Dissociation of methane hydrate granules

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Abstract. The methane hydrate dissociation at negative temperatures and under external pressure of 1 bar is studied experimentally. It is shown that the dissociation rate of the gas hydrate depends on the granule diameter and heat transfer. The dissociation curve has an extremum. The dissociation rate initially increases due to the temperature increase and reaches the maximum value and then sharply falls due to the curvature of the granules. When describing dissociation kinetics of the spherical granules, it is important to take into account the granule size and their composition.

1. Introduction
Currently, increasingly greater attention worldwide is given to investigations on gas hydrates formation and dissociation. The growth and dissociation of gas hydrates [1, 2] are determined by many key factors: the external pressure and temperature, subcooling degree of pellets, structural characteristics of gas hydrate surface and sample defects. There are several main structures of gas hydrates which are most often found in studies: cubic structure (sI); cubic structure (sII); hexagonal structure (sH) [1]. Methane gas hydrates have structure (sI). Gas hydrate deposits contain huge reserves of natural gas and will be promising alternative sources in the coming decades [2]. Theoretical and practical studies on generation and dissociation of artificial methane hydrates are being carried out intensively. Much attention is paid to the problems of transportation and storage [3] of methane granule hydrates in large containers [2, 4]. The tankers carry liquefied natural gas at the temperatures below 111 K. Pelleted gas hydrates can be stored for a long period due to the self-preservation phenomenon at the temperatures of about 253 K. Besides, the decay rates depend on the grain size and the thickness of powder layer. The dissociation at different heating rates were studied in Ref. [5]. It is shown that a slow heating can significantly affect the dissociation intensity. When changing rate of heating from 0.2 to 1 K/h, the dissociation rate may differ by tens of percent. In the literature, there is practically no data on the methane hydrate dissociation at heat flux variations by tens times. High heat fluxes and high dissociation rates are realized by burning methane hydrate [6, 7]. Experimental investigation of flame spreading over pure methane hydrate in a laminar boundary layer were studied in Refs. [8, 9]. Of course, for a turbulent incoming stream, it is necessary to evaluate the effect of external turbulence and the mechanisms of turbulent transport, which are considered in [10,11]. The efficiency of burning the methane hydrate depends on the organization scheme of the oxidant flow. The best method
corresponds to the combination of the longitudinal flow and the transverse one through the granule layer [12]. High rates of the decomposition and the gas hydrates formation are realized by the explosive boiling of liquid gases in water at atmospheric pressure. High rates of evaporation and hydration growth are caused by the large area of small gas bubbles formed during boiling [13, 14]. The decomposition kinetics of the methane hydrate granules taking into account the influence of porosity is considered in Refs. [15, 16]. The porosity can be formed at both destruction and formation of gas hydrates [17]. Gas hydrates dissociation of the porous granule layers are considered in Ref. [18]. The technique for obtaining thermal imaging measurements with multiple magnification, used in this paper, was considered in Ref. [19, 20].

Lately, the increased attention is paid to the phenomenon of "self-preservation" [21-24] when abnormally low rates of dissociation is achieved. The phenomenon is important for storage and transportation of methane contained in the hydrates. To date, the self-preservation mechanism and its descriptions are still far from fundamental understanding. Most of the works associate the abnormally stable properties of gas hydrates with formation of a solid ice crust and the appearance of characteristic structures during annealing [25]. It is shown, based on Microfocus X-ray Computed Tomography, that the ice crust increases in the direction from the outer shell to the granule center.

Thus, the study of the influence of porosity and granule size is important both for the development of storage and transportation technologies of methane hydrate and for combustion technologies of environmentally friendly raw materials.

2. Experimental method and analysis

The experimental setup and is presented in [6, 7]. The external pressure was 1 atm. The setup was located in a closed shell, and the outer temperature was kept constant. In the experiment, initial methane mass concentration in the methane hydrate synthesized under the laboratory conditions corresponded to 12.1-12.4 wt.%. Methane hydrate was consistent with sI structure. Formula of the elementary cell is 2D·6T·46H2O, or taking into account the number of edges and faces 2(512)+6(51262). The cell consists of 46 water molecules, two small and six large areas. Characteristics of methane hydrate powder were determined by gravimetric and volumetric methods. The methane concentration values closely match with the weight measurements by gas hydrate dissociation.

Figure 1. Dissociation rate of methane hydrate. Curve 1 – Experimental data for dissociation rate; Curve 2 – temperature variations of powder surface
Figure 1 shows the methane gas hydrate dissociation rate \( j = \Delta V_i/V_0 \cdot 100\% \) depending on time. Despite the fact that the temperature of the granules continuously increases, the dissociation curve has an extremum. The dissociation rate initially increases due to the temperature increase and reaches an extremum. With increasing temperature, the deviation of the thermodynamic system from an equilibrium increases. Reduction in dissociation rate in the range where \( t > 400 \, s \) is associated with the curvature of the granules. As the granule decays, and when the granules (sphere) approach the center, the surface area of the reaction (decay) decreases sharply. Therefore, the amount of methane released from the powder is sharply reduced. Since the decay rate of the methane powder depends on the curvature, i.e. it depends from the average diameter of the granules, it is necessary to take into account the granular composition in the modeling of dissociation.

![Figure 1](image1.png)

**Figure 1.** shows the methane gas hydrate dissociation rate \( j = \Delta V_i/V_0 \cdot 100\% \) depending on time.

**Figure 2.** The change in the dissociation rate as a function of the diameter of methane hydrate granules

Fig. 2 represents experimental data of the dissociation rate of methane hydrate versus the granules diameter and for powder temperature \( T = 225\, K \). The decomposition of the gas hydrate begins at a temperature of 193 K. The temperature of the powder continuously increases and when \( T = 225\, K \) the total amount of methane removed from the granules is measured by the weight method. The average conditional dissociation rate is characterized by the ratio \( \Delta V_i/V_0 \), where \( \Delta V_i \) is the amount of gas released from the powder at \( T=225\, K \), \( V_0 \) is the total initial amount of methane in the powder before the dissociation beginning. As can be seen from the figure, the rate of distraction decreases substantially with the growth of granules diameter. The strong influence of the diameter is probably determined by two main reasons: 1) the effect of heat transfer (as the diameter of the granule grows, the mass grows as \( R^3 \), and the heat transfe area as \( R^2 \)). 2) With increasing diameter, the effect of self-preservation is more pronounced. The phenomenon of "self-preservation" is observed at annealing temperatures \( (T > 235K) \) when observed abnormally low rates of dissociation.

**Conclusion**

Thus, the experimental studies of nonisothermal dissociation of methane hydrate were implemented. The significant influence of the granules diameter on the decay rate during dissociation was established. Despite the continuous increase in the temperature of the powder and the increase in the deviation of the methane hydrate from the equilibrium state, the decay curve is essentially nonlinear. The dissociation curve has an extremum. The dissociation rate initially increases due to the
temperature increase and reaches the maximum value. Reduction in dissociation rate in the range where \( t > 400 \) s is associated with the curvature of the granules. As the granule decays, and when the granules approach the center, the decay surface area decreases sharply. Therefore, the amount of methane released from the powder is sharply reduced. The distraction rate of methane hydrate substantially decreases with the growth of granules diameter. Hereby, it is necessary to take into account the granular composition in the modeling of dissociation.

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