

Estimation of ultra-stability of methane hydrate at 1 atm by thermal conductivity measurement

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Abstract

Thermal conductivity of methane hydrate was measured in hydrate dissociation self-preservation zone by means of the transient plane source (TPS) technique developed by Gustafsson. The sample was formed from 99.9% (volume ratio) methane gas with 280 ppm sodium dodecyl sulfate (SDS) solution under 6.6 MPa and 273.15 K. The methane hydrate sample was taken out of the cell and moved into a low temperature chamber when the conversion ratio of water was more than 90%. In order to measure the thermal conductivity, the sample was compacted into two columnar parts by compact tool at 268.15 K. The measurements are carried out in the temperature ranging from 263.15 K to 271.15 K at atmospheric pressure. Additionally, the relationship between thermal conductivity and time is also investigated at 263.15 K and 268.15 K, respectively. In 24 h, thermal conductivity increases only 5.45% at 268.15 K, but thermal conductivity increases 196.29% at 263.15 K. Methane hydrates exhibit only minimal decomposition at 1 atm and the temperature ranging from 263.15 K to 271.15 K. At 1 atm and 268.15 K, the total gas that evolved after 24 h was amounted to less than 0.71% of the originally stored gas, and this ultra-stability was maintained if the test was lasted for more than two hundreds hours before terminating.

Key words

methane hydrate; self-preservation; dissociation velocity; thermal conductivity

1. Introduction

Great amount of natural gas (mainly methane) hydrate deposits are found worldwide in sediments of outer continental margins and polar permafrost areas. It has been estimated that such kinds of methane hydrates contain at least twice as much combustible carbon as in all other fossil fuels on the earth [1]. Being a potentially promising future energy source, hydrate thermal properties play an important and crucial role not only in the assessments of gas production from natural deposits, sea floor stability of hydrate-bearing oceanic sediments, but also in the studies of global climate change, submarine slide formation, and hydrate plug dissociation in oil and gas pipelines [2].

For equilibrium stability of methane hydrates in sl at atmospheric pressure, temperature must be lowered to 193 K. However, if the polycrystalline methane hydrates are formed on the surface of ice at high pressures, an anomalous sta-

bility for methane hydrates occurs when pressure is lowered to 1 atm within a temperature window between 245 and 270 K [3,4]. Yakushev et al. [5] and Gudmudsson et al. [6] conducted experimental study on the mechanism of self-preservation, and pointed out the approximate temperature zone of self-preservation. Stern et al. [3] measured the dissociation velocity of methane hydrate at 1 atm and temperature ranging from 193 K to 273 K. The result showed that 242–271 K is the temperature zone of self-preservation and the dissociation velocity of methane hydrate is the lowest in the ranging from 265 K to 271 K. Shiota et al. [7] studied the dissociation velocity of methane hydrate at 1 atm and temperature ranging from 265.65 K to 273.15 K, and the result was approximately agreeable with that of Stern et al. The range of 265.65–270.50 K is the temperature zone of self-preservation and the dissociation velocity of methane hydrate is the lowest at 268.15 K. Circone et al. [8] reported that at temperatures above or below the anomalous stability envelope, methane

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hydrates decompose at the rates with the orders of magnitude greater than those when methane hydrates were in the metastable window. Zhang and Rogers [9] also reported that the comparable ultra-stabilities of natural gas hydrates as well as methane hydrates could be achieved in the laboratory at 1 atm and 268.2 K, and the ultra-stability of natural gas hydrates could be extended to a temperature as high as 270.2 K. Meanwhile, ultra-stability of natural gas hydrates in sII could be maintained for as long as 256 h with decomposition amounted to be only 0.040% of the original gas occluded.

The thermal properties play an important role in hydrate dissociation. If the dissociation of methane hydrate is carried out below ice point, a thin ice film, impermeable to gas molecules, forms on hydrate surface during depressurization and it interrupts further dissociation of hydrate [10]. In this process, the effective thermal conductivities of both ice film and methane hydrate that does not dissociate were varied in company with the ice mass ratio. Based on this point, we attempt to establish a model and algorithm expression to predict the dissociation velocity of methane hydrate at different temperature in self-preservation zone by thermal conductivity measurement.

Here, we designed an experiment that measured thermal conductivity of methane hydrate at 1 atm and the temperature ranging from 263.15 K to 271.15 K and investigated relationship between thermal conductivity and time at 263.15 K and 268.15 K, respectively.

2. Experimental

2.1. Apparatus and materials

Two sets of facilities were used in this work. One is for methane hydrate formation, which was described in detail by Huang et al. [11,12]. In this system, the cell is made of stainless steel with 250 mm height and 50 mm inside diameter and the maximal operating pressure is 32 MPa. Pt100 RTD measuring the temperature change in hydrate formation process is placed in the cell and its precision is ± 0.01 K. Data of the temperature and gas flux are logged by the Agilent 34901A. The cell is immersed in the alcohol bath that controls the temperature in the range from 228.15 K to 313.15 K.

The thermal conductivity measurement system is shown in Figure 1. The system mainly consists of a low temperature testing chamber and a Hot Disk thermal constants analyzer. The volume of the testing chamber is about 10 m^3 and it can accommodate two or three persons to conduct the experiment. The temperature range of the testing chamber can be adjusted from 253.15 K to 313.15 K. Hot Disk thermal constants analyzer is made by Sweden Hot Disk AB Company and based on transient plane source (TPS) technique developed by Gustafsson et al. [13,14]. The details of the thermal conductivity measurement system are shown in the References [11,12].

In order to promote the formation of methane hydrate, sodium dodecyl sulfate (SDS) solution was used instead of distilled water. Methane gas (purity 99.9 vol%) was purchased

from Guangdong Nanhai Gas Co. Ltd and SDS with its purity higher than 98 wt% was from Guangzhou Chemical Reagent Factory.

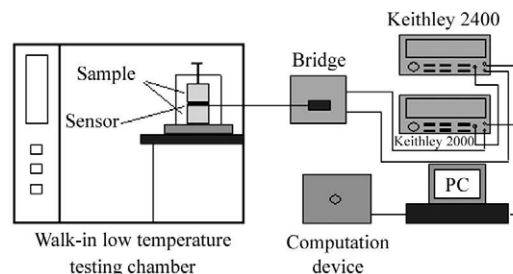


Figure 1. The schematic of the system for thermal conductivity measurement

2.2. Procedure

The initial temperature of the alcohol bath was set at 273.15 K and 70 g 280 ppm SDS aqueous solution was injected into the cell. After the pipeline and the cell were vacuumed, the gauge of the methane gas was opened and set to 6.6 MPa. The hydrate formation system was maintained in 273.15 K and 6.6 MPa. The water was transformed into hydrate almost completely under such conditions after it lasted for about 12 h, and no any change could be further detected in temperature and gas flux. The conversion ratio of water was 97.3% at that time. After three days, the methane hydrate sample was taken out of the cell and moved into the testing chamber. At 268.15 K, the sample was compacted in two cylindrical pieces by compacting tool under certain pressure. Then the two pieces of sample and the Hotdisk probe were fixed in the test holder. The holder was placed in the testing chamber and the Hotdisk thermal constants analyzer was outside. By temperature programming, the thermal conductivity could be measured in the temperature range from 263.15 K to 271.15 K at 1 atm at an interval of 1 K. The time interval between adjacent two temperatures is 30 min.

3. Modeling and algorithm

As the former concerned, the self-preservation phenomenon is caused by the fact that thin ice films, impermeable to gas molecules, are formed on the hydrate surface. Therefore, the thermal conductivity of methane hydrate measured during its dissociation is the effective thermal conductivity of ice film and methane hydrate that does not dissociate yet. Here, we applied the arithmetic mixed model for the effective thermal conductivity in the following equation:

$$\lambda(T) = \varepsilon_{\text{ice}}(T)\lambda_{\text{ice}}(T) + [1 - \varepsilon_{\text{ice}}(T)]\lambda_{\text{NGH}}(T) \quad (1)$$

In Equation (1), $\varepsilon_{\text{ice}}(T)$ is the volume fraction of ice at temperature T , $\lambda_{\text{ice}}(T)$, $\lambda_{\text{NGH}}(T)$ is thermal conductivity of ice and methane hydrate at temperature T , respectively.

The volume fraction of ice at temperature T , $\varepsilon_{\text{ice}}(T)$, can be expressed in Equation (2):

$$\varepsilon_{\text{ice}}(T) = \frac{W_{\text{ice}}(T)}{\rho_{\text{ice}}} = \frac{M_{\text{H}_2\text{O}}[n_0 - n(T)]H}{n(T)M_{\text{NGH}} + M_{\text{H}_2\text{O}}[n_0 - n(T)]H} \cdot \frac{1}{\rho_{\text{ice}}} \quad (2)$$

In Equation (2), $W_{\text{ice}}(T)$, $\rho_{\text{ice}}(T)$ are mass fraction and density of ice at temperature T , respectively. n_0 is mole number of methane hydrate at initial time at which methane hydrate did not begin to dissociate, $n(T)$ is mole number of methane hydrate at temperature T . $M_{\text{H}_2\text{O}}$ and M_{NGH} is mole mass of H_2O and methane hydrate, respectively. H is hydration number of methane hydrate. For ideal methane hydrate, H is 5.75.

The dissociation velocity at temperature T can be expressed as:

$$k(T) = -\frac{dn(T)}{dt} \quad (3)$$

Here, t is the time.

So, the average dissociation velocity from T_i to T_{i+1} can be expressed as:

$$k_{\Delta T_i} = \frac{n(T_{i+1}) - n(T_i)}{\Delta t_i} \quad (4)$$

In Equation (4), $n(T_i)$ and $n(T_{i+1})$ are mole number of methane hydrate at temperature T_i and T_{i+1} , respectively. $i = 1, 2, \dots, N$, N represents the amount of temperature point. Using the Equations (1), (2) and (4), $k_{\Delta T_i}$ can be calculated. Transient dissociation velocity at temperature T_i can be expressed as:

$$k(T_i) = -\frac{dn(T_i)}{dt} = -\frac{dn(T_i)}{dT} \cdot \frac{dT}{dt} \quad (5)$$

Where $n(T_i)$ ($i = 1, 2, 3, \dots, N$) can be determined by the Equations (1) and (2), and can be fitted as:

$$n(T) = f_1(T) \quad (6)$$

The velocity of temperature change can be determined by experiment procedure and the relationship between temperature and time can be fitted as:

$$T = f_2(t) \quad (7)$$

So transient dissociation velocity $k(T_i)$ can be calculated by Equations (5), (6) and (7).

4. Results and discussion

4.1. $\lambda(T_i)$ measured results and $n(T_i)$, $k_{\Delta T_i}$ calculated results

The effective thermal conductivity of methane hydrate sample at 1 atm and 263.15–271.15 K is shown in Table 1. Using the Equations (1), (2) and (4), $n_0 = 0.676$ mol, and assuming $\lambda_{\text{ice}}(T) = 2.12$ W/mK, $\lambda_{\text{NGH}}(T) = 5.75$ W/mK, $H = 5.75$, $\rho_{\text{ice}}(T) = 0.920$ g/cm³, we calculated $n(T_i)$ and $k_{\Delta T_i}$ (i represents each temperature point from 263.15 K to 271.15 K). The results are also shown in Table 1.

Table 1. $\lambda(T_i)$ measured, $n(T_i)$ and $k_{\Delta T_i}$ calculated at different temperature or temperature intervals

T/K	$\lambda(T)/(\text{W/mK})$	$n(T)/\text{mol}$	$k_{\Delta T_i}/(\text{mol/s})$
263.15	0.594	0.664	
264.15	0.722	0.609	3.06×10^{-5}
265.15	0.805	0.574	1.94×10^{-5}
266.15	0.838	0.560	7.78×10^{-6}
267.15	0.843	0.557	1.67×10^{-6}
268.15	0.840	0.556	5.56×10^{-7}
269.15	0.8439	0.555	5.56×10^{-6}
270.15	0.846	0.551	2.22×10^{-6}
271.15	0.873	0.538	7.22×10^{-6}

In Table 1, the value of $k_{\Delta T_i}$ is very small, namely, the dissociation velocity of methane hydrate is very low since self-preservation exists in the temperature zone from 263.15 K to 271.15 K. At 1 atm and 268.15 K, total gas that evolved after 24 h is less than 0.71% of originally stored gas, and even if the test was lasted to more than two hundreds hours before terminating. This can be considered as ultra-stability and it was similar to the results that Zhang and Rogers reported in Ref. [9].

4.2. $k(T_i)$ calculated results

Based on the previous calculated results, $n(T)$ can be fitted as:

$$n(T) = 1745.92 - 195.27T + 0.72807T^2 - 9.0488T^3 \quad (R^2 = 0.9989) \quad (8)$$

In this work, the velocity of temperature change is 1/30 K/min. So transient dissociation velocity $k(T_i)$ can be calculated.

Figure 2 illustrates the transient dissociation velocity at different temperatures from 263.15 K to 271.15 K. Here, the dissociation velocity at 268.15 K is the lowest. Hence, 268.15 K can be considered to be the best temperature point to store methane hydrate. This result is in good agreement with the work reported by other researchers such as Circone et al. [8]. And it approved that our method to predict the dissociation velocity of methane hydrate by thermal conductivity is feasible.

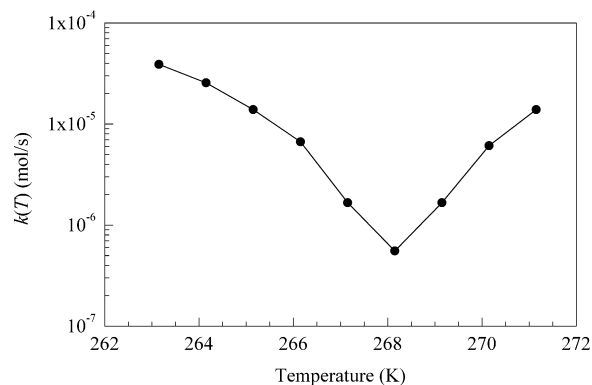


Figure 2. Transient dissociation velocity at different temperatures from 263.15 K to 271.15 K

4.3. $\lambda(t)$ at different temperatures

Using the same methane hydrate sample, we measured its thermal conductivity at different times at 263.15 K and 268.15 K, respectively. The results are shown in Figure 3 and Figure 4.

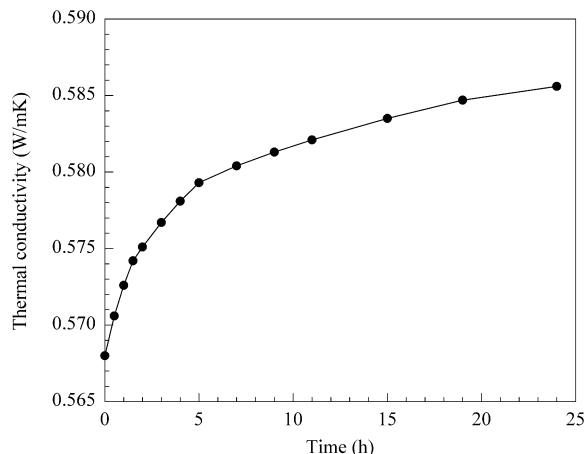


Figure 3. The relationship between thermal conductivity and time at 268.15 K

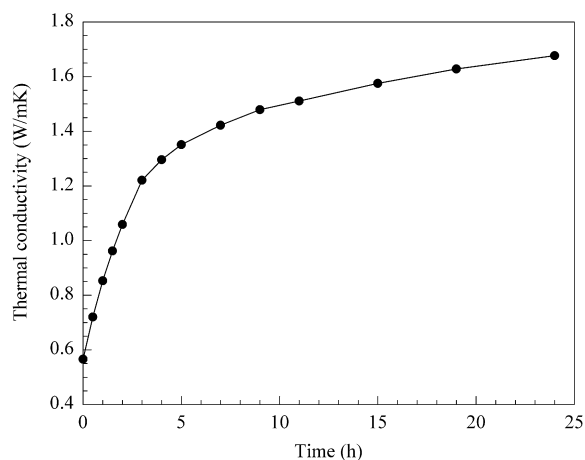


Figure 4. The relationship between thermal conductivity and time at 263.15 K

After 24 h, thermal conductivity increases only 5.45% at 268.15 K, but thermal conductivity increases 196.29% at 263.15 K. Increasing of thermal conductivity is due to the increasing of the ice fraction with much larger thermal conductivity. In other words, the dissociation velocity of methane hydrate at 268.15 K is much lower than that at 263.15 K.

4.4. Postulated mechanism for ultra-stability of methane hydrate

One may suspect that the stability contributed by a given ice-shield thickness which was produced around methane hydrate varies with the particle size. The stress of a cylindrical shell pressurized internally is given by the following Equation [15]:

drical shell pressurized internally is given by the following Equation [15]:

$$\sigma_L = 2\sigma_t = \frac{pD}{4\delta} \quad (9)$$

Here, σ_L and σ_t are the axial stress and the circumferential stress (shown in the Figure 5), respectively; δ is the required minimum wall thickness to maintain an internal pressure p in a cylindrical shell of diameter D ; The allowable stress σ_f in the wall material is often less than the circumferential stress σ_t .



Figure 5. The compaction test sample and the stress analysis

Wall thickness is proportional to the diameter of the ice shell. Assuming that hydrate equilibrium pressures prevail inside an ice-coated shell, we use Equation (9) to compare the stabilities with their different sizes.

For our cylindrical sample, D is 50 mm, and p is 2.2 MPa (phase equilibrium pressure). The required minimum wall thickness of ice is more than 50 mm if we assumed that the allowable stress is 0.7 MPa. The tensile strength of ice varies from 0.7 MPa to 3.1 MPa and the compressive strength varies from 5 MPa to 25 MPa over the temperature ranging from 263 K to 253 K [16], hence the tensile strength of ice is less than 0.7 MPa at 268 K. Apparently, the ice shell only creates a weakening internal pressure. The allowable stress cannot stabilize the hydrate long time and sustain the ice film not to fracture. In addition, the stability created by the ice-shield can not prohibit the dissociation of some hydrates without self-preservation effect, such as Xe, H₂S, etc. [17]. Moreover, Melnikov et al. [18] found that the dissociation of small methane hydrate samples formed from water droplets with the size of 0.25–2.5 mm, which was investigated below the ice melting point in the temperature range of 240–273 K, where the self-preservation effect is observed for bulk hydrates. They also found that the dissociation pressure for small hydrate samples fell on the extension of the water-hydrate-gas equilibrium curve into the metastable region in the temperature range of 253–273 K. It seems that liquid water can reduce the strength of ice film, but the lower dissociation pressure can make the hydrate in a metastable state.

It is of the opinion that the hydrates surrounding by many voids and having strength greater than ice are able to maintain hydrate equilibrium pressures within defect spaces [9]. If it has no significant ice or water impurities, the mechanical strength of methane gas hydrate exceeds hexagonal water ice strength by a factor of 40 [19]. Therefore, in a mass of hydrate small voids surrounded by hydrates instead of ice would afford the greatest stability.

Based on the above analysis, we suggest that if methane hydrates are preserved at about 268 K and small hydrate particles are packed into some void spaces, which are surrounded by hydrates instead of ice, their greatest stability would be obtained.

5. Conclusions

In this work, a model and an algorithm were established to predict dissociation velocity of methane hydrate at different temperatures in its dissociation self-preservation zone by thermal conductivity. The dissociation degree of gas hydrate can be calculated by the measurement of the effective thermal conductivity. The dissociation process can be characterized by thermal conductivity instead of microscopic method such as X-ray diffraction. The results calculated by the model and algorithm showed that the dissociation velocity of methane hydrate is the lowest at 268.15 K and thermal conductivity changed a little. Methane hydrates exhibit only minimal decomposition at 1 atm and the temperature ranging from 263.15 to 271.15 K. At 1 atm and 268.15 K, the total gas that evolved in 24 h amounted to less than 0.71% of originally stored gas, and this ultra-stability was maintained when the test was lasted to more than two hundreds hours before terminating.

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