Production of Concentrated Methane Hydrates in Bulk, at Medium Pressure

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Two procedures have been tested to produce concentrated methane hydrates in bulk, at medium to low pressure, avoiding the use of the high-pressure spray process. Both procedures have in common a first step of formation of the hydrate (30 % to 40 % mass fraction of water converted to hydrate) at (4 to 5) MPa and 275.16 K in a stirred reactor, starting from water and methane. Following this step, more hydrate was formed in the first procedure by cycling the temperature through the ice melting point. In the second procedure, pressure and temperature were cycled (after the first step) close to the hydrate stability boundary (about 4.3 MPa and 279.16 K). The second procedure is more effective, giving higher conversion yields, up to about 90 % water converted to hydrate.

Introduction

Gas hydrates are crystalline nonstoichiometric compounds in which hydrogen-bonded water molecules are arranged in an icelike framework, forming polyhedral cavities occupied by small guest molecules such as CH_4, CO_2, C_2H_6, and others.[1]

Methane hydrate is mostly important because of the huge amount of natural gas stored in oceanic sediments and permafrost, so that hydrate reservoirs have been considered as a substantial energy resource as well as a metastable reservoir of a greenhouse gas that participates in the long-term natural climatic change.[2,3]

Because hydrates concentrate methane by a factor higher than 160 at the same pressure, a number of transportation and storage systems for natural gas using gas hydrates have been investigated, and some of them are nearing practical use.[4,5] In these systems, the hydrate is produced as a slurry by a spray process at about 7 MPa and then shaped into transportable pellets.[5] A spray process, instead of a conventional stirred vessel, is necessary to reach high hydrate concentrations (nearly 90 % water converted to hydrate) in the hydrate−water system.

In previous unpublished experiments, we have noticed an apparently anomalous behavior during the hydrate decomposition process. By increasing the temperature, a pressure decrease was detected near the equilibrium curve. Because a pressure increase is an indicator of the hydrate decomposition while pressure decrease is linked to hydrate formation,[6] we interpreted the observation as an indication that some hydrate had formed just before the decomposition.

Such an effect was also noted, although not emphasized, in the experimental procedure adopted by Behar et al.[7] to study the plugging problem during hydrocarbon production and transport (Figure 1). During the study of the HCFC141b hydrate growth process, Yingming et al.[8] noticed the continuous hydrate formation along the surface of the heat transfer tube. They also described the phenomenon of fast nucleation of hydrate from melting ice. According to these experiments, they suggested the possibility of forming hydrates from melting ice and/or along a heat transfer surface. A nearly complete conversion of ice to CO_2 hydrate was obtained by Circone et al. as the temperature of the sample was cycled through the melting point of ice.[9,10]

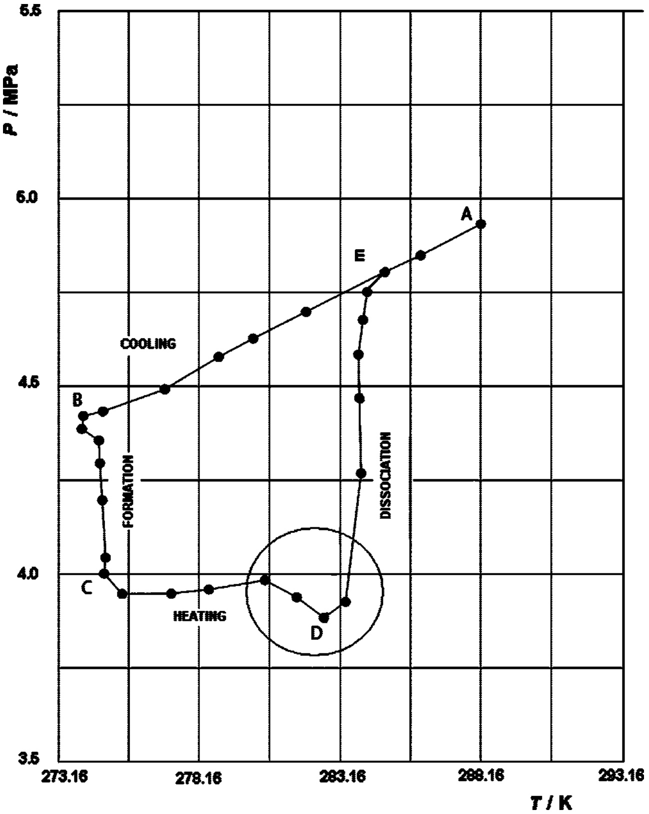

Figure 1. Experimental procedure for hydrate equilibrium curve measurement,[7] which shows hydrate formation just before decomposition (point D).

In the present work, we have studied a new procedure to produce a bulk of concentrated methane hydrate in a static traditional reactor at moderate pressure, controlling the pressure at (4 to 5) MPa and temperature in the interval between ice melting (273.16 K) and the hydrate equilibrium curve (about 279.16 K).

The importance of due control over the experimental parameters, especially the heating gradient near the equilibrium

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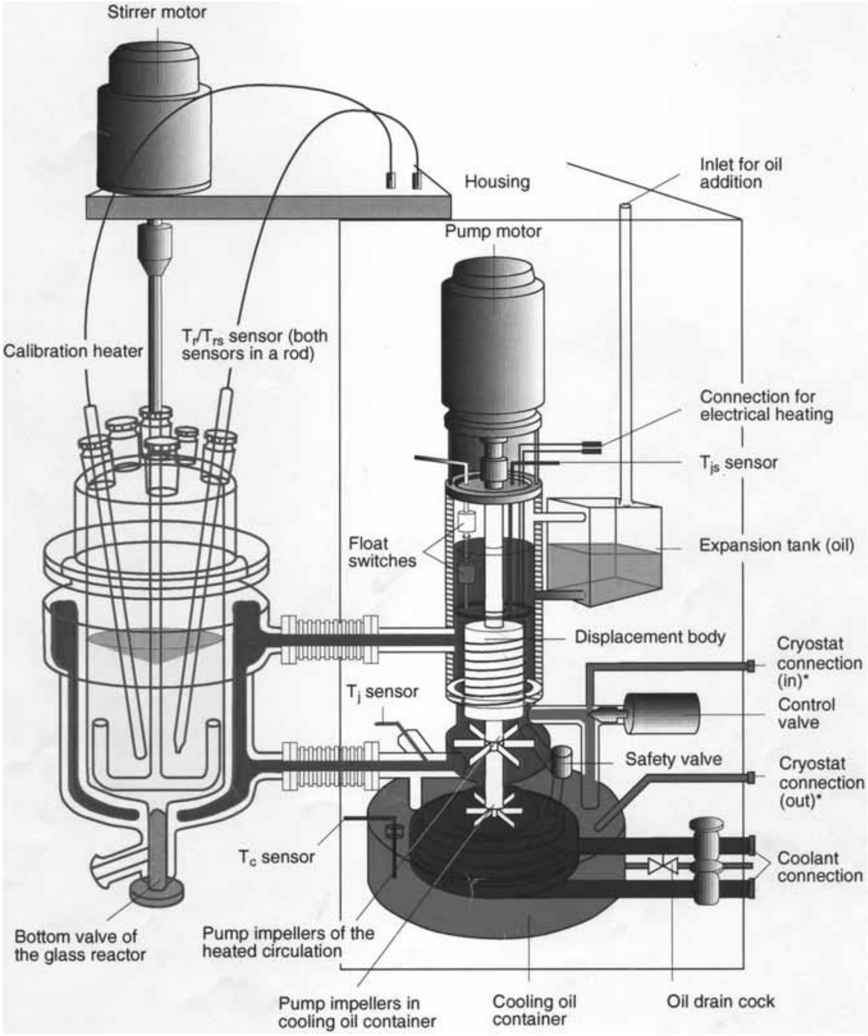

Figure 2. Scheme of the RC1 reactor.

conditions, has been previously underlined by Circone et al.[9] and Gjersten and Fadnes.[11] A too high heating rate may lead to erroneous hydrate equilibrium predictions.

Experimental

Apparatus. The experimental apparatus consisted of a jacketed stainless steel reactor (RC-1 Mettler Toledo) with an internal volume of 2 L, equipped with an anchor stirrer working at 400 rpm. A schematic view is shown in Figure 2. Pressure, temperature, and stirrer revolutions were transmitted to a computer through a data acquisition board and were recorded at 3 s intervals. The uncertainty was ($P \pm 0.001$) MPa and ($T \pm 0.01$) K. For hydrate formation, CH_4 gas (99.9 %) was supplied from a cylinder bottle in the reactor containing the required amount of distilled water. An external oil circulation loop was attached to the chamber, and the rate at which cold oil flowed through this loop was controlled by a plunger pump. During all experiments, it was possible to control the rate of heat transfer to the reactor by varying the temperature difference between the jacket fluid (T_j) and the reactor interior (T_r).

Hydrate Formation. The normal procedure in our laboratory for producing hydrates from gas and water consisted of purging the reactor chamber (containing about 560 g of water, at 283.16 K) and pressurizing it with methane to about (4 to 5) MPa. The temperature was lowered to 275.16 K to enter the hydrate stability zone in the equilibrium diagram (Figure 3, step 0 → 1). Hydrate formation began immediately after the stirring was started (400 rpm) and was detected by a pressure decrease and a temperature increase (T increase spike not shown, Figure 3, step 1→2).

The hydrate mass fraction concentration in the system ice + hydrate produced was normally about (30 to 35) % (water converted to hydrate), and the final reactor pressure was about 2.8 MPa. Any further repressurization at 275.16 K had no apparent effect on the formation of new hydrate. Figure 4 shows experimental pressure and temperature curves during the normal procedure of hydrate formation. Following this step, two procedures were tested to increase the hydrate concentration in the bulk.

Procedure A. Procedure A is represented in Figure 3, where all steps are marked out by numbers.

After the normal procedure (step 0 → 1 and 1 → 2), the reactor temperature was lowered to 268.16 K (2 → 3), and the reactor was then repressurized with methane to about 4 MPa (3 → 4). In these conditions, there were two mixed solid phases in the reactor: hydrate and ice.[6,12] The temperature was then increased from 268.16 K to an average value of 273.3 K (4 → 5). At the end of this heating phase, there was a new hydrate formation due to the partially melted ice and shown by a pressure decrease and by a small temperature increase (not shown) (5 → 6). The new hydrate formation ended when the ice melting was complete.

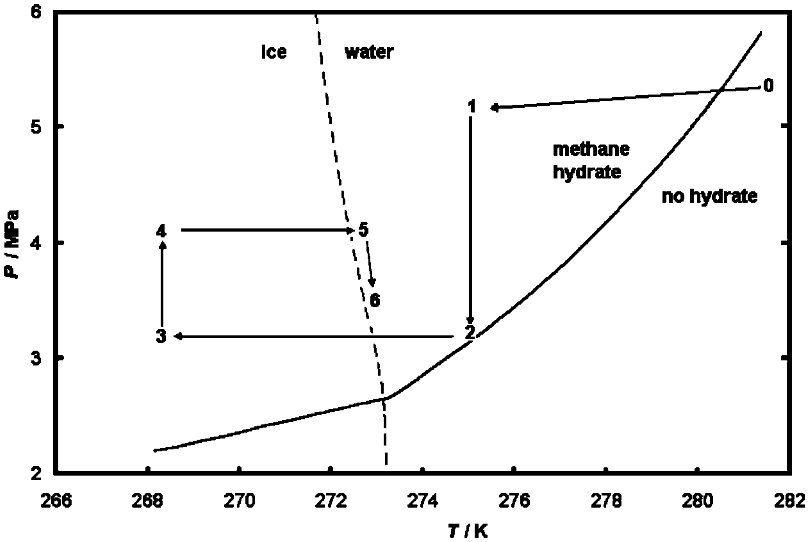

Figure 3. Procedure A: hydrate formation from melting ice. The normal procedure previously adopted follows only the path from zero to two.

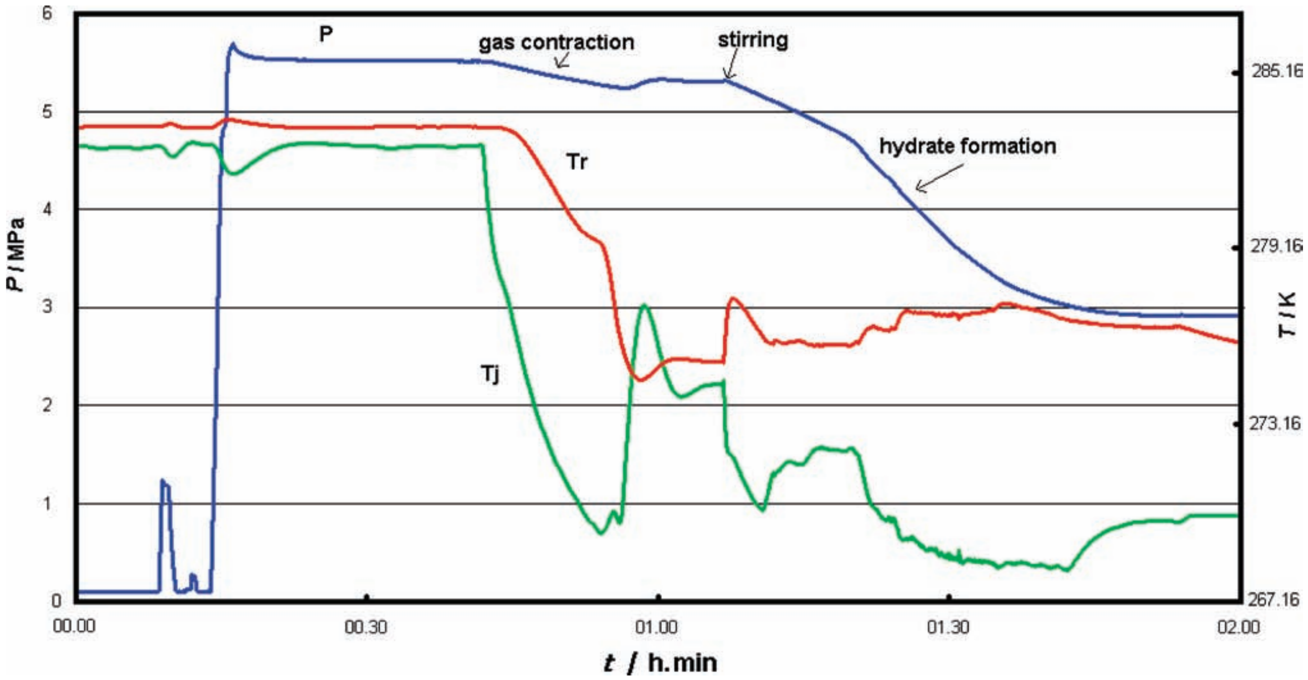

Figure 4. Typical pressure and temperature trend during hydrate formation. T_r, reactor temperature; T_j, cooling jacket temperature (K); P, reactor pressure (normal experimental procedure). Time in the abscissa is expressed in hours and minutes. "Gas contraction" indicates the pressure drop due to the contraction of the gas on cooling, while "hydrate formation" indicates the pressure drop due to hydrate formation. "Stirring" indicates the start of stirring.

Procedure B. Procedure B is represented in Figure 5. After the normal formation procedure (step 0 → 1 and 1 → 2), the reactor was repressurized with methane to about 4.3 MPa (2 → 3), and the temperature was then increased to near the decomposition value, at about 279.2 K (3 → 4). The pressure drop clearly indicated a new formation of gas hydrate (4 → 2). In this step, the temperature was decreased at a rate of 1 K/h to obtain pressure and temperature values close to the hydrate dissociation conditions. To further increase the hydrate conversion, the reactor was pressurized again to about 4.3 MPa at 275.5 K. It was then heated at 279.2 K, and the conversion cycle 2−3−4−2 was repeated.

Results and Discussion

A. Hydrate Formation from Melting Ice. An example of the *P*,*T* experimental curves is shown in Figure 6 where the formation steps previously described are indicated by the same numbers in Figure 3. The first hydrate formation (step 1 → 2) occurred starting at about 5 MPa and decreasing the temperature to 275.16 K, when the stirrer was started. The pressure drop was about 2.3 MPa. The reactor was cooled to 268.16 K (step 2 → 3) to transform the free water into ice and then was repressurized to 4.4 MPa (3 → 4) and slowly heated to the ice melting point (step 4 → 5). This was obtained by gradually increasing the jacket temperature T_j from (268.16 to 274.16) K to equalize the reactor and jacket temperature.

The hydrate formation from melting ice started at 4.4 MPa and 273.3 K (starting with step 5 → 6) and was detected by a pressure decrease and temperature increase. The conversion rate was $5.7 \cdot 10^{-5}$ CH_4 mol·s^{-1} calculated by the pressure change due to the hydrate formation.

In this example, the conversion obtained during the normal formation procedure (step 0 → 1 and 1→2) was about 35 % mass fraction, while the conversion obtained in the following

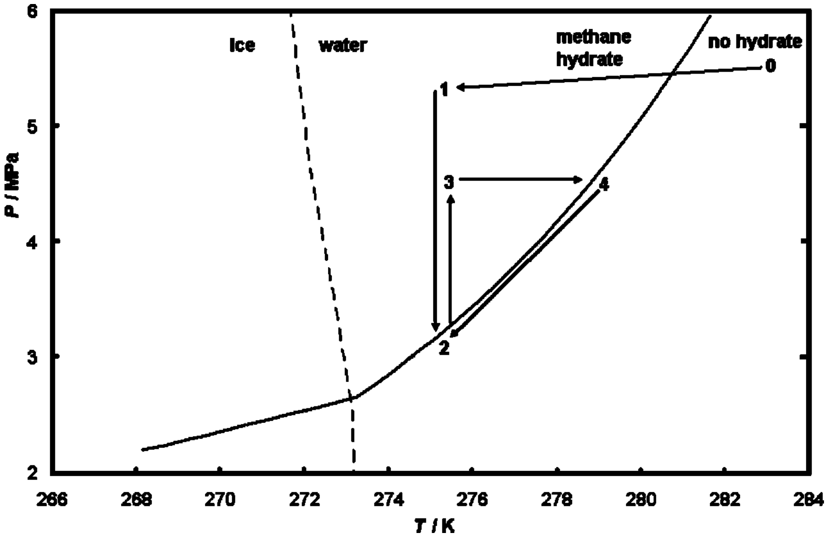

Figure 5. Procedure B: hydrate production near the equilibrium curve.

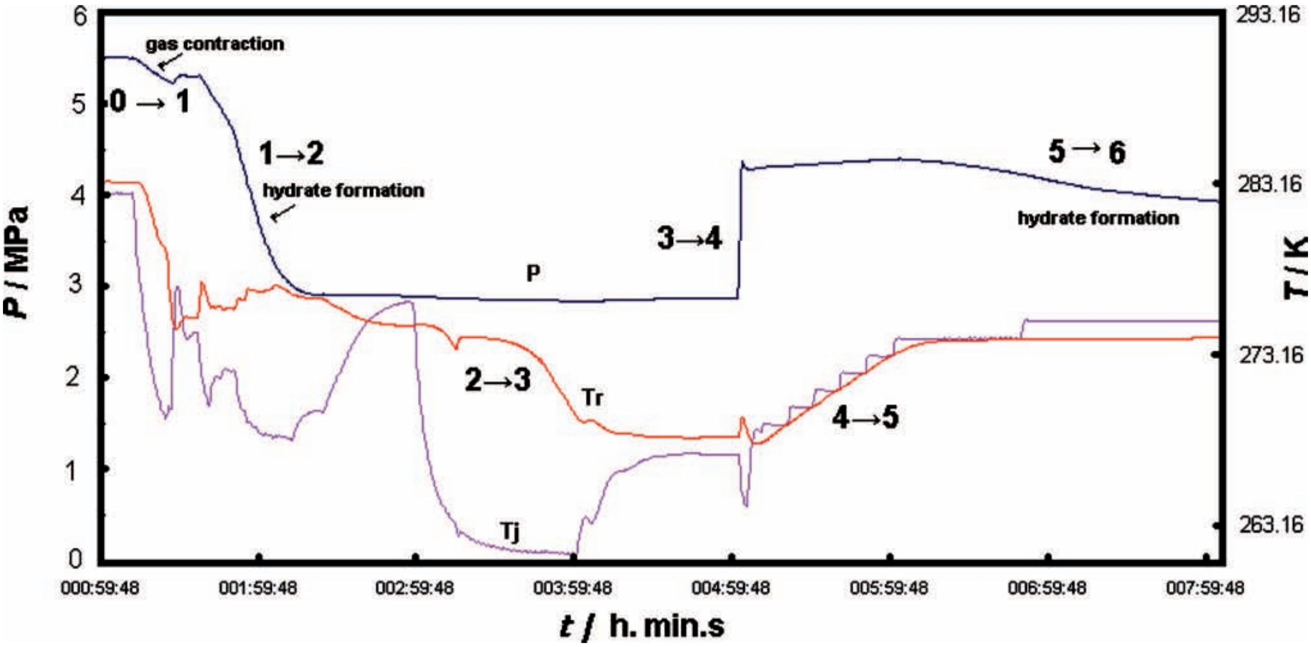

Figure 6. Experimental $P-T$ curves of the hydrate formation from melting ice (procedure A). Temperature is expressed in K, and pressure in MPa. The time in the abscissa is expressed in hours, minutes, and seconds. "Gas contraction" indicates the pressure drop due to the contraction of the gas on cooling, while "hydrate formation" indicates the pressure drop due to hydrate formation. "Stirring" indicates the start of stirring.

steps was about 23 % mass fraction, so that the total conversion was about 58 % mass fraction. The conversion yields calculated from the pressure drop during formation were confirmed by the pressure release during the complete dissociation of the sample.[6] Higher conversion yields could be obtained by increasing the starting pressure and/or by adding a further step 5 → 6 (i.e., by repressurizing the reactor). An important parameter for the formation process was the difference between T_r and T_j; in fact, as shown in Figure 7, the highest formation rate was reached when the difference $T_j - T_r$ was 0.88 K. Such a temperature difference probably produced the water content most favorable to the reaction, in terms of gas−water interface. The availability of a premelting layer on the surface of the ice particles provides sufficient interfacial contact between water−gas. Conversely, if the ice is melted too much, the increased surface area is not available for interfacial gas−water contact. Too little melting leads to conversion of ice to hydrate which is far too slow. This confirms the importance of the control of the heating gradient during the hydrate formation.[11]

B. Hydrate Formation near the Equilibrium Curve. Figure 8 shows an example of the P,T experimental curves relating to the second formation procedure: the formation steps are indicated by the same numbers in Figure 5. The numerical values are shown in Table 1.

Also, in this case, the first hydrate formation (1 → 2) occurred starting at 5.3 MPa and 274.3 K when the stirrer was started, and the pressure drop was about 2.5 MPa. The reactor was repressurized to 4.3 MPa (2 → 3) and then heated to a temperature close to the equilibrium curve (step 3 → 4). During heating, the reactor pressure increased up to 4.4 MPa and the temperature to 279.2 K, where an inversion of the pressure trend was noticed and the formation of a new hydrate started (step 4 → 2).

During the hydrate formation in this step, the temperature of the jacket was held at about 278.2 K for 3 h and then gradually decreased to reach a temperature of 274.3 K inside the reactor, where the pressure was just under 3 MPa. The reactor was then repressurized to 4.4 MPa, and the formation cycle was repeated

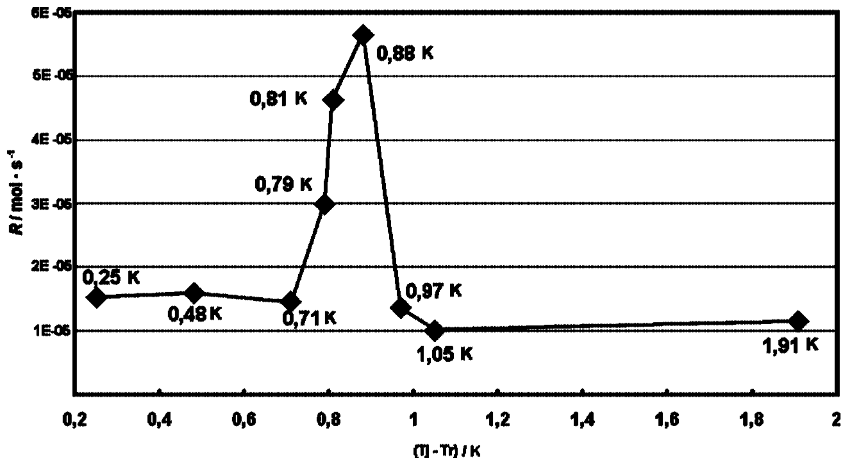

Figure 7. Procedure A: the influence of the difference between the jacket temperature (T_j) and reactor temperature (T_r) on the formation rate (R). Temperature expressed in Kelvin.

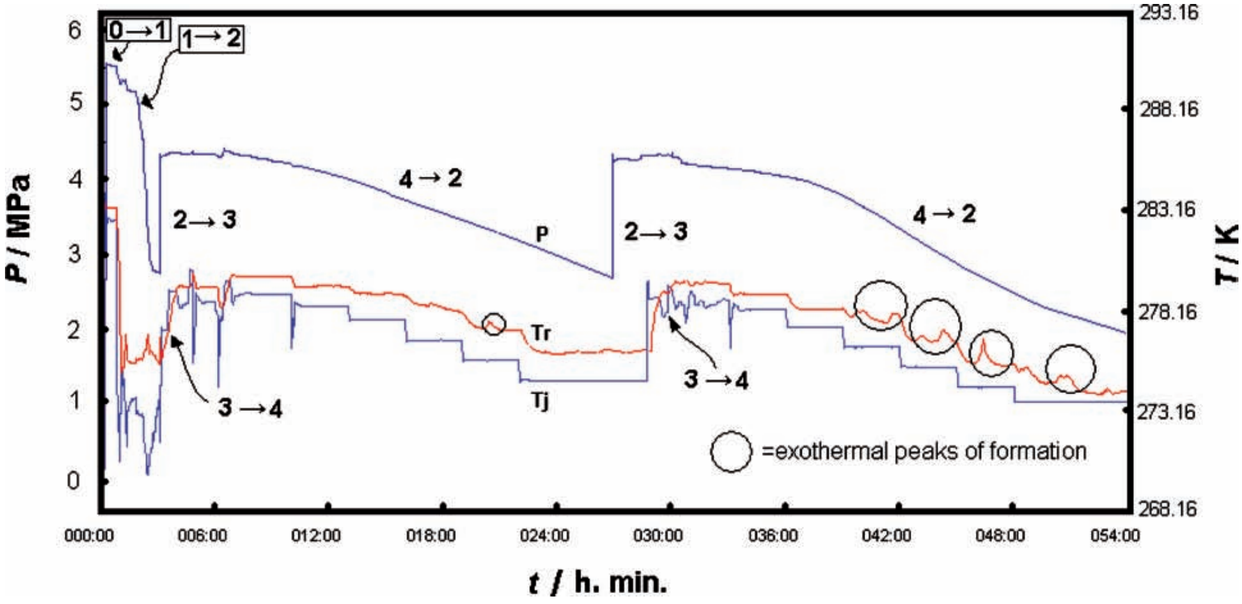

Figure 8. Experimental $P-T$ curves of the hydrate formation following procedure B. Time in the abscissa is expressed in hours and minutes.

Table 1. Numerical Values of the Hydrate Formation Following Procedure B

step	P/MPa	T_r/K	T_j/K
0	5.5	283.16	283
1	5.3	274.3	273
2	2.8	274.3	273
3	4.3	274.6	273
4	4.4	279.2	278.2
2	2.8	275.2	274.3
3	4.3	275.5	274.2
4	4.4	279.2	279.2
2	2.8	274.2	274.2

(from step 2 to step 4). The new hydrate formation is shown in Figure 8 by a pressure drop and by various (circled) exothermic peaks on the T_r curve.

After three to four cycles, about 90 % of the free water was converted to hydrate. In the described example, the formation of "new hydrate" (steps 4 → 2) was about 53 % mass fraction. By adding the conversion obtained with the normal procedure (step 0 → 1 and step 1 → 2), the total conversion was 88 % mass fraction.

Conclusion

Of the two proposed procedures for hydrate formation, the second one (B) seems more efficient, giving higher conversion yields, up to about 90 % water converted to hydrate in our experimental conditions, that is, (4 to 5) MPa and two to three cycles. Methane hydrate is produced with a portion of "unreacted" interstitial water and seems suitable for the development of gas hydrate storage and transport technologies. Compared to the spray process[5] and to other experimental techniques which produce concentrated hydrates,[13] procedure B reported here requires more time but makes use of simpler equipment and can be performed at lower pressures.

The formation from melting ice (procedure A, fast nucleation) has been explained by Yingming et al.[8] according to the hypothesis of Sloan et al.[14] and Zhou:[15] when the temperature is above 273.16 K, a part of hydrogen bonding in the ice crystals breaks and produces "ice fragments", immediately changing into mainly dodecahedron units (5^{12}). These empty cages could easily form more stable hydrate crystals.

Circone et al.[9] have observed that complete conversion of the free water to CH_4 or CO_2 hydrate occurred in only a few days when the temperature was increased above H_2O solidus and held near the hydrate stability boundary. They inferred that the hydrate growth was then dominated by diffusion of the gas through the external hydrate layer to the unreacted free water core.

The formation near the equilibrium curve (procedure B) could possibly be explained in terms of surface free energy which is in favor of hydrate formation at the borderline between the hydrate stability zone and no hydrate zone.[8] The hydrate film on the liquid−liquid interface is a kind of porous media so that gas and water can permeate into the other side of this film.[16]

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