Research on Formation Prediction Model of Gas Hydrate

Jianwei Lin

Oil Production Service Branch of CNOOC Energy Technology & Services Limited, China

201922000466@stu.swpu.edu.cn

Abstract. In the process of gas extraction, gathering and transportation, etc., the formation of hydrates will cause blockage of mining facilities and pipelines and affect normal production, and even there are hidden dangers, causing difficulties in gas development. Therefore, the building of the hydrate prediction model is an urgent problem to be solved in the prevention and control of hydrate; it plays an important role in accurately and efficiently predicting the specific position and time of hydrate formation. In this paper, The formation mechanism and conditions of gas hydrate were described, and the prediction models of hydrate were introduced from two aspects: whether there are inhibitors (alcohols and electrolytes) in the hydrate system, respectively, the VdW-P model, a series of thermodynamic models based on it, and Chen Guo model based on hydrate dynamics were mainly described. Under different application conditions, the appropriate prediction model can effectively predict the formation of hydrate.

Keywords: gas hydrate; formation mechanism; formation condition; prediction model.

1. Introduction

Gas hydrate is similar to ice-snow shape solid form appearance, in which the weight of gas is only about 15%, and the overall density is about 0.9g/cm³, which varies with the difference of gas composition. At present, according to the known findings of the crystal structure of natural gas hydrates, we generally divide them into three types: type I, type II, and type H. In addition, research shows that we want to make the hydrate crystal exist stably, then specific conditions are needed, namely, the hydrocarbon molecules in the hydrate can reach a certain void occupancy, and the crystal structure will vary with the temperature and the change of the hydrocarbon gas molecules [1-2].

In 1810, Davy discovered gas hydrate, and since then he began research on hydrate. Hummerschmidt discovered hydrate in pipelines which transport gas in 1934; this phenomenon attracted much attention of the oil and gas industry. According to previous research experiences, the formation conditions of gas hydrate are the theoretical basis of prevention and control of gas hydrate, which can provide technical support for the related work of prevention and control of gas hydrate, and are the crux. Therefore, if we want to reach a deeper level in the research field of gas hydrate, we first need to have a clear understanding of the formation conditions of gas hydrate, so as to provide a more scientific and accurate basis for predicting and judging the specific position of hydrate formation. At present, experts and scholars at home and abroad have achieved great results in the following two aspects for research of gas.
hydrate: (1) In allusion to studies on the prediction conditions of gas hydrate, a series of thermodynamic models for predicting hydrate formation have been produced and developed, these models are mainly improved and developed based on the VdW-P model; (2) In allusion to prevention and control of gas hydrate, whether hydrate in the wellbore or pipeline network, as well as in the deep sea or on land, hydrate inhibitors are used for prevention and control at home and abroad, by studying the generating structure of hydrate and the thermodynamics and dynamics of hydrate formation, people are committed to developing new hydrate inhibitors.

2. Formation Mechanism and Conditions of Gas Hydrate
The gas hydrate is a crystalline solid from the appearance, it is composed of N₂, CO₂, H₂S and other gases, alkane gas and some heavy hydrocarbon composition, and it needs to be formed at a certain low temperature and high pressure. To put it simply, gas hydrate includes two parts: host molecule and guest molecule. Among them, the water molecule is the host molecule, and the light hydrocarbon or non-light hydrocarbon molecule is the guest molecule.

The network structure of gas hydrate is formed by water molecules under the action of hydrogen bonds, and there are some lattice holes in the hydrate, and light hydrocarbon or non-light hydrocarbon molecules exist in these holes. Under the action of intermolecular force, water molecules combine with light hydrocarbon or non-light hydrocarbon molecules to form hydrate in the end. Therefore, it is obvious that the structure and stability of gas hydrate will be affected by factors such as the type and size of guest molecules and external conditions, and there are certain differences.

According to the dynamics of hydrate formation, the crystalline hydrate which gas generates mainly includes the following three stages [3]:

According to the generating dynamics of hydrate, the crystalline hydrate from generated by gas mainly includes the following three stages [3]:

1. The induction period when gradually forms crystal nucleus with a certain size;
2. The rapid growth period when the crystal nucleus size keeps increasing;
3. The stable period when the crystal nucleus continues to increase and tends to be stable after adsorbing gas and water molecules.

The formation of hydrate generally requires the following conditions:

The formation of hydrate generally requires the following conditions:

1. The gas contains liquid water or supersaturated water vapor;
2. A certain high pressure and a certain low temperature state;
3. The air velocity is very high when passing through pipes or facilities;
4. Pressure fluctuation caused by the change of gas flow direction or sudden change of flow speed;
5. There are small hydrate crystals with induction effect;
6. There are components such as CO₂ or H₂S, because these acid gases are more soluble in water.

It is worth noting that hydrate does not always form with infinite increase of pressure at low temperatures, the formation of hydrate has its critical temperature, when the temperature is higher than the critical temperature, and hydrate will no longer be generated.

3. Hydrate Prediction Model without Inhibitor System
Since the 1940s, scientists had begun prediction research work of the formation of hydrocarbon gas hydrate (excluding acid gases). The phase equilibrium study of gas hydrate can provide important data of physical properties for studying gas hydrate, and it is the key and basis for studying gas hydrate. In recent years, as domestic and foreign experts and scholars have conducted in-depth research on the field of gas hydrate, the studies on phase equilibrium of natural gas hydrate have also achieved rapid development. At present, we generally divide the prediction models of gas hydrate in system without inhibitors into two categories, one is the VdW-P model and a series of thermodynamic models based on it; the other is Chen Guo model based on hydrate formation dynamics and using statistical thermodynamics.
3.1. VdW-P model
To put it a little crassly, the formation process of gas hydrate is visualized, in fact, it first develops from the pure water phase (α phase) to an water hydrate phase (β phase), and then develops to the gas-filled hydrate crystal lattice (H phase) and W phase (water-rich phase). In the process of transforming pure water into hydrate, different chemical states have different energy, so their activity levels are also different, among them, the state with the lowest chemical potential is in an advantageous position in energy. Here, water is taken as the reference object, because hydrate is generated in this equilibrium system, according to the thermodynamic phase equilibrium theory, the chemical potential of water in the hydrate H phase and the water-rich phase (called W phase) should be equal, namely:

\[
\mu^H = \mu^W
\]  

In the formula: \( \mu^H \) is the chemical potential of water in the hydrate phase; \( \mu^W \) is the chemical potential of water in the W phase.

If the chemical formula potential \( \beta \mu \) of completely empty hydrate lattice is used as the reference state, then the equilibrium condition is as follows:

\[
\mu^H - \beta \mu = \mu^W - \beta \mu
\]  

Or

\[
\Delta \mu^H = \Delta \mu^W
\]  

In the formula: \( \Delta \mu^H \) is the chemical potential difference between the filled crystal lattice and the air hydrate lattice phase, J\( \text{mol}^{-1} \); \( \Delta \mu^W \) is the chemical potential difference between the water-rich phase and the empty hydrate crystal lattice phase, J\( \text{mol}^{-1} \).

In 1959, Van Der Waals and Platteeum proposed the thermodynamic model based on the classical adsorption theory; in 1964, Satio [4] used this model to propose the complete model for predicting formation conditions of hydrate:

\[
\ln \frac{1}{v_{ij}} = \sum_i v_i \ln \left( 1 - \sum_j \theta_j \right)
\]  

\[
\theta_j = \frac{C_{ji} f_j}{1 + \sum_i C_{ij} f_i}
\]

In the formula: R is the gas state parameter constant; T is the temperature, K; \( v_i \) is the percentage of i-type crystal pore; \( \theta_j \) is the percentage of gas component j in the hole; \( f_j \) is the fugacity of gas component j, Pa, calculated by equation of state; \( C_{ji} \) is the Langmuir constant of the gas component j in the i-type crystal pore, the parameter reflecting the pore shape of the hydrate, and it is related to temperature.

3.2. Parrish-Pransnitz model
In 1972, Parrish and Pransnitz gave the empirical formula of the Langmuir constant, which greatly simplified the Van Der Waals model. For type I and type II structure:

\[
C_{ji} = \frac{A_{ji}}{T} \exp \left( \frac{B_{ji}}{T} \right)
\]  

For hydrate with H-type structure:
\[ C_j = \frac{A_j}{T} \exp \left( \frac{B_j}{T} \left( 1 - \frac{T}{T_0} \right) \right) \]  

(7)

\[ A_j = A_{ji} \exp \left( \frac{B_j}{T_0} \right) \]  

(8)

In the formula: \( A_{ji} \) and \( B_{ji} \) are test fitting parameters.

Since then, a series of improved models based on the Vdw-P theoretical model have been formed (as shown in Table 1).

Table 1. Simple form of the improved model of the Vdw-P model [5]

| Model                  | Formula                                                                 | Improvement                                                                 | Effect                                                                 |
|------------------------|-------------------------------------------------------------------------|----------------------------------------------------------------------------|----------------------------------------------------------------------------|
| Parrish-Prausnitz[6]   | \( C_j = \frac{A_j}{T} \exp \left( \frac{B_j}{T} \right) \)            | calculate Langmuir constant \( C_{ji} \) with empirical relation          | simplify the calculation of Langmuir constant                             |
| Ng-Robinson[7]         | \( \Delta \mu = RT \left( \prod \left[ 1 + 3(a_j - 1) \gamma_i^2 - 2(a_j - 1) \gamma_i^2 \right] \right) \times \sum \gamma_i \ln \left( 1 + \sum C_{ji} \gamma_i \right) \) | correct chemical potential difference \( \Delta \mu \) of the hydrate phase in the vdw-P model | solve the problem of higher results when predicting system containing polar substances in the Parrish-Prausnitz model |
| Holder-John[8]         | \( C = C^* Q^* \)                                                       | use disturbance factor and three-layer sphere model improve gas adsorption model | closer to the actual hydrate model, the result is closer to reality         |
| Du-Guo[9]              | \( C_j = \frac{A_j}{T} \exp \left( \frac{B_j}{T} + \frac{D_j}{T^2} \right) \) | correctly correct Langmuir parameter                                      | have good prediction effect for system containing propane or above        |
| Yoon-Chun[10]          | \( f_w = P \exp(\varphi_w \exp(\int_{p_w=0}^{p_w} \frac{v^w}{RT} dp)) \) | the SRK equation of state [11] and the improved second-order Huron-Vidal equation [12] are used to calculate the fugacity of all components when the gas and liquid phase are mixed | the average absolute deviation of forming simple hydrates is 0.6%-9.3%; the average absolute deviation is 2.9%-16.6% for mixed guest system |
| Ballard-Sloan[13]      | \( \frac{\Delta \mu}{RT} = \sum \gamma_i \ln \left( 1 - \sum \theta_j \right) + \ln \gamma_{w,H} \) | introduce the activity coefficient in the hydrate phase to characterize the non-ideality of the hydrate | high accuracy can be maintained under high pressure                        |
| Javanmardi[14]         | \( \nu^{\mu} = \nu^{\mu_0} \exp \left( \frac{K_{H}}{K_{H}^{p}} \left( \exp \left( -K_{H}^{p} P \right) - 1 \right) \right) \) | consider the influence of volume change of pure liquid water and empty hydrate crystal lattice on the formation of hydrate | consider the influence of volume change of pure liquid water and empty hydrate crystal lattice on the formation of hydrate |
3.3. Chen-Guo model
In 1996, Chen-Guo [15] put forward a model which is completely different from Van Der Walls, they believed that the quasi-chemical equilibrium and physical adsorption equilibrium phenomena must exist in the process when gas generate hydrate. Therefore, in order to verify such research ideas, first of all, some stoichiometric basic hydrate were needed, Chen-Guo completed a series of corresponding quasi-chemical reactions for such needs. However, there will be some empty voronoi cells among the basic hydrate, and these empty voronoi cells will cause some small molecules to be adsorbed in them, thus causing the hydrate to be transformed into non-stoichiometric types. This model is based on the mechanism of hydrate generating dynamics and uses statistical thermodynamics to deduce the fugacity formula of guest molecule j:

\[
f_j = a \exp \left( \frac{b}{T - c} + \frac{\beta p}{T} \right) \alpha_w^{\frac{1}{\lambda_1}} \left(1 - \theta^\Delta \right)^{\lambda_2}
\]  

(9)

In the formula: \(\alpha_w\) is the water activity, mol/cm\(^3\); \(\lambda_1\) is the number of small pores per water molecule; \(\lambda_2\) is the number of large pores per water molecule; a, b, c are test fitting parameters; \(\beta\) is the parameters of hydrate structure, it is only related to the type of hydrate and dimensionless.

This model has a clearer physical meaning, which simplifies the calculation (avoid directly calculate \(\Delta\mu^w\)), and also improves the prediction accuracy.

3.4. Klauda-Sandler model
Klauda and Sandler [16] believe that the Chen-Guo model has limitations and is not accurate enough. Because the Antoine relation does not have universality, the generated vapor pressure range fluctuates when it exceeds a certain range, it does not achieve enough stability and accuracy, and the parameters of Chen-Guo model are based on the energy parameters in VdW-P model or Antoine relation, thus getting correlation formula of calculating fugacity. Therefore, its results may also be affected by Antoine relation. Therefore, they believe that the Chen-Guo model cannot accurately predict when it exceeds a certain range. The model proposed by Klauda and Sandler does not need to use the reference parameters mentioned in the VdW-P model, so this model greatly reduces the error, and its applicability also increases with the expansion of the temperature range. Their model introduced the Kihara potential model parameters and the second Virial coefficient, and effectively combined with quantum mechanics methods, thus calculating the fugacity of water and other components in the gas phase. This model has significantly reduced errors in the calculation results in comparison with the traditional VdW-P model and its improved model, as well as Chen-Guo model. In addition, this model has stronger applicability when predicting the formation conditions of hydrate in the three-phase system. Zhang et al. [17] used the PRSV equation of state calculate the fugacity for the liquid phase based on the Klauda-Sandler model when the temperature was lower than 300K, and used two variable parameters calculate the equilibrium pressure of pure gas hydrate. Martin and Peters [18] proposed a relatively novel idea and direction for predicting hydrate, what is very different from the traditional thermodynamic model is that they advocated using cubic equations of state (CPA-EOS) to describe on how to describe the gas phase and the liquid phase, and they used the number reduced by regression parameters for the lattice distortion of gas hydrate. Moradi and Khosravani [19] proposed the thermodynamic model of hydrate-liquid water-steam and hydrate-liquid water-liquid hydrocarbon phase equilibrium, the most prominent feature of this model is that it can accurately predict pure gas or mixed gas hydrate at any temperature, they used the PRSV2 equation of state and van Laar binary parameter mixing rules establish liquid and gas phase model. The results show that this prediction method, which avoids using different models in the liquid phase and the gas phase, greatly reduces the prediction error of hydrate and improves the prediction accuracy in comparison with the previous model.
4. Hydrate Prediction Model with Inhibitor System

According to the structure types, gas hydrate can generally be divided into type I, type II and H type structure.

(1) The fugacity $f_j$ of each component in the gas phase is calculated by PR equation of state:

$$f_j = \frac{1}{C_{ji}} e^{\frac{\Delta \mu_j}{RT}} \left(1 - \theta_j\right)^{\frac{\lambda_1}{\lambda_2}} \left(1 - \theta_i\right)^{\frac{\lambda_2}{\lambda_1}} \left(1 - \theta_j\right)^{\frac{\lambda_1}{\lambda_2}}$$  \hspace{1cm} (10)

For type I hydrate, $\lambda_1=1/23$, $\lambda_2=3/23$; for type II hydrate $\lambda_1=2/17$, $\lambda_2=1/17$; for type H hydrate, $\lambda_1=5/34$, $\lambda_2=1/34$.

(2) For type I and II hydrate, the Langmuir constant $C_{ji}$ can be calculated by formula (6); for H-type hydrate, the Langmuir constant $C_{ji}$ can be calculated by formula (7) and formula (8).

(3) The Javanmardi model is used to calculate the water activity ($\alpha_w$):

$$\alpha_w = \frac{\phi_{w}^{el-al}}{\phi_{w}^{EOS}}$$  \hspace{1cm} (11)

$$\ln \phi_{w}^{el-al} = \ln \phi_{w}^{EOS} + \ln \gamma_{w}^{el} + \ln \gamma_{w}^{al}$$  \hspace{1cm} (12)

In the formula: $\phi_{w}^{el-al}$ is the total fugacity coefficient of water in the hydrate containing electrolyte and alcohol mixed system; $\phi_{w}^{EOS}$ is fugacity coefficient when the PT equation of state combines the mixing rule based on local composition concept to make it suitable for the of the (EOS) aqueous solution without electrolyte under the condition that temperature is 273.15k and the pressure is 0; $\phi_{w}^{EOS}$ is fugacity coefficient when the PT equation of state combines the mixing rule based on local composition concept to make it suitable for the of the (EOS) aqueous solution without electrolyte under the general condition; $\gamma_{w}^{el}$ is the influence value of electrolyte on water activity coefficient; $\gamma_{w}^{al}$ is the influence value of alcohol on water activity coefficient.

(4) $\Delta \mu^H$ is calculated by formula (4) and (5), and the calculating expression of $\Delta \mu^W$ was given by Holder [20] et al (1980).

$$\Delta \mu^W = \frac{\Delta \mu_w^0}{RT} - \int_0^T \frac{\Delta h_w}{RT^2} \, dT + \int_0^p \frac{\Delta V_w}{RT} \, dp - \ln \alpha_w$$  \hspace{1cm} (13)

In the formul: $\Delta \mu_w^0$ is the chemical potential difference of water in the completely empty hydrate phase and the water-rich phase under the condition of 273.15K temperature and 0 pressure; $\Delta h_w$ is the mole enthalpy difference chemical when water in completely empty hydrate crystal lattice and water-rich phase; $J/mol$; $\Delta V_w$ is the volume difference of water in completely empty hydrate lattice and water rich phase, cm$^3$/mol.

(5) According to $\Delta \mu^H$ and $\Delta \mu^W$, the relative error of the two is calculated, and the relative error and the allowable value (usually 1×10^-4) are compared to determine whether it is less than the allowable error. If the relative error meets the condition of less than the allowable error, the temperature value obtained in this iteration is the formation temperature of the structure hydrate under the pressure; if the relative error is greater than the allowable error, return to step (1) again for calculation, until meet the requirements.
5. Outlook
At present, in the field of natural gas industry, the most widely used in the formation prediction of hydrate are the VdW-P model and its improved model, as well as the Chen-Guo model. However, these models still have their own limitations, requiring oil workers to persist in overcoming problems for too long.

(1) At present, there are few studies on the prediction of hydrate with H-type structure, and there is no substantial breakthrough. The prediction studies on type I and type II hydrates have been relatively mature. Therefore, it is necessary to gradually shift the research focus to the prediction field of hydrate with H-type structure in the future, in order to achieve an early breakthrough.

(2) At present, we cannot avoid the acid gas components such as H2S and CO2 in gas hydrate in actual production. Therefore, it is a trend to invest more energy and carry out more research work in the prediction of the formation conditions of sour gas hydrate.

(3) The thermodynamic prediction models of formation conditions of gas hydrate have been relatively mature and widely used; therefore, it will be an inevitable trend to focus on studying phase equilibrium model based on hydrate dynamics, and it is of far-reaching significance for the scientific and efficient utilization of hydrate energy in the future.

(4) Regarding hydrate containing inhibitor system (alcohols, electrolytes), such prediction models are still lacking and have many shortcomings and limitations, therefore, the studies on the prediction model of the hydrate formation conditions of this complex system is very necessary.

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