

Dissociation and specific heats of methane hydrate under high pressure

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Gas hydrates are crystalline clathrate compounds composed of water and gases, and are stable at low temperatures and high pressure conditions. Clarification of their role in the terrestrial environment is expected because methane gas, which is the main component of gas hydrates in marine and lake sediments, is one of the greenhouse gases. Thermodynamic properties of gas hydrate determine their stability themselves. In this study, dissociation and specific heats of synthetic methane hydrate were measured under high pressure by using a heat-flow type calorimeter.

Tian-Calvet type heat-flow calorimeter (Setaram BT2.15) was located in a cold room (temperature: 255K). The sample cell was a small pressure chamber (volume: 3.7ml) and connected with a pressure gauge and a vacuum pump. Ice powder (1.5g) was put into the sample cell and pressurized by methane up to 5MPa. The calorimeter was then heated from 263K to 278K at the rate of 0.01K/min to form methane hydrate. The sample was cooled and heated again from 263K to 288K at the same rate of 0.01K/min. Dissociation heat (kJ/mol) was calculated by an integration of the peak of heat flow and the amount of dissociated gas, which was obtained from the weight of water and hydrate number by NMR.

Large negative peak of heat flow was detected in a temperature range 279-282K at a pressure of about 5MPa. Dissociation heat of methane hydrate was calculated as 18.25 (kJ/mol) and agreed well with the value obtained by Handa (1986). While Handa obtained the specific heat of methane hydrate in a temperature range between 85K and 270K, we obtained it in the range 264-277K which covered the bottom water temperatures in the Sea of Okhotsk and the Lake Baikal. 4-277K which covered the bottom water temperatures in the Sea of Okhotsk and the Lake Baikal.