



Preliminary study on measurement technology for hydrate phase equilibrium



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ABSTRACT

The phase equilibrium of gas hydrate is the important foundation for hydrate research and accurate equilibrium data are obtained mainly by experiments. In order to improve the accuracy of hydrate equilibrium, the research effort focused on measurement technology itself. Firstly, intensive variables under three-phase equilibrium were analyzed in terms of the Gibbs phase rule. Then the multi-step heating dissociation method was investigated in detail after a brief review of measurement technologies. No leakage and gas saturation must be ensured in sample preparation stage. During data processing, the endpoint of complete hydrate dissociation usually is regarded as phase equilibrium condition, which corresponds to the largest pores in sediment, initial concentration of solution and initial gas composition. The experimental results indicate that CH₄ hydrate phase equilibrium in 0.0003 mass fraction Sodium dodecyl sulfate (SDS) solution is not changed, but the “climbing wall effect” changes CH₄ hydrate equilibrium in silica sand saturated by SDS solution. Hydrate phase equilibrium of 0.180 mol fraction CO₂-N₂ mixture in 0.004 mol fraction tetrahydrofuran (THF) solution is changed obviously. Additionally, the accuracy of CO₂ hydrate phase equilibrium using heating rate of 0.2 K/h is higher than using 0.6 K/20 min which shows that a low heating rate can improve the accuracy. The study also indicates that isolated CO₂ hydrate in 0.009 mol fraction NaCl solution is different from that of bulk hydrate. Suggestions to control heating rate and judge isolated hydrate are also proposed.

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1. Introduction

Natural gas hydrates widely occur in marine sediments and permafrost zone that are considered as one of the most promising new energy because of rich natural gas resources [1,2]. In recent years, many countries in the world pay much attention to the resources survey, development and assessment of natural gas hydrates. Moreover, hydrate-based technologies including gas storage/transportation, gas separation, seawater desalination, cold storage, CO₂ capture and separation etc., have been widely studied [3–8]. Whether hydrate resources development or the applications of hydrate-based technologies, hydrate phase equilibrium must be understood firstly. Natural gas hydrates generally occur along the three phase equilibrium (hydrate–water–vapor) boundary where they are very sensitive to the change of temperature and pressure.

In other words, a small change of ambient temperature or pressure can cause the dissociation of gas hydrates. For a specific hydrate reservoir, the sensitivity of the front boundary of hydrate dissociation to temperature and pressure is actually the restricting degree of sediment and pore water on hydrate equilibrium condition. In addition, the present issues for the industrial purposes of hydrate-based technologies are the high equilibrium pressure, low formation rate and low gas capacity etc. Hydrate formation is always the first step in any of the technologies mentioned above and it may control the rate of the whole process. Thus, to investigate hydrate phase equilibrium and reduce hydrate formation pressure is crucial for the industrial application of hydrate-based technologies.

Like other media such as reservoir oils, hydrate phase equilibrium can be predicted or measured [9–11]. Since hydrate phase equilibrium is affected by many factors including temperature, pressure, gas composition, sediment and pore water etc. [12–20], the requirement for experiments and models are relatively high. In general, hydrate phase equilibrium in the presence of pure water or solution can be predicted relatively accurately by the existing calculation software or referred to the related literatures

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[21–33]. The existing prediction models of hydrate phase equilibrium are proposed generally based on van der Waals and Platteeuw (vDWP) model [21]. As we know, the establishments or verifications of these models still need a large number of experimental data. Especially, some model predictions are highly sensitive to experimental data. Besides, if these models are applied to phase equilibrium of sediment hosting hydrate, the error may be great. For improving the prediction, Clarke et al. [34] introduced interfacial tension between liquid/ice and solid particles and employed Young–Laplace equation to calculate the pressure difference between liquid phase and vapor phase. Wilder et al. [35] assumed that hydrate phase, liquid phase and vapor phase were in equilibrium and the capillary forces of liquid–hydrate and liquid–vapor could not be ignored in porous media. Seo et al. [36] improved the model of pore water activity by taking the pore capillary force into consideration. Klauda and Sandler [37,38] proposed a hydrate equilibrium model for natural sediments, but both Klauda–Sandler model and Wilder model applied hydrate growth model to describe the dissociation behavior of hydrate defined in pores. Llamedo et al. [39] presented the fugacity formula by introducing the capillary pore pressure, but did not consider the effect of pressure and clay on pore size. Therefore, the errors of the equilibrium models for sediment hosting hydrate are significantly larger, especially for actual sediment with complex composition and uneven particle size. It is usually obtained accurately through experiments.

At present, although there are some experimental methods for hydrate phase equilibrium, unfortunately, one is difficult to confirm the accuracy or correctness of equilibrium data due to the lack of the specific research on measurement technique. Tohidi et al. [40,41] investigated the impact of the amount of water phase, experimental methods and procedure on the accuracy of hydrate dissociation point. Ivanic et al. [42] proposed a modified experimental method to eliminate the metastability associated with hydrate formation and dissociation. Anderson et al. [43] and Mohammad-Taheria et al. [44] considered that the step heating technique provided a more-reliable method for isochoric determination of hydrate equilibrium conditions, when compared to the continuous-heating technique. Beltran et al. [45] clarified the common mistake existing in literatures. Hydrate formation condition in the sense of kinetics is different from hydrate phase equilibrium condition although sometimes it also refers to the phase equilibrium condition indiscriminately. The kinetic formation condition has the characteristics of metastability, randomness and low repeatability, which depends on many factors, such as cooling rate, super-cooling degree, water history, ice particle, crystal nucleus, etc. So the experiment of hydrate formation condition is like looking for a “moving target”. Hydrate phase equilibrium belongs to the category of thermodynamics that has the characteristics of repeatability. The experiment of phase equilibrium is like looking for a “fixed target”. Generally, the accuracy of kinetic parameter measured or calculated is lower at least an order of magnitude than the corresponding

thermodynamic parameter [11,46]. In fact, to improve measurement technology of hydrate phase equilibrium is to make the measured data infinitely approach the real value (the target). Hydrate phase equilibrium is generally obtained by dissociation method, which is easily mistaken for no metastability. Actually, the metastability can occur if the heating rate is too fast [47,48], or anomalous self-preservation region does on a rapid depressurization [49–52]. In summary, it is very necessary to investigate measurement technology of hydrate phase equilibrium itself. Based on phase rule, the measured/controlled parameters, equipments and methods of phase equilibrium in various systems were analyzed in this work. Thereby, the key issues including hydrate sample preparation, data processing, hydrate formation promotion, heating rate and isolated hydrate were discussed. This work is very important for a higher accuracy of hydrate phase equilibrium measurement.

2. Phase equilibrium theory

Hydrate phase equilibrium obeys the Gibbs phase rule that is the theory basis of equilibrium measurement. For a given hydrate system, the number of degrees of freedom F = the number of components C – the number of phases P + 2. The number of degrees of freedom represents the number of intensive variables, i.e., the number of independent parameters to be controlled/measured in experiments. For a single component gas + water system (CO_2 + water) as an example, the number of components $C = 2$, the number of phases ($L_{\text{W}}\text{--}H\text{--}V$) $P = 3$, thus the number of degree of freedom $F = 1$. During hydrate phase equilibrium experiment, the only pressure p or temperature T can be controlled for a given temperature T or pressure p under the condition of three-phase equilibrium. However, the temperature and the corresponding pressure should be given together to verify a real equilibrium. For a binary gas mixture + water system ($\text{CO}_2 + \text{N}_2 + \text{water}$), the number of degree of freedom $F = 2$ under three-phase equilibrium because $C = 3$ and $P = 3$ according to Gibbs phase rule. Thus two intensive variables are required to be controlled. Experimentally, the temperature and pressure are selected as the controlled variables and the vapor phase molar fraction is usually selected as the third variable to ensure a real equilibrium. Similarly, for a single component gas + aqueous solution (or sediment) system ($\text{CO}_2 + \text{NaCl}$ aqueous solution or silica sand), the number of degree of freedom $F = 1$, so the temperature or pressure is usually considered as the controlled variable during equilibrium experiments. But the temperature, pressure and the concentration (or sediment parameters such as particle size or pore size) need to be reported together.

3. Experiment

3.1. Experimental materials

In this work, various materials were used as shown in Table 1, including CH_4 , CO_2 , $\text{CO}_2\text{--N}_2$ binary mixture, NaCl, Sodium dodecyl

Table 1
Experimental materials.

Material	Purity	Supplier
CH_4	0.9999 mol fraction	Qingdao Ruifeng Gas Co., Ltd.
CO_2	0.9999 mol fraction	Qingdao Ruifeng Gas Co., Ltd.
$\text{CO}_2\text{--N}_2$ ($x_{\text{CO}_2} = 0.180$)	Each gas >0.99 mol fraction	Qingdao Ruifeng Gas Co., Ltd.
NaCl	0.995 mass fraction	Sinopharm Chemical Reagent Co., Ltd.
SDS	>0.980 mass fraction	Sinopharm Chemical Reagent Co., Ltd.
THF	0.990 mass fraction	Sinopharm Chemical Reagent Co., Ltd.
Silica sand	$\text{SiO}_2 > 0.999$ mass fraction	Lingshou BaoLei Mineral Processing Co., Ltd.
Deionized water		Laboratory-made

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