pressure are entered at a temperature obtained in stage (2). Seperator of values on the length axis is w determined in stage four.

Hydrate formation prediction based on the thermodynamic model:

Solid-vapor equilibrium constant based on molar ratio of a compound in the gas phase is defined with the same ratio in the solid phase, wher both of them are on waterless base.

3 ($$Kvs = \frac{y_8}{x_i^s}$$

Kvs is vapor-solid equilibrium ratio, yi is a mole fraction of component i in the vapor phase in waterless base, and X_i^s is mole fraction of component i in hydrate phase on waterless base.

Calculating the temperature and pressure when hydrate is formed from a gas phase is like calculating dew point for saturated steam. Therefore, we will have:

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

The tables for Kvs for ethane, methane, propane, and isobutene were prepared by Carson and Katz in 1942. In addition, Katz and his coworkers prepared Co2 and H2s tables. Robinson and his coworkers prepared a Kvs table for nitrogen and a corrected table for isobutene. Poettman suggested a Kvs table for normal butane at a temperature and pressure above normal butane-hydrate formation. This Kvs table can be found in the book of information of oil Research Center of the US and gas product associations (GPA). In addition, to facilitate the application of these tables, several authors have developed numerical ratios for the Kvs tables in a calculator app.

Recently, it has been proved that hydrate mixtures in hydrocarbon fluids are not restricted to n-butane (Ripmeester et al, 1991). Therefore, separating heavier mixtures such as non-hydrate species is not justifyable. In fact, oil and compressed gas systems include a key result of medium and heavy hydrocarbon mixtures that are heavier than n- Bhutan. It was reported in previous years that the samples of hydrate structure just exist for benzene (Danesh et al, 1993) cyclohexane (Tohidi et al, 1996a) and cyclopentane, which are structure II. In a recent study, it has been proved that heavy hydrate species structure II refer to a free zone of real fluids. For this purpose, heavy hydrates of structure II can not be ignored and must be considered for more valid theories in hydrate free zone. Preparing a developed practical method of Kvs which includes species of heavy Hydarthay structure II requires tables for these compounds. Based on the above-mentioned information, the method used in the formation of Kvs tables for heavy hydrates structure II is highly detailed. In addition, for each combination, an corresponding equation is introduced, which facilitates Kvs method in a computer program. In addition, prediction of free hydrate through Kvs method is the same as laboratory data. Therefore, closed thermodynamic model is proved with satisfactory results.

A practical method for Kvs tables:

The closed thermodynamic modelused for making Kvs for each species of heavy hydrate is predictable from boundary phase of hydrate. A selected equation of each phase, i.e the reform of Valder Rama, is used in all liquid phases through Patel-Teja equation to calculate the fugacity of each component. Hydrate phase was set thorugh van der waals- plateuo solid solution hydrate phase and then developed by Parrish and Prausnitzd. In 1963 McKay and Synagogue, a reliable detailed explanation is provided for this model. In 1996, Tahiti determined Bell Mtqa coefficient between water and HHF by measuring the composition and predicting the solvability. Bell Mtqa effect of dual parameters is defined as sudden effect of molecules· the initiative shapes of all components are the same. For each HHF, three data sets of hydrate equilibrium in four phases have been created: broad, aquatic zone, liquid hydrocarbon, steam and hydrates, two paired and one triple with methane or nitrogen are used as auxiliary gas. This model has been validated in the laboratory against independent data and the collection of existing data.

In the creation of K Values, the only data having been used for HHf pairs is methane or nitrogen based on Gibbs phase rule. As a result, combinations of different phases and finally Kvs wont be a function of combining ingredients. The method used by List Square for multisentence equation is a good process to determine Kvs Value. Then, the Kvs calculated by multisentence equation is evaluated against the kvs determined by the closed model. Finally, Kvs used in the equation is used to calculate the separation of binary and ternary HHF with methane or nitrogen. Anyway, the tables for KVs must be used simultaneously.

5 ($K_{C1} = -0.75542 - 1.84557(T) + 0.22749(T^2) + 0.27531(T^3) - 0.45391\ln(p)$

6) $K_{N2} = -748.741 + 765.036(T) - 260.609(T^2) + 29.7205(T^3) - 0.91722\ln(p)$

Where, T is the intended temperature in unit K, and P is the pressure in Mpa unit. the results will be compared with the laboratory data and predictions of closed thermodynamic model.

Discussion and conclusion:

Description of the model for determining the appropriate Kvs through closed model of benzene, cyclopentane, and cyclohexane as described above made a substantial impact.

$$Kvs = \exp\left(\frac{a + bT + cT^2 + dT^3 + eT}{P + PT + g\ln(P)}\right)$$

The parameters a to g are constants that can be obtained using the related tables. The equation for neopentane is as follows:

$$K_{Neopantane} = -113.25 + 115.664(T) - 39.2699(T^2) + 4.5612(T^3)$$

8(

$$+ 0.04645(T/P) - 0.02106\ln(P/T)$$

Where, T is the temperature in Kelvins, and P is pressure in Mpa.

In reference books such as GPSA handbook, cyclopentane, cyclohexane, and neopentane are shown as functions of temperature at different pressures. For example, in these graphs, the Kvs calculated from the above equation for benzene is compared with the predictions made by the thermodynamic model. The results show List Square method has been successful. The present table shows the average percentage of absolute deviation (% AAD) derived from the equation 7. Here, the Kvs calculated from the equation or through the

closed model are compatible. In addition, although HHF methane- nitrogen data is not used in determining the Kvs, the esults ae satisfactory.

$$\%AAD_{2\text{-}1} = 100\left(\sum_{i=1}^{N}\frac{|Q_2 - Q_1|}{Q_1}\right)/N \quad (9$$

Where, Q1, and Q2 are Kvs calculated by equation or closed model (albeit approximately), and N is the number of laboratory points given. The predictions of hydrate phase bonds are matching with the laboratory data and the maximum error in the prediction of hydrate pressure formation will not be greater than 1 degree Kelvin. HHF nitrogen methane experimental data observed have not been used in the optimization of parameters model or in determining the Kvs for HHF at all. There is an acceptable match between the experimental results and predicted pressure separator for the above systems in the graphs, which indicates that the method of determining the Kvs has been successful.

Tables and equations of solid vapor equilibrium ratios have been developed for four species of heavy hydrates structure II, namely benzene, cyclopentane, cyclohexane, and neopentane. The equation for each component has 6 constants, which facilates the use of computer programs. The tables above can be used in predicting free zone of hydrate for HHF inbinary and triple compounds with methane or nitrogen. As a result, Kvs method should be extended to include the species of heavy hydrate structure II for more accurate prediction of free zone hydrate for the fluid reservoirs.

Results:

1. Based on the two-stage mechanism proposed for hydrate formation and the reported concepts, new models of hydrate will be available.

2. Complicated algorithm of hydrate formation, simplification of the calculations, direct calculation of $\Delta\mu w$, complex evaluations based on Langmuir C constant, and optional selection of suitable parameters for evaluating $\Delta\mu w$ and C will not be possible.

3. Composition change of methane hydrate, when mixed with a small amount of propane can be physically addressed and investigated.

4. The results of the various experiments show that the proposed new models of hydrate are suitable for practical engineers, especially for natural gas compositions.

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