

Calorimetric measurements of enthalpy of dissociation for methane hydrate containing ice

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Enormous amounts of natural gases stored in hydrate crystals in marine sediments and permafrost play an important role as a great reserve of carbon in the world. Gas hydrates release or absorb large latent heat in phase changes and affect their thermal condition themselves. To understand the formation, dissociation and maintenance processes of gas hydrates in nature, thermal properties of gas hydrates are required. For example, enthalpy of dissociation of gas hydrate has been interested and measured by researchers. Direct measurements using heat-flow calorimeter are suitable to obtain thermal properties of natural gas hydrate; enthalpy of dissociation and heat capacity.

Although thermodynamic properties of synthetic gas hydrates have been investigated, there are few reports for naturally occurring gas hydrates because they are rare and unavailable. These samples stored in liquid nitrogen usually contain a lot of free water (ice) and it makes difficult to get a thermograph of gas hydrates. In this work, an experimental device was designed to weigh the hydrate sample in the temperature of liquid nitrogen and to obtain enthalpy of dissociation of gas hydrate which contains a lot of ice using calorimetric method.

Heat-flow calorimeter (Setaram BT2.15) was used for thermodynamic measurements of gas hydrates under high-pressure and low-temperature conditions. About 1g of synthetic methane hydrate and ice mixture was ground up in liquid nitrogen and put into a small pressure cell. It was weighed and put into the calorimeter at about 100K. The sample was then heated from 100K to 300K at the rate of 0.15K per minute. Preliminary results showed that the signals of hydrate dissociation and ice melting were clearly distinguished each other. Assuming the hydrate number, the enthalpy of dissociation of methane hydrate was obtained by the thermograph and the weight of the hydrate calculated from those of whole sample and ice.