

GAS HYDRATES

METASTABLE STATES OF GAS HYDRATES AT PRESSURES BELOW
THE 'ICE-HYDRATE-GAS' EQUILIBRIUM

V.P. Melnikov, A.N. Nesterov, L.S. Podenko, A.M. Reshetnikov, V.V. Shalamov

*Institute of Earth's Cryosphere, Siberian Branch of the Russian Academy of Sciences,
PO box 1230, Tyumen, 625000, Russia; nesterov@ikz.ru*

Reported are experimental results on the behavior of methane, propane, and carbon dioxide hydrates at temperatures below 273 K and pressures below the 'ice-hydrate-gas' equilibrium, when ice is the stable phase. The study has furnished evidence for the formation of intermediate supercooled (metastable) water during gas hydrate dissociation. The pressures of hydrate dissociation into supercooled water and gas were measured at the temperature ranges 253–273 K for methane hydrate, 263–273 K for propane hydrate, and 249–273 K for carbon dioxide hydrate. The gas hydrates have been recognized to keep metastable for a long time within the P - T area in the phase diagram bounded by the 'ice-hydrate-gas' and 'supercooled water-hydrate-gas' metastable equilibrium lines. Contrary to what has been assumed for self-preservation of gas hydrate, their metastability has no relation with ice coating on hydrate particles.

Gas hydrates are crystalline compounds forming from water and low-molecular gases. In nature they exist as hydrates of natural gases and are widespread in submarine environments below depths 350–400 m or below 200–250 m in the permafrost zone [Istomin and Yakushev, 1992]. Within the latter, gas hydrates can exist also outside their present-day geological stability zone even at 150–200 m depths due to self-preservation in the pore space of frozen rocks. These are the so-called relic gas hydrates [Istomin and Yakushev, 1992] which store large amounts of natural gas and thus have good economic prospects [Yakushev et al., 2005].

Self-preservation of gas hydrates has been commonly attributed to ice coating that forms upon hydrate particles at the onset of their dissociation and precludes free gas release [Davidson et al., 1986; Istomin and Yakushev, 1992]. Ice formation on dissociation of hydrates has been proven experimentally but its very mechanism remains poorly understood.

One self-preservation mechanism, which was theoretically grounded in terms of equilibrium thermodynamics, implies that hydrates dissociated at temperatures below 273 K can go through intermediate metastable phases of supercooled water and cubic ice [Istomin et al., 2006]. However, there was no reliable experimental evidence for the existence of these metastable phases before our studies.

Below we present main highlights of our study aimed at checking experimentally whether the metastable states of gas hydrates can exist during gas hydrate dissociation below the ice melting point.

The experiments were performed with methane, propane, and carbon dioxide hydrates. The gas hydrate dissociation was studied using visual microscopy technique combined with P - T measurements.

Details of the experimental setup and procedure used in this work are given elsewhere [Reshetnikov, 2010]. In brief, gas hydrates were formed in a high-pressure reactor placed inside a thermostatic cooler in order to maintain the required temperature. Optical observation was carried out through viewing windows on the reactor's lateral surface using a cathetometer with its telescope ocular fitted with a digital camera. The digital image was displayed on a monitor in real-time mode and saved on DVD.

The samples of gas hydrates were prepared in the following way. Distilled water (1.0–1.5 g) was sprayed over a Plexiglass plate set vertically inside the reactor between the viewing windows. Before that, both the reactor and the plate were cooled down to 253–258 K to let ice form on the plate surface as a spherical segment with the 0.15–2.5 mm base diameter and a height of 0.3 mm. After vacuuming and charging with the hydrate-forming gases, the reactor was heated slowly to above the ice melting point. The formation of hydrates was inferred from visual absence of liquid in the samples on the plate.

For gas hydrate dissociation, first the chosen temperature was set up in the reactor and then pressure was decreased slowly. In the course of dissociation, the gas hydrate samples changed their surface patterns as insular liquid appeared with gas releasing from it. The pressure at which the first change became visible was assigned the dissociation pressure P_d .

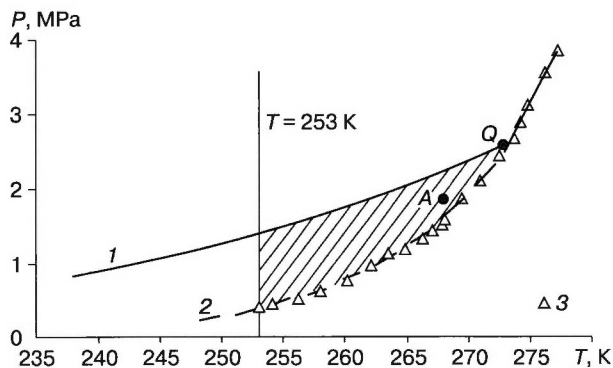


Fig. 1. State diagram of the 'water-methane' system (with excess gas), a fragment:

1 – equilibrium line 'ice (water at $T > 273$ K)–gas hydrate–gas' [Istomin and Yakushev, 1992]; 2 – predicted metastable extension of the 'water–gas hydrate–gas' equilibrium line at $T < 273$ K [Istomin et al., 2006]; 3 – gas hydrate dissociation pressure P_d , our data; $T = 253$ K is the temperature limit at which supercooled water formation on methane hydrate dissociation was observed; Q is the quadrupole point corresponding to coexistence of ice + water + gas hydrate + gas; A is the point on the phase diagram corresponding to P – T conditions of the experiment with metastable methane hydrate (see text for explanation).

Table 1. Coefficients A and B in Equation (1)

Hydrate-forming gas	A	B, K	Temperature range, K
Methane	24.763	6509.1	253–273
Propane	54.607	15 402.0	263–273
Carbon dioxide	28.61	7774.7	249–273

Figure 1 shows P_d for methane hydrate. At temperatures above those at the quadrupole equilibrium point (T_Q), the P_d values coincide with the equilibrium dissociation pressure of bulk hydrates. At temperatures below T_Q and up to $T = 253$ K, the P_d values fall on the predicted extension of the 'water–hydrate–gas' equilibrium line into the area where supercooled water can exist. Similar results were obtained for propane and CO_2 hydrates, with the only difference that P_d were measured till 263 K for the former and 249 K for the latter.

Least-square processing of the data has yielded the following temperature dependence of the dissociation pressure (with the regression coefficient 0.998):

$$\ln(P_d/P_0) = A - B/T, \quad (1)$$

where $P_0 = 1$ MPa, T is the temperature in K, and A, B are the empirical coefficients (Table 1).

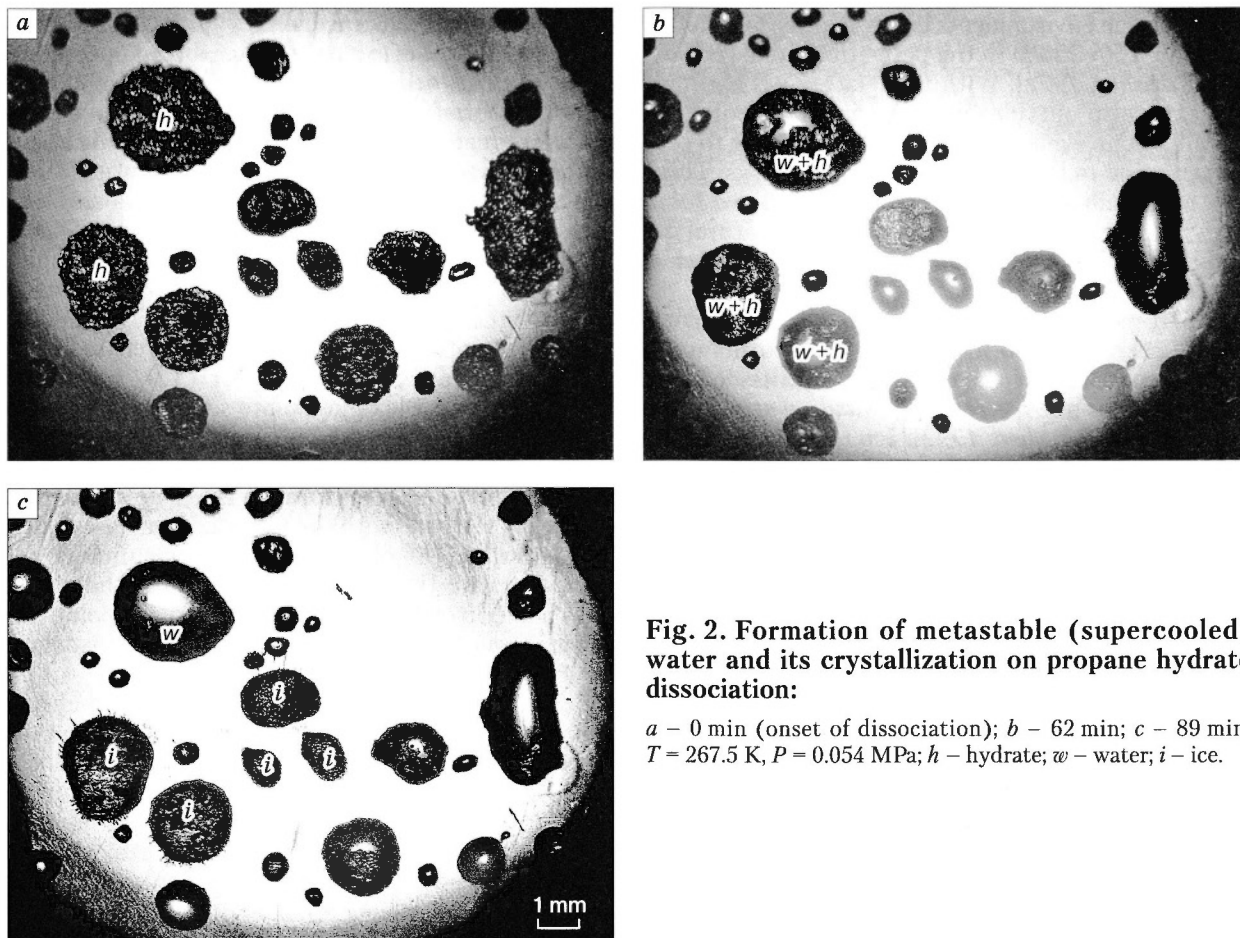


Fig. 2. Formation of metastable (supercooled) water and its crystallization on propane hydrate dissociation:

a – 0 min (onset of dissociation); b – 62 min; c – 89 min; $T = 267.5$ K, $P = 0.054$ MPa; h – hydrate; w – water; i – ice.

The dissociation enthalpy ΔH was calculated using the measured pressures P_d with the Clausius–Clapeyron equation: $\Delta H = 51.7$ kJ/mol for methane hydrate, $\Delta H = 129.4$ kJ/mol for propane hydrate, and $\Delta H = 58.4$ kJ/mol for carbon dioxide hydrate. The predicted enthalpy values agree well with the published ones for dissociation of the respective hydrates into water and gas.

Figure 2 shows an example of successive visible changes observed during dissociation of propane hydrate at 267.5 K. At this temperature, propane hydrate is known to dissociate into ice and gas at the equilibrium pressure 0.137 MPa [Sloan and Koh, 2008]. However, the first change in the samples was observed at a pressure as low as 0.054 MPa when propane hydrate dissociated into supercooled water and gas (Fig. 2, *a, b*). Some drops of supercooled water remained in the metastable state and did not crystallize even 1.5 hr after having appeared (Fig. 2, *c*).

The gas hydrate samples behaved in an unusual way within the P – T area bounded by the 'ice-hydrate-gas' equilibrium line and 'supercooled water-hydrate-gas' metastable equilibrium line (hatched area in the phase diagram of Fig. 1). When the methane hydrate samples showed no visible signature of dissociation for 14 days of continuous examination at 268 K and 1.9 MPa (point *A* in Fig. 1), we began to reduce pressure in the reactor while maintaining the same temperature. Water formed immediately following the intersection of 'supercooled water-hydrate-gas' metastable equilibrium line. The formation of supercooled water means that the hydrate samples were free from ice. Indeed, had there been ice in the samples, no supercooled water would have been observed: this water crystallizes rapidly as it can never coexist with ice. Therefore, the stability of the methane hydrate samples in the metastable state (point *A* in Fig. 1) has no relation with self-preservation through ice coating of hydrate particles. The long-term existence of metastable hydrates in the P – T area where ice is a stable phase and the appearance of supercooled (metastable) water as an intermediate phase is thermodynamically forbidden, is evidence that the dissociation of hydrates into ice and gas in the form of a direct solid-solid transition is kinetically impeded.

Similar behavior was observed also for other methane hydrate samples in the area bounded by the 'ice-hydrate-gas' equilibrium line and 'supercooled water-hydrate-gas' metastable equilibrium line and the 253 K isotherm, as well as for propane and CO₂ hydrates in the area bounded by the same lines and the 263 K and 249 K isotherms, respectively.

Thus, the laboratory tests have proven that the metastable states (gas hydrate, supercooled water) on dissociation of gas hydrates can really exist for a long time (on the experiment scale) at the temperature below 273 K. As inferred from the measured metastable equilibrium pressure for the systems 'water-methane hydrate', 'water-propane hydrate', and 'water-carbon dioxide hydrate', the gas hydrate stability within the P – T area bounded in the phase diagram by the 'ice-hydrate-gas' and 'supercooled water-hydrate-gas' lines has no relation with self-preservation but is rather due to kinetic impediment of dissociation into ice and gas.

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