Dissociation and specific heats of methane and ethane hydrates under submarine and sublacustrine environment

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Gas hydrates are stable at low temperatures and high-pressure conditions and exist in submarine and sublacustrine sediments. It was confirmed that natural gas hydrate discovered in Kukuy K-2 mud volcano of Lake Baikal contained high concentration of ethane. In this study, dissociation and specific heats of synthetic methane and ethane hydrates were measured under high pressure by using a heat-flow type calorimeter.

Heat-flow calorimeter (Setaram BT2.15) was located in a cold room (temperature: 255K). The sample cell was a small pressure chamber and connected with a pressure gauge and a vacuum pump. Ice powder (about 1.5g) was put into the sample cell and pressurized by methane and ethane up to 5MPa and 2MPa, respectively. The calorimeter was then heated from 263K to 278K at the rate of 0.01 K min⁻¹ to form gas hydrate. The sample was cooled and heated again from 263K to 288K at the same rate of 0.01 K min⁻¹. Dissociation heat (kJ mol⁻¹) was calculated by an integration of the peak of heat flow and the amount of dissociated gas.

Large negative peaks of heat flow were detected in a temperature range 279-282K at a pressure of about 5MPa for methane hydrate and 283-286K at 2MPa for ethane hydrate, respectively. Dissociation heats from methane and ethane hydrates to water and gases were calculated as $55.3 \text{ (kJ mol}^{-1})$ and $71.1 \text{(kJ mol}^{-1})$, respectively, which agreed well with Handa (1986). While Handa obtained the specific heat of methane hydrate in a temperature range between 85K and 270K for methane and between 85K and 260K for ethane, respectively, we obtained the specific heats in the range 264-277K for methane and 264-282K for ethane, those covered the bottom water temperatures in the Sea of Okhotsk and Lake Baikal.