

RESEARCH NOTES

Rigorous Approach to the Prediction of the Heat of Dissociation of Gas Hydrates

Ji-Ho Yoon,^{*,†} Yoshitaka Yamamoto,[†] Takeshi Komai,[‡] and Hironori Haneda[‡]

Institute for Energy Utilization and Institute for Geo-Resources and Environment, National Institute of Advanced Industrial Science and Technology, 16-1 Onogawa, Tsukuba, Ibaraki 305-8569, Japan

Taro Kawamura

Graduate School of Engineering, Hokkaido University, Kita-13 Nishi-8 Kita-ku, Sapporo 060-8628, Japan

This paper presents a theoretically correct method for predicting the heat of dissociation of gas hydrates using a fugacity-based model. Based on the Clausius–Clapeyron equation, the proposed approach takes into account the difference in compressibility by phase transition and the solubility of a guest component in the liquid phase. It is found that, for specific gas hydrates, the effect of two correction factors on the prediction of the heat of dissociation is not negligible. All corresponding properties including the hydrate number, compressibility, solubility of gas in water, water content in the vapor phase, and heat of dissociation are calculated and compared with experimental values in part.

Introduction

A variety of research papers related to gas hydrates have been published over the past 50 years. A study on natural gas hydrate has been carried out because it was recognized that the plugging of gas pipelines in natural gas transportation was primarily due to gas hydrate formation between water and gas composed of methane, ethane, propane, and other light hydrocarbons. A large amount of the dissociation equilibrium data for gas hydrates have been reported in the literature and are well summarized by Sloan¹ and Bercz and Balla-Achs.² To exploit methane gas from gas hydrates in deep-ocean sediments or the permafrost region, it is necessary to possess a lot of information on thermal properties as well as phase equilibria of gas hydrates. However, only a few experimental measurements for thermal properties of gas hydrates have been reported in the literature. Most of the past investigations on gas hydrates have been limited to the crystalline structure and phase equilibria such as pressure–temperature behavior as described previously.

For practical applications, one of the most important thermal properties of gas hydrates is the heat of dissociation (in other words, the enthalpy of dissociation). A thorough and correct investigation on the heat

of dissociation of clathrate hydrate has been carried out by Handa et al.³ and Handa.^{4–7} They used an automated Tian-Calvet heat-flow calorimeter to determine the composition, heat of dissociation, and heat capacity of gas hydrates over a wide range of temperatures. Measurements were made on not only laboratory-synthesized hydrates but also naturally occurring gas hydrates. A differential scanning calorimeter (DSC) can also be used to determine both the heat capacity and heat of dissociation of gas hydrates. Using a high-pressure, constant-volume cell in DSC, the thermal properties of gas hydrates have been determined successfully.⁸ Lievois⁹ and Lievois et al.¹⁰ measured the heat of dissociation of methane hydrate by using a high-pressure heat-flux calorimeter which was nearly the same as that used by previous researchers.^{3–7} An isothermal microcalorimeter has also been used for measuring the hydrate number and heat of dissociation of gas hydrates.¹¹

The objective of this work is to develop a method for accurately predicting the heat of dissociation of gas hydrates. In general, the Clausius–Clapeyron equation has been used for predicting the heat of dissociation of gas hydrates.^{1,2,12–14} This work differs from most other studies in that we take into account the difference in compressibility by phase transition and the solubility of a guest component in the liquid phase. It is found that the effect of these two correction factors on the prediction of the heat of dissociation is not negligible.

Theory

The heat of dissociation of gas hydrates has usually been determined from three-phase equilibria using the

* To whom correspondence should be addressed. Tel & Fax: +81-298-61-8701. E-mail: jh-yoon@aist.go.jp. Permanent address: Environmental Research Group, Korea Electric Power Research Institute, 103-16 Munji-dong, Yusung-ku, Taejeon 305-380, Korea.

[†] Institute for Energy Utilization.

[‡] Institute for Geo-Resources and Environment.

Clausius–Clapeyron equation as follows:

$$\frac{d \ln P}{d(1/T)} = - \frac{\Delta H_d}{zR} \quad (1)$$

where P is the equilibrium dissociation pressure at T , ΔH_d is the heat of dissociation of gas hydrates, z is the compressibility factor of gas at P and T , and R is the gas constant. The slope of hydrate dissociation pressures on the logarithmic scale against reciprocal temperature gives the calculated value of the heat of dissociation of gas hydrates. It is widely known that this method can provide promising results for the determination of the thermal properties of simple hydrate formers. However, it is also obvious that this equation does not well predict the heat of dissociation of gas hydrates such as carbon dioxide and hydrogen sulfide that are highly soluble in water. Furthermore, the change in volume between hydrate and ice (or water) phases by phase transition should not be neglected for hydrate systems in which phase transition occurs at relatively high pressure. Considering these two aspects, we provide a new expression for the heat of dissociation using the Clausius–Clapeyron equation as follows:

$$\frac{d \ln P}{d(1/T)} = - \frac{\Delta H_d + nx_g \Delta H_s}{z^* R} \quad (2)$$

where

$$z^* = \frac{1}{y_g} \left(1 - \frac{nx_g}{1 - x_g} \right) z^{\text{vap}} - n \frac{P \Delta v}{RT} \quad (3)$$

n is the hydrate number, ΔH_s is the heat of dissolution of a guest component in water, x_g is the mole fraction of a guest component in water, y_g is the mole fraction of a guest in the vapor phase, z^{vap} is the compressibility factor of the vapor phase, and Δv is the difference in volume per mole of water between hydrate and ice (or water). In this work, we do not take into account the compressibility of the solid phase. Thus, it is assumed that the value Δv is always constant and only depends on the type of hydrate structure. If we choose two points in a narrow region on a three-phase dissociation line, the heat of dissociation can be expressed by

$$\Delta H_d = \frac{\bar{z}^* R \ln(P_2/P_1)}{\frac{1}{T_1} - \frac{1}{T_2}} - \bar{n} \bar{x}_g \Delta \bar{H}_s \quad (4)$$

where

$$\bar{z}^* = \frac{1}{\bar{y}_g} \left(1 - \frac{\bar{n} \bar{x}_g}{1 - \bar{x}_g} \right) \bar{z}^{\text{vap}} - \bar{n} \frac{\bar{P} \Delta v}{RT} \quad (5)$$

and an overbar quantity is defined as the average value between T_1 and T_2 . The hydrate number, compressibility factor of the vapor phase, and all phase compositions are calculated by our model developed in a previous work.¹⁵ Without further modification, for the heat of dissolution of gas in water, we use the values obtained using the correlation equation¹⁶ and the Clausius–Clapeyron relation.¹⁷ The fugacity of all components in the vapor and liquid phases coexisting with hydrates is calculated by using the Soave–Redlich–Kwong equation of state¹⁸ incorporated with the modified Huron–

Table 1. Hydrate Number and Heat of Dissociation for Simple Hydrate Formers

guest	hydrate system ^a	T (K)	n	ΔH_d (kJ/mol)	ref
CH ₄	H = I + G	272.90	6.07	17.53	this work
		273.15	6.00	18.13	Handa ⁵
	H = L + G	273.15	6.07	53.81	this work
		273.15	6.00	54.19 ^c	Handa ⁵
		285	6.15 ^b	54.67	Rueff et al. ⁸
		278.15	5.97	57.65	Lievois et al. ¹⁰
C ₂ H ₆	H = I + G	273.10	7.77	24.83	this work
		273.15	7.67	25.70	Handa ⁵
	H = L + G	273.15	7.77	71.34	this work
		273.15	7.67	71.80 ^c	Handa ⁵
		273.13	17.0	26.97	this work
		273.15	17.0	27.00	Handa ⁵
C ₃ H ₈	H = I + G	273.13	17.0	26.97	this work
		273.15	17.0	27.00	Handa ⁵
	H = L + G	273.15	17.0	129.5	this work
		273.15	17.0	129.2 ^c	Handa ⁵
		272.12	6.23	20.60	this work
		273.15	6.21	57.66	this work
CO ₂	H = I + G	272.12	6.23	20.60	this work
		273.15	6.21	57.66	this work
	H = L + G	273.65	7.23	65.22	Kang et al. ¹¹
		272.89	6.10	26.33	this work
		273.15	6.10	63.10	this work
		273.06	7.69	23.92	this work
C ₂ H ₄	H = I + G	273.06	7.69	23.92	this work
		273.15	7.69	68.15	this work
	H = L + G	273.05	17.0	23.56	this work
		273.15	17.0	125.3	this work
		271.93	6.34	12.18	this work
		273.15	6.28	49.54	this work
C ₃ H ₆	H = I + G	271.93	6.34	12.18	this work
		273.15	6.28	49.54	this work
	H = L + G	273.65	5.94	65.81	Kang et al. ¹¹
		272.26	6.30	11.52	this work
		273.15	6.26	49.16	this work
		273.15	6.26	49.16	this work

^a The general formula for gas hydrates is usually written as $M \cdot nH_2O$. Here M is a guest molecule, and n is the hydrate number of gas hydrates. Thus, $H = I + G$ and $H = L + G$ mean $M \cdot nH_2O$ (hydrate) $\leftrightarrow nH_2O$ (ice) + M (gas) and $M \cdot nH_2O$ (hydrate) $\leftrightarrow nH_2O$ (liquid water) + M (gas), respectively. ^b Assumed value. ^c Calculated values using the heat of fusion of ice at 273.15 K.

Vidal second-order (MHV2) mixing rule.^{19,20} Thus, it is not necessary to use Henry's constant correlation to describe gas solubility in liquid water. The UNIFAC group contribution model is also used as the excess Gibbs energy for the MHV2 model. The fugacity of water in the hydrate phase can be expressed by the following equation:

$$\hat{f}_w^H = f_w^L \exp \left[\frac{\Delta \mu_w^0}{RT} - \int_{T_0}^T \frac{\Delta H_w^{\text{MT-I}} + \Delta h_w^{\text{fus}}}{RT^2} dT + \int_0^P \frac{\Delta v_w^{\text{MT-I}} + \Delta v_w^{\text{fus}}}{RT} dP - \sum_m \nu_m \ln(1 + \sum_j C_{mj} \hat{f}_j^N) \right] \quad (6)$$

A more detailed description on the thermodynamic model for calculating the phase equilibria of gas hydrates is given elsewhere.¹⁵

Results and Discussion

In Table 1, the predicted results by model calculation are well summarized and compared with the literature data measured calorimetrically. Only nine hydrate-forming gases have been considered in this work because the modified UNIFAC interaction parameters between solvent groups and gases are not sufficiently available in the literature. Upon calculation of the heat of dissociation for phase transition of hydrate to ice and gas, the lower quadruple point of each hydrate system

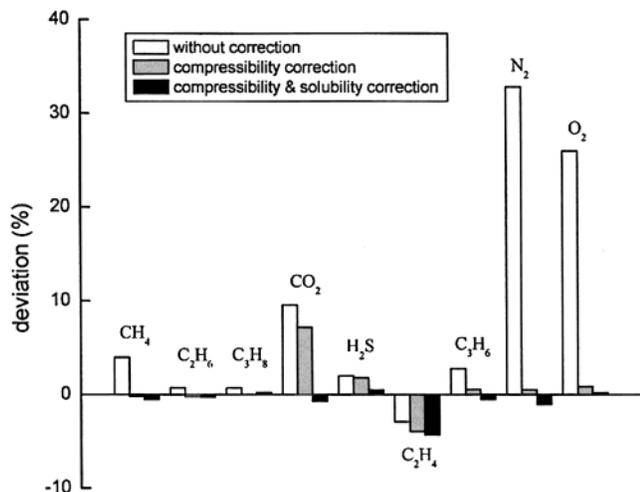


Figure 1. Deviation between calculated and experimental heats of fusion of ice at 273.15 K. Deviation (%) means $(\Delta H_f^{cal} - \Delta H_f^{exp})/\Delta H_f^{exp} \times 100$.

has been chosen as a reference standard state because it serves as a temperature limitation under which ice can coexist with hydrates. However, in the region of phase transition of hydrate to water and gas, the heat of dissociation and hydrate number of gas hydrates are calculated at the standard state 273.15 K. As shown in Table 1, for methane, ethane, and propane hydrates, the agreement between the predicted and experimental values for both the hydrate number and heat of dissociation is remarkably excellent. The predicted values in the table are calculated using eq 4 with both corrections of solubility and compressibility. In a comparison of the data by Handa,⁵ the absolute average percent deviations (% AAD) between the predicted and experimental values for the hydrate number and heat of dissociation are found to be within 1 and 1.5, respectively. We note that all experimental data measured by Handa⁵ are accurate within 1%. Unfortunately, for carbon dioxide and nitrogen hydrates, the agreement between the calculated and experimental values with an accuracy of 2%¹¹ is not satisfactory: % AAD values of 10 and 18 for the hydrate number and heat of dissociation, respectively.

Obviously, the difference in slope between the hydrate–ice–gas (H–I–G) and hydrate–liquid–gas (H–L–G) regions is due to the heat of fusion of ice to water.⁴ We assume that there is no change in the heat of dissociation of hydrate to ice and gas between the lower quadruple point and 273.15 K because the correction to the standard state for dissociation of gas hydrate to ice is quite small.⁵ Thus, the heat of fusion for the phase transition of ice to water at 273.15 K can be easily obtained from the difference in the heats of dissociation calculated using the H–I–G and H–L–G dissociation lines. The deviation between the calculated and literature values is depicted in Figure 1. Only compressibility correction indicates that the concentration of a guest component in the liquid phase, x_g in eqs 4 and 5, is assumed to be zero. Without any correction, the heat of dissociation of gas hydrates is calculated using the original Clausius–Clapeyron relation equation (1). As shown in Figure 1, the effect of compressibility correction on the calculation of the heat of fusion becomes sensitive and large, particularly for nitrogen and oxygen hydrate systems. This implies that all kinds of volume changes by phase transition should be taken into

account correctly to calculate the heat of dissociation at high-pressure conditions. For carbon dioxide and hydrogen sulfide hydrates, the effect of dissolution of gases in water by phase transition on the model calculation is not negligible as shown in Figure 1. It should be noted that the calculated results are strongly affected by both the heat of dissolution and the change in compressibility correction by high solubility of gas in water. For ethylene hydrate, we used the Kihara potential parameters for interaction between water and gas molecules determined in our previous work.¹⁵ Of particular interest is a sharp rise occurring at about 291 K in the slope of the H–L–G three-phase curve.²¹ The Kihara potential parameters determined previously cover over a wide range of temperature and pressure including the abrupt change region in the H–L–G slope. This may lead to an increase in the error of calculation in a specific region even though it has the smallest error value over the entire range. Thus, we have revised the Kihara potential parameters for ethylene hydrate by fitting the model to the experimental dissociation data ranging only from 269 to 290 K. Upon calculation with the newly determined Kihara potential parameters, $\sigma = 3.2710 \text{ \AA}$ and $\epsilon/k = 173.0 \text{ K}$, the hydrate number is 7.33 and the heats of dissociation for the phase transition of H–I–G and H–L–G are 23.21 and 66.90 kJ/mol, respectively. As a result, the absolute deviation for ethylene hydrate in Figure 1 becomes less than 1% and % AAD for all hydrate systems considered in this work becomes less than 0.5.

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Literature Cited

- (1) Sloan, E. D., Jr. *Clathrate Hydrates of Natural Gases*; Marcel Dekker: New York, 1998.
- (2) Berez, E.; Balla-Achs, M. *Gas Hydrates*; Elsevier: Amsterdam, The Netherlands, 1983.
- (3) Handa, Y. P.; Hawkins, R. E.; Murray, J. J. Calibration and Testing of a Tian-Calvet Heat-Flow Calorimeter Enthalpies of Fusion and Heat Capacities for Ice and Tetrahydrofuran Hydrate in the Range 85 to 270 K. *J. Chem. Thermodyn.* **1984**, *16*, 623.
- (4) Handa, Y. P. Calorimetric Determination of the Compositions, Enthalpies of Dissociation, and Heat Capacities in the Range 85 to 270 K for Clathrate Hydrates of Xenon and Krypton. *J. Chem. Thermodyn.* **1986**, *18*, 891.
- (5) Handa, Y. P. Compositions, Enthalpies of Dissociation, and Heat Capacities in the Range 85 to 270 K for Clathrate Hydrates of Methane, Ethane, and Propane, and Enthalpy of Dissociation of Isobutane Hydrate, as Determined by a Heat-Flow Calorimeter. *J. Chem. Thermodyn.* **1986**, *18*, 915.
- (6) Handa, Y. P. Calorimetric Studies of Laboratory Synthesized and Naturally Occurring Gas Hydrate. AIChE Annual Meeting, Miami, FL, Nov 1986.
- (7) Handa, Y. P. A Calorimetric Study of Naturally Occurring Gas Hydrates. *Ind. Eng. Chem. Res.* **1988**, *27*, 872.
- (8) Rueff, R. M.; Sloan, E. D.; Yesavage, V. F. Heat Capacity and Heat of Dissociation of Methane Hydrates. *AIChE J.* **1988**, *34*, 1468.
- (9) Lievois, J. S. Development of an Automated, High Pressure Heat Flux Calorimeter and its Application to Measure the Heat of Dissociation of Methane Hydrate. Ph.D. Thesis, Rice University, Houston, TX, 1987.
- (10) Lievois, J. S.; Perkins, R.; Martin, R. J.; Kobayashi, R. Development of an Automated, High Pressure Heat Flux Calorimeter and its Application to Measure the Heat of Dissociation and Hydrate Numbers of Methane Hydrate. *Fluid Phase Equilib.* **1990**, *59*, 73.

(11) Kang, S.-P.; Lee, H.; Ryu, B.-J. Enthalpies of Dissociation of Clathrate Hydrates of Carbon Dioxide, Nitrogen, (Carbon Dioxide + Nitrogen), and (Carbon Dioxide + Nitrogen + Tetrahydrofuran). *J. Chem. Thermodyn.* **2001**, *33*, 513.

(12) Sloan, E. D.; Fleyfel, F. Hydrate Dissociation Enthalpy and Guest Size. *Fluid Phase Equilib.* **1992**, *76*, 123.

(13) Skovborg, P.; Rasmussen, P. Comments on: Hydrate Dissociation Enthalpy and Guest Size. *Fluid Phase Equilib.* **1994**, *96*, 223.

(14) Sloan, E. D.; Fleyfel, F. Reply to Comments on: Hydrate Dissociation Enthalpy and Guest Size. *Fluid Phase Equilib.* **1994**, *96*, 233.

(15) Yoon, J.-H.; Chun, M.-K.; Lee, H. Generalized Model for Predicting Phase Behavior of Clathrate Hydrate. *AIChE J.* **2002**, *48*, 1317.

(16) Leites, I. L. Some Trends and a Prediction of the Solubility of Gases in Liquids and the Heat of Dissolution. *Sep. Purif. Technol.* **1997**, *12*, 201.

(17) Sander, R. Henry's Law Constants. In *NIST Chemistry WebBook, NIST Standard Reference Database Number 69*,

Linström, P. J., Mallard, W. G., Eds.; National Institute of Standards and Technology: Gaithersburg, MD, July 2001 (<http://webbook.nist.gov>).

(18) Soave, G. Equilibrium Constants from a Modified Redlich-Kwong Equation of State. *Chem. Eng. Sci.* **1972**, *27*, 1197.

(19) Dahl, S.; Michelsen, M. L. High-Pressure Vapor-Liquid Equilibrium with a UNIFAC-Based Equation of State. *AIChE J.* **1990**, *36*, 1829.

(20) Dahl, S.; Fredenslund, A.; Rasmussen, P. The MHV2 Model: A UNIFAC-Based Equation of State Model for Prediction of Gas Solubility and Vapor-Liquid Equilibria at Low and High Pressures. *Ind. Eng. Chem. Res.* **1991**, *30*, 1936.

(21) van Cleef, A.; Diepen, G. A. M. Ethylene Hydrate at High Pressures. *Recl. Trav. Chim.* **1962**, *81*, 425.

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