

GAS HYDRATE FORMATION

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KINETICS GROWTH OF GAS HYDRATE
OF FREON-12 DURING THERMAL CYCLING OF SAMPLEA.G. Zavodovsky¹, M.Sh. Madygulov^{1,2}, A.M. Reshetnikov^{1,2}¹Earth Cryosphere Institute, Tyumen Scientific Centre SB RAS,
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The article presents the results of experiments involving differential thermal analysis to study the kinetics of growth of a freon-12 hydrate sample at the cyclic change in the temperature in the range of 263–276 K. The radial growth rate of the gas hydrate cake initially formed at the temperature of 263 K on ice granules with the mean size of 150 μm has been measured. Comparative analysis has been carried out for the growth rate of the hydrate among the samples, depending on the presence of water or ice in them. It has been found that hydrate growth is determined by the diffusion properties of the inhomogeneous gas hydrate cake: there are inclusions of either water or ice in it, depending on the sample temperature. The main factors have been identified to contribute to the maximum content of gas hydrate in a sample.

Growth kinetics, disperse ice, gas hydrate, differential thermal analysis, crystallization, diffusion

INTRODUCTION

Increased emission of gases of anthropogenic origin into the Earth's atmosphere (CO_2 , CH_4 , N_2O , etc.) negatively affects the cryogenic formations of the Earth: the glaciers' melting rate increases, degradation of permafrost zones takes place, relic gas hydrates get destroyed, accompanied by methane emission, etc. [Kisilev and Reshetnikov, 2013].

The gas hydrate technologies being developed are aimed at utilization of the greenhouse gases of anthropogenic origin [Gudmundson et al., 2000; Chuvilin and Guryeva, 2009], their storage and transportation [Dawe et al., 2003; Levin et al., 2011]. In these technologies, gas hydrates are used, formed from water molecules and low-molecular gases under specific thermobaric conditions [Sloan and Koh, 2008]. Those areas of the permafrost zone of the Earth where such conditions are met may be used as gas hydrate storages [Melnikov et al., 2009].

The prospects of using gas hydrate technologies are mainly determined by the degree of water transformation into a hydrate, which can be significantly raised by different methods of expanding the surface of interaction between water (ice) and hydrate-forming gas [Sloan and Koh, 2008]. Therefore, it is economically advantageous to use artificial disperse ice or loose snow in implementing gas hydrate technologies in the regions of Extreme North. However, as time goes, the rate of transformation of ice particles into ice significantly decreases, as they build up on the surface of the gas hydrate cake [Yakushev et al., 2008]. The scope of retardation of gas hydrate forma-

tion is described, for example, in [Groisman, 1985], where the time of transition natural gas in hydrate when ice granules sized 200–400 μm were used at a temperature of 260 K and a pressure of 5 MPa was 6 days. Much greater retardation of gas hydrate formation was observed for pure methane in using ice particles with the mean size of 50 μm under practically the same experimental conditions: after 5 days, only 60 % ice became gas hydrates [Kuks et al., 2006].

As one of the ways to intensify gas hydrate formation, the technology of cyclic change of the sample temperature is used in the atmosphere of hydrate-forming gas, with its mandatory transit through the ice melting point [Wright et al., 1998; Chuvilin et al., 2002; Vlasov et al., 2011a]. However, in order to improve and further develop this technology, it is necessary to ascertain the causes and the degree of influence of the phase state of water on the intensity of the gas hydrate growth. This can be done in investigating the growth of the gas hydrate cake by the method of differential thermal analysis (DTA), which allows study of phase transformations and evaluation of the amount of water transformed into the gas hydrate [Zavodovsky et al., 2014].

In this study, we suggest using the same model of the gas hydrate system as that proposed in [Vlasov et al., 2011a]. This will allow us to compare the DTA data with the measurement results obtained by the nuclear magnetic resonance (NMR) method and to reduce the number of uncontrollable factors affecting the kinetics of the gas hydrate growth, which will

contribute to the study of the mechanisms of gas hydrate formation from water and ice in the presence or absence of the gas hydrate cake.

THE OBJECT OF STUDY

In the study using the DTA method, a large amount of the particles of freon-12 hydrate (Fig. 1) was used, the adhesion of which, according to [Uchida *et al.*, 2015], was assumed to be insignificant. The gas hydrate particles were prepared on the basis of ice granules with the mean size of $\sim 150 \mu\text{m}$, obtained by crushing monolithic ice formed in freezing of distilled water. The ice was crushed and a narrow fraction of the particles was separated with a system of sieves in a freezing chamber at the temperature of 263 K. To crush the ice, a mechanical chopper (a coffee-grinder) was used for 60 s at a speed of 1600 rpm. The obtained ice powder was fractioned by vibration using a PE-6700 vibration machine, with sieves with the mesh size 94 and 200 μm , respectively, used.

As hydrate-forming gas, freon-12 (R-12) was used, with the volume content of CCl_2F_2 not less than 99.7 %. The gas hydrate of freon-12 is related to hydrates of the structure of the s-II type and is characterized by the low pressure of hydrate formation [Byk *et al.*, 1980], which essentially simplifies the experimental conditions.

THE EXPERIMENTAL SETUP

The DTA setup, the schematic of which is shown in Fig. 2, is meant for synthesizing and studying gas hydrates with low pressure of hydrate formation. It is based on two identical cells located in a Julabo FM50-ME liquid thermostat. A hydrate sample was synthesized and measured in one of the cells. The other cell was used as an etalon for DTA measurements and was partly filled with liquid Thermal H5S, which did not have any phase transitions in the range of temperatures of 263–276 K used in the experi-

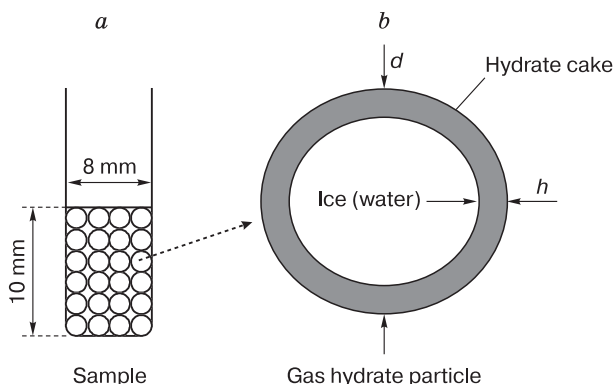


Fig. 1. The sample used in the DTA experiment (a) and a model of a gas hydrate particle (b).

d – particle diameter; h – thickness of the gas hydrate cake.

ment. The original DTA-signal $\Delta T = T_m - T_s$ was formed on the basis of the temperature values T_m and T_s , measured with the accuracy of ± 0.1 K in the center of the sample and of the etalon, respectively.

The hydrate-forming gas was injected into the reactor from a gas cylinder containing freon-12. To lower the pressure in the sample-containing cell, a vacuum pump 2FY-1B was used. Gas pressure in the reactor was controlled with a digital manometer DM5002G UHL with the accuracy of ± 1.5 kPa throughout the entire measuring range. Manual adjustment of the pressure rate in the reactor was possible from 0.1 to 20 kPa/min at the stage of gas injection and pumping out, using needle valves. Signals converted with an ADC (analog-to-digital converter) from the temperature sensors and from the digital pressure manometer and the DTA-signal were recorded on a personal computer (PC) in the real-time mode.

THE EXPERIMENTAL PROCEDURE

To prepare a hydrate sample, the reactor cooled to the temperature of 263.2 K was filled with ground ice up to the height of ~ 10 mm. Then it was placed into the thermostat with the temperature of 263.2 K. After brief vacuuming of the reactor containing ice, freon-12 was injected into it to reach the pressure of 150 kPa. At the sample temperature equal to 263.2 K, this value of pressure exceeds the equilibrium pressure of hydrate formation but is lower than the respective pressure of saturated vapor of freon-12 [Byk *et al.*, 1980].

In the state with the pressure of ~ 150 kPa and the temperature of 263.2 K, the sample was kept for

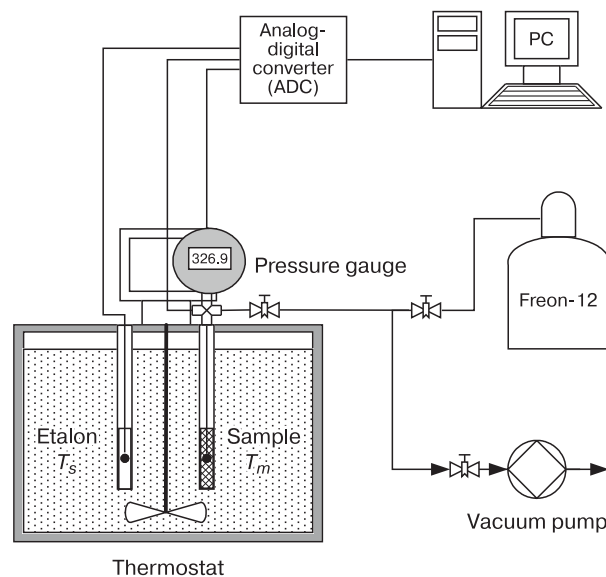


Fig. 2. Configuration of the DTA installation for studying gas hydrates (see the explanations in the text).

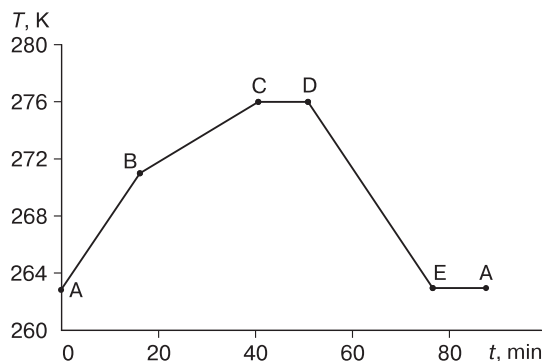


Fig. 3. A schematic of a thermal cycle used in the synthesis of the freon-12 hydrate (see the explanations in the text).

105 minutes, with periodic compensation of the reduction in the gas pressure due to hydrate formation. During this time, the effectiveness of hydrate growth decreased, indicated by noticeable decrease in the gas consumption and eventually by establishment of practically constant pressure in the cell containing the sample.

To activate the growth of the hydrate, the temperature of the sample varied by to the scheme (Fig. 3), developed in accordance with the results [Vlasov et al., 2011a]. In this scheme, the heating of the sample from 263 to 276 K corresponds to line segment AB and BC with heating rates of 0.5 and 0.2 K/min. The sample was kept at the temperature of 276 K on the line segment CD during 10 min, and then it was cooled to the temperature of 263 K at the rate 0.5 K/min (line segment DE). At the final stage of the cycle, the sample was kept at the temperature of 263 K for 10 min (line segment EA).

In cyclic change of the sample temperature, the pressure of the hydrate-forming gas was maintained manually at the level of ~150 kPa, in order to ensure duration of the process of hydrate formation with a constant driving force. The cycle was repeated several times, in order to obtain the maximum amount of the gas hydrate in the sample. The total duration of a cycle was 87 min.

RESULTS AND DISCUSSION

Kinetics of the freon-12 hydrate growth

Shown in Fig. 4 is the thermal DTA curve obtained by repeated thermal cycling of a sample of freon-12 hydrate in accordance with the above described scheme. The observed reduction of the areas of the DTA peaks of water crystallization and ice melting qualitatively indicates the growth in the amount of the formed freon-12 hydrate as time goes (as the number of the cycles increases). The values of the areas of these peaks were used by the authors to evaluate the degree of transformation of water/ice

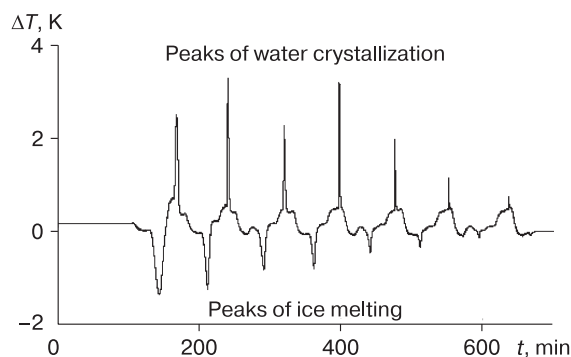


Fig. 4. A DTA – thermogram of the synthesis of freon-12 hydrate at multiple cyclic change of the sample temperature in the range 263–276 K.

into a hydrate (the degrees of hydrate formation of the sample $P_h(k)$) according to the formula [Zavodovskiy et al., 2014]

$$P_h(k) = \frac{S_0 - S_k}{S_0} \cdot 100\%, \quad (1)$$

where S_0 is the area of the ice melting peak (of water crystallization) in air; S_k is the area of the melting peak of non-reacted ice (of crystallization of non-reacted water) in the atmosphere of freon-12 in the k -th cycle ($k = 1, 2, 3, \dots$). It is to be noted that in order to obtain the peak of ice melting and the subsequent peak of water crystallization in air, we took ice granules of the same mass as in the original amount of ice used in obtaining the gas hydrate.

The results of calculating P_h according to formula (1) are shown in Fig. 5, where, just as in the study using the pulse NMR method [Vlasov et al., 2011a], slowing down of the growth of the freon-12 hydrate is observed as the number of the cycles increases. Such behavior of the hydrate is quite understandable, since, as the number of the cycles grows, the thickness of the gas hydrate cake increases and thus the access of the gas molecules to the hydrate formation front decreases [Rivera and Janda, 2012]. In that, the multi-stage character of hydrate formation is manifested (Fig. 5), due to the influence of different mechanisms on the hydrate growth [Kuhns et al., 2006].

It should be noted that in experiments using the DTA method regarding complete conversion of the aqueous phase to hydrate was indicative of the absence of peaks of crystallization and melting of water and ice that did not convert into hydrate. In further thermal cycling of the sample, the fact of obtaining 100%-hydrate was also confirmed by practically constant gas pressure in the control points of the cycle, which were the temperatures 263 and 276 K. Complete conversion of the aqueous phase into hydrate indicates that for a cyclic change in the sample temperature, a monolithic mass of gas hydrate is not formed. To prove that, a DTA experiment was conducted

on formation of freon-12 hydrate based on bulk ice of the same mass as in the experiments with the ice granules. Based on the results of this experiment, the authors found that in thermal cycling of the sample according to the model presented in Fig. 3, the degree of conversion of the water phase into hydrate was less than 2 % after 10 cycles.

Unfortunately, the authors were unable to obtain convincing visual evidence of adhesion or lack of adhesion of the particles of freon-12 hydrate seemingly taking place during thermal cycling of the sample. Yet, in accordance with the results of [Uchida *et al.*, 2015], where the authors observed adhesion of the particles of the CO₂, C₂H₆ and CH₄ hydrates, formed on ice granules, we may assume that adhesion and partial accretion of the freon-12 hydrate particles may principally take place.

According to the analysis of the results of [Uchida *et al.*, 2015], the “spot” of accretion of two particles of the studied hydrates is insignificant (<1 %) during the time equal to 1000 min, which is commensurable with the full time spent in the authors’ experiments on thermal cycling of the sample. Supposing the same insignificant adhesion of the hydrate particles takes place for the particles of freon-12 hydrate, then the total area of the “spots” on the surface of a particle of freon-12 hydrate (the maximum number of the “spots” for the given particle is 6) will be small compared to its “working” surface (<6 %). The authors understood that adhesion of the particles of freon-12 hydrate took place due to the increase of the mechanical strength of the sample (it does not precipitate like powder does and gets separated into small fragments under little mechanical impact).

Correctness of the values of P_h shown in Fig. 5 is confirmed by the NMR results and by the results of

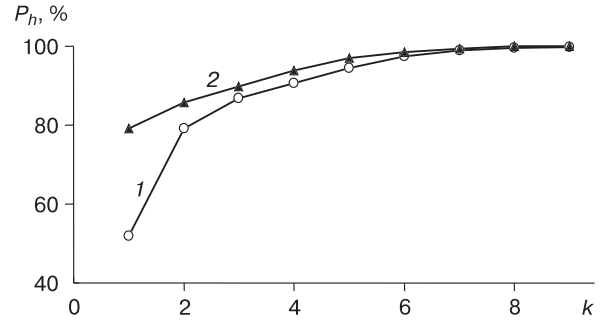


Fig. 5. Increase of the degree of hydrate formation as the number of the melting–freezing cycles increases.

The values of P_h were obtained on the basis of respective DTA-peaks: 1 – melting of ice not turned into hydrate; 2 – crystallization of water not turned into hydrate.

P – V – T -measurements in using identical samples, other conditions being equal. It turned out that the values of P_h obtained in this study are in most cases close to the results of the NMR measurements, and their maximum deviation from the results obtained on the basis of P – V – T -measurements does not exceed 5 %.

The values of $P_h(k)$ shown in Fig. 5 were used later for calculating the thickness of the gas hydrate cake according to the formula [Vlasov *et al.*, 2011a]

$$h = 0.5d \left(1 - \sqrt[3]{(1 - P_h(k) / 100)} \right),$$

where d is the particle diameter.

To analyze the kinetics of the growth of the thickness of the hydrate cake, we divided the time of the gas hydrate formation in the sample into intervals Δt_j ($j = 1, 2, 3, \dots, N$; N is the total number of inter-

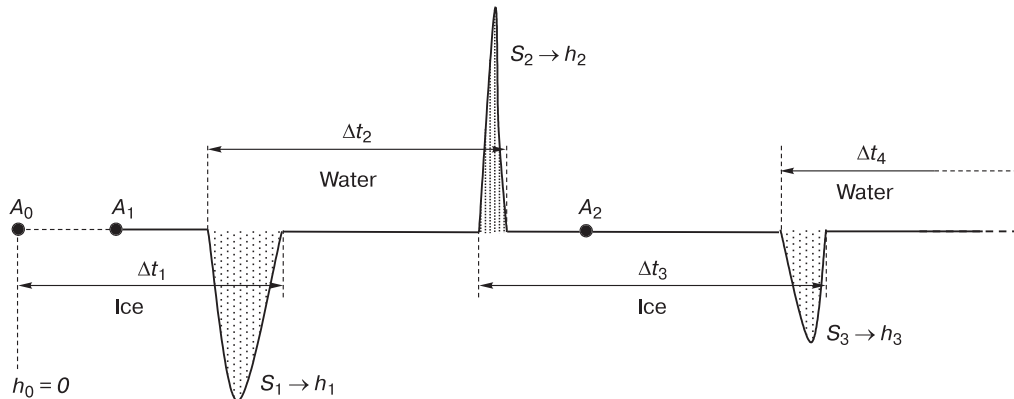


Fig. 6. The basic diagram of division of the total sample cycling time into intervals corresponding to the growth of hydrate from water and ice.

A_0 – the beginning of the experiment; A_1, A_2 – the beginning of the first and second cycles, respectively; $\Delta t_1, \Delta t_3$ – time intervals of the stay of water not turned into hydrate in a solid state; $\Delta t_2, \Delta t_4$ – time intervals of the stay of water not turned into hydrate in a liquid state; h – thickness of the hydrate cake at the beginning of the experiment (h_0), at the end of recording ice melting peaks (h_1, h_3) and water crystallization peaks (h_2); S – the area of the melting peaks (S_1, S_3) and the crystallization peak (S_2) of ice and water not turned into hydrate, respectively.

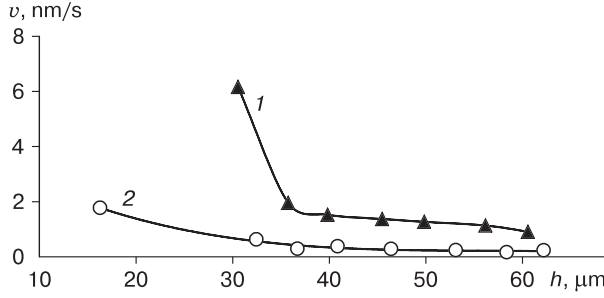


Fig. 7. Change in the radial velocity of the hydrate cake growth (v) as its thickness increased (h) in the case of hydrate formation from water (1) and ice (2).

vals), corresponding to the synthesis of the hydrate from water and ice in full agreement with the observed DTA peaks of crystallization and melting of the hydrate-turned water phases (Fig. 6). For each of these time intervals, the increments of the hydrate cake Δh_j were determined, and the mean values of the radial velocity of the growth of the freon-12 hydrate were calculated according to the formula

$$\bar{v}_j = \Delta h_j / \Delta t_j = (h_j - h_{j-1}) / \Delta t_j.$$

The results of these calculations shown in Fig. 7 demonstrate the high growth rate of the hydrate from water compared to ice, with the thickness of the gas hydrate cake being equal, the difference was by an order of magnitude. It is interesting that, independently of the phase state of water which does not turn into hydrate, the radial velocity of the growth of the hydrate cake decreases as its thickness increases. As a first approximation, this indirectly indicates the manifestation of the diffusion mechanism of hydrate formation.

The diffusion properties of the freon-12 hydrate cake

It is to be remembered that, given the gas hydrate cake, the growth rate of the studied gas hydrate is influenced by several factors: the intensity of the inflow of gas molecules to the hydrate formation front, heat outflow from the boundary of the phase transition water (ice) \rightarrow hydrate, the rate of formation of an elementary cell of the hydrate (the phase transition velocity), etc. In our experiments, the small size of the gas hydrate particles and of the sample as a whole contributed to the intense outflow of heat from the boundary of the hydrate formation (Fig. 1). Proceeding from this, further the authors limited themselves to analysis of the contributions to the growth rate of the gas hydrate cake made by the diffusion motion of the gas molecules to the hydrate formation front and by the water (ice) \rightarrow hydrate phase transition.

To evaluate the diffusion coefficient D of the freon-12 molecules diffusing through the hydrate cake, we use Groisman's formula for the velocity of the hydrate formation front in gas hydrate particles of a spherical shape (the radial velocity of the hydrate growth v) [Groisman, 1985]:

$$v = \frac{(1 - X_f) r_0}{(r_0 - h) X_f h} D.$$

Here $r_0 = d/2$; $X_f = M_h / (M_h + nM_w)$, where $n = 17$ – hydrate number; $M_h = 120.9 \cdot 10^{-3}$ kg/mol, $M_w = 18 \cdot 10^{-3}$ kg/mol – molar mass of freon-12 and of water, respectively. Hence, considering the above numerical values, we obtain the desired expression for the diffusion coefficient:

$$D = (1 - 2h/d) hv / 2.53. \quad (2)$$

The results of calculating D by formula (2), performed on the basis of the data presented in Fig. 7, indicate decrease of the diffusion coefficient as the thickness of the hydrate cake increases and its dependence on the phase state of the water that has not passed into the gas hydrate. Thus, as the hydrate cake thickness varies from 30 to 60 μm , the diffusion coefficient decreases from $4.4 \cdot 10^{-14}$ to $0.4 \cdot 10^{-14}$ m^2/s in the presence of water in the sample, and in the presence of ice it decreases from $0.5 \cdot 10^{-14}$ to $0.1 \cdot 10^{-14}$ m^2/s .

Dependence of the diffusion coefficient of the hydrate cake on its thickness and the phase state of the water that has not passed into hydrate suggests its non-homogeneity. Considering the porous structure of the freon-12 hydrate formed, just as in our study, on the basis of disperse ice [Vlasov *et al.*, 2011b], it is logical to assume that inhomogeneity of the hydrate cake in our case is related to the presence of water or ice not turned into hydrate, depending on the sample temperature. It is to be mentioned that non-uniform hydrate formation in ice particles has been reported previously in [Kawamura *et al.*, 2002]. The authors of this study account for the dynamics of the changes in the combinational scattering (CS) spectra in the process of the growth of the CO_2 hydrate by the presence of ice inclusions in the hydrate cake. Considering the inhomogeneity of the freon-12 hydrate cake, the above-mentioned diffusion coefficients should be treated as effective diffusion coefficients.

It is clear that pores heal with the time, and inclusions of water and ice turn into hydrate. As a result, the hydrate cake becomes more homogeneous. Therefore, it is quite logical that the increase in the thickness of the gas hydrate cake results in the reduction and approximation of the considered rates of its growth (Fig. 7). This, in its turn, testifies to approximation of the respective effective diffusion coefficients, which, as the hydrate cake achieves its maximum thickness, approach the diffusion coefficient of

freon-12 molecules in the gas hydrate under study. In our estimate, its value is $\sim 10^{-15}$ m²/s in the range of temperatures 263–276 K and at the pressure of 150 kPa.

It is quite unlikely that the rates of the water \rightarrow hydrate and ice \rightarrow hydrate phase transitions essentially influence the difference in the growth rates of the hydrate cake observed in Fig. 7. To ascertain that, we will first evaluate the characteristic times of forming the elementary cells of the hydrate from water $t_w = a/v_w$ and ice $t_i = a/v_i$. Here $a = 1.73$ nm is the characteristic size of an elementary cell of the gas hydrate of the s-II structure [Byk *et al.*, 1980]; v_w , v_i are the linear growth velocities of an elementary cell of the gas hydrate from water and ice in the direction of movement of the front hydrate formation. As for freon-12, the values of the velocities v_w and v_i are unknown; to evaluate the times t_w and t_i , we will use the values of the hydrate growth velocities from water v_{0w} and ice v_{0i} in the absence of the hydrate cake ($h = 0$). It is evident that in reality $v_w \geq v_{0w}$ и $v_i \geq v_{0i}$.

To find v_{0w} and v_{0i} , we approximate the dependences $v(h)$ shown in Fig. 7 by polynomials to the n -th degree with the maximum approximation reliability R^2 . As a result, we have $v_{0w} = 321$ nm/s ($n = 4$, $R^2 = 0.994$), and $v_{0i} = 5$ nm/s ($n = 4$, $R^2 = 0.985$). Hence, under the thermodynamic conditions realized in the experiment, the unit cell of the freon-12 hydrate is formed from water 64 times faster than from ice: $t_w = 5.4$ ms and $t_i = 346$ ms. This qualitatively corresponds to the results of [Melnikov *et al.*, 2010], where, other conditions being equal, the hydrate formation front of propane, forming, just as freon-12, the hydrate of the s-II structure, moved on the water surface faster by an order of magnitude than on the surface of ice.

To compare the contributions of the above mechanisms to the growth velocity of the hydrate cake, we can evaluate the respective times of diffusion of the freon-12 molecules through the hydrate cake with thickness h according to the formula $t_d = h^2/D$ and compare them with t_w and t_i . The calculations demonstrate that, given water not turned into hydrate in the sample, the value t_d is $\sim 2 \cdot 10^4$ s with cake thickness $h = 30$ μ m and grows to $\sim 9 \cdot 10^5$ s with $h = 60$ μ m, which is much greater than time t_w . Fulfillment of the condition $t_d \gg t_w$ with the values $h \geq 30$ μ m recorded in the experiment indicates that in this case the growth of the gas hydrate cake is determined by the diffusion of the freon-12 molecules to the hydrate formation front. In its turn, given ice not turning into hydrate in the sample, the limiting role of the diffusion processes is manifested by the thickness values $h \geq 15$ μ m recorded in the experiment. It is to be noted that in reality, based on the obtained evaluations of time t_w , t_i and t_d , the diffusion processes play the major role in forming the gas hydrate cake for sizes much less than those indicated above. It is most likely

that the rate of forming an elementary hydrate cell will essentially affect the process of gas hydrate formation as the hydrate cake appears at the initial stage of its growth.

CONCLUSION

In obtaining gas hydrate particles on the basis of ice granules, the growth of the hydrate slows down with the time, which is related to the shielding action of the gas hydrate cake forming on its surface. In this case, the procedure of thermal cycling of the hydrate sample has a positive effect for initializing and further growth of the hydrate, with mandatory realization of the ice formation and melting stages.

The use of the simplest model system of gas hydrate in the DTA experiments reduced the number of the uncontrollable factors which affect the kinetics of the gas hydrate growth and allowed the possibility of ascertaining the main mechanisms which influence the hydrate formation process for different aggregate states of water. The following results were obtained.

1. In thermal cycling of the freon-12 hydrate sample, the hydrate more actively grows from water than from ice, both in the presence and absence of the hydrate cake, as:

- a) the effective diffusion coefficient of the freon-12 molecules for diffusion through the hydrate cake, given water inclusions in it, exceeds the effective diffusion coefficient given ice inclusions by more than an order of magnitude;

- b) for the freon-12 gas hydrate, the water–hydrate phase transition speed exceeds the ice–hydrate phase transition speed more than 60 times.

2. In the DTA experiments, with the hydrate cake thickness being $h \geq 15$ μ m (for ice) and $h \geq 30$ μ m (for water), the growth rate of the gas hydrate cake is determined by the diffusion of the gas molecules to the hydrate formation front.

3. The gas hydrate cake is not homogeneous in its composition: depending on the temperature of the sample, it has inclusions of water or ice not turned into hydrate or ice, which eventually transform themselves into hydrate.

4. The value of the diffusion coefficient of the molecules of the hydrate forming gas in the freon-12 hydrate is $\sim 10^{-15}$ m²/s in the range of temperatures 263–276 K at the pressure of 150 kPa.

To enhance the effectiveness of gas hydrate formation and to improve the process of thermal cycling of a sample, it is necessary to reduce the time of stay of the water not turned into hydrate in the solid state and to decrease the size of the gas hydrate particles.

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