

Measurement of dissociation heat of N₂, O₂, and Ar hydrates

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Gas hydrates are crystalline clathrate compounds composed of gas and water molecules, and stable under low temperature and high pressure conditions. Dissociation heats (enthalpies) of gas hydrates have been obtained from their phase diagrams using the Clapeyron equation; however, the application has also been difficult due to low quality of the phase data. Dissociation heat of N₂ hydrate was reported by Kang *et al.* (2001), but the value is thought to be overestimated because it is larger than that of methane hydrate. Dissociation heat of O₂ and Ar hydrates have not reported yet. In this study, we applied calorimetric technique to determine their dissociation heat.

The samples of gas hydrates were synthesized from fine ice powder and guest gases at 273.2 K and the pressure condition of 20MPa (N₂) and 16MPa (O₂ and Ar). The ice powder started to melt and formed these gas hydrates. Approximately 1 g of each hydrate sample was set in a pressure cell specially designed for a Tian-Calvet type heat-flow calorimeter, and its dissociation monitored. The experimental setup and technique were the same as the one that was used previously by Hachikubo *et al.* (2009; 2012).

Dissociation heats of N₂, O₂, and Ar hydrates from hydrate to gas and ice are 12.8±0.2 [kJ mol⁻¹], 12.6±0.1[kJ mol⁻¹], and 13.2±0.1[kJ mol⁻¹], respectively. Yoon *et al.* (2003) reported that dissociation heats of N₂ and O₂ hydrates are 12.18 [kJ mol⁻¹] and 11.52 [kJ mol⁻¹], respectively, using the Clausius-Clapeyron equation. Therefore, our data are several percent smaller than the previous report.

References

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