



Dissociation enthalpy of methane hydrate in salt solution



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ABSTRACT

The dissociation enthalpy of methane hydrate is an important thermal parameter for hydrate-related work. In this paper, the dissociation enthalpies of methane hydrate in various salt solutions are calculated using the previously measured H-L_W-V equilibrium data by the Clapeyron equation and the Clausius-Clapeyron equation, respectively. The calculated results by the Clapeyron equation do not show temperature dependence and the order of the dissociation enthalpy of methane hydrate in different salt solutions is 0.5NaCl > 0.5MgCl₂ > 0.5CaCl₂ > 1.0NaCl > 1.0CaCl₂ > 2.0NaCl > 1.0MgCl₂, the corresponding value of which is 52.6 ± 0.1 kJ/mol, 51.3 ± 0.3 kJ/mol, 50.4 ± 0.5 kJ/mol, 49.4 ± 0.3 kJ/mol, 46.0 ± 0.2 kJ/mol, 45.1 ± 0.2 kJ/mol and 44.0 ± 0.3 kJ/mol. Both the values and the errors calculated by the Clausius-Clapeyron equation are bigger than those by the Clapeyron equation. Moreover, the calculated values obtained by the Clausius-Clapeyron equation decrease with the temperature increase. Cations have less effect on the dissociation enthalpy than anions due to the different ability in affecting the ambient water networks. However, how the two effects (the colligative effect and the salting out effect) combine to influence the dissociation enthalpy of hydrate needs to be investigated further.

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1. Introduction

Naturally occurring gas hydrates envelop huge resource of natural gas, which mainly occur in marine sediments. Natural gas hydrates are considered as the ideal alternative energy in the future so that much work is focused on the exploration and development of gas hydrates in the world such as resource assessment, production technology, environment effect, etc. Moreover, gas hydrate-technologies, e.g. gas separation, gas storage and transportation, cold storage and carbon dioxide capture, have also been developed rapidly [1–7]. However, both hydrate resource and hydrate-technology research involve the hydrate phase transition process, so the important basic parameter of formation and decomposition enthalpy (heat) of gas hydrate has to be used. The formation enthalpy and dissociation enthalpy of gas hydrate are two different manifestations of phase change heat, i.e., the formation enthalpy is the heat released during hydrate formation; the dissociation enthalpy is the heat absorbed during hydrate

dissociation. In terms of quantity, the formation enthalpy and dissociation enthalpy are substantially the same. There are two methods to determine the dissociation enthalpy of gas hydrate, namely direct measurement and indirect measurement [1]. Direct measurement method includes calorimetric technique, differential thermal analysis (DTA), differential scanning calorimetry (DSC), etc. Due to the stochastic nature and large metastable state of hydrate nucleation, the heating dissociation method is usually used to measure the dissociation enthalpy of gas hydrate. For indirect measurement method, the dissociation enthalpy of gas hydrate is calculated employing the Clapeyron equation or the Clausius-Clapeyron equation. Handa [8], Rueff et al. [9] and Lievois et al. [10] earlier measured the dissociation enthalpies of methane hydrate, ethane hydrate and propane hydrate using the calorimetric technique. Afterward, the dissociation enthalpies of various hydrates (trimethylolethane trihydrate, cyclopentane hydrate, carbon dioxide hydrate, methane hydrate, ethane hydrate, propane hydrate, carbon dioxide-nitrogen hydrate, carbon dioxide-nitrogen-neohexane (2, 2-dimethylbutane, NH) hydrate, etc.) were successively determined using direct measurement method [11–19]. If the phase equilibria of gas hydrate have been measured, and then the dissociation enthalpy of gas hydrate can be calculated easily by the Clapeyron equation or the Clausius-Clapeyron equation. Van der

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Waals and Platteeuw [20] proposed that the Clapeyron equation could be applied to calculate the dissociation enthalpy of gas hydrate along the three-phase equilibrium line. Recently Anderson [21,22] calculated the dissociation enthalpies of carbon dioxide hydrate and methane hydrate using the Clapeyron equation. He found that the calculated values were in good agreement with measured data and the results did not show any temperature dependence. This conclusion is also proved by Gupta et al. [16]. However; the Clapeyron equation requires much detailed information, e.g., the solubility of gas in solution. The Clausius-Clapeyron equation is the simplified Clapeyron equation that assumes the molar volumes of the hydrate and water are equal and the volume change can be approximated by the molar volume of gas [23–30]. The calculated values by the Clausius-Clapeyron equation are in relatively good agreement with the measured data under low pressure condition, but the error is large under high pressure condition.

Natural gas hydrates generally exist below the sulfate reduction zone where Cl^- is much more predominant than other anions such as PO_4^{3-} and CO_3^{2-} [31]. However, the dissociation enthalpy of methane hydrate in similar salt solution has not been reported. We have investigated the three phase equilibrium (hydrate-water rich liquid-vapor, H-L_W-V) of methane hydrate in various concentrations of NaCl, MgCl₂ and CaCl₂ solution by the isochoric multi-step heating dissociation method [32]. In this paper, an analysis on the accuracy of two calculation methods is conducted and then the equilibrium data in these solutions are employed to calculate the dissociation enthalpies of methane hydrate using the Clapeyron equation and the Clausius-Clapeyron equation, respectively, and. This work will provide important basic thermal data for gas hydrate-related studies.

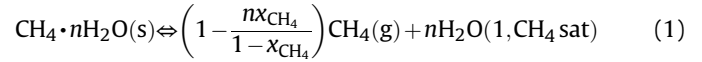
2. Experiment

In experiments, the isochoric multi-step heating dissociation method was used to investigate the H-L_W-V equilibrium of methane hydrate in various salt solutions. The experimental equipment and procedure were described in greater detail in the literature [32–34]. Experimental materials include NaCl, MgCl₂, CaCl₂, deionized water and methane gas, as shown in Table 1.

3. Calculation methods

3.1. The Clapeyron equation

In the H-L_W-V equilibrium state, free methane gas is released from methane hydrate and the salt solution is saturated with methane gas. Suppose that the mole fraction of CH₄ in the solution in equilibrium with methane hydrate is x_{CH_4} . When 1 mol of methane hydrate is dissociated, n moles of water are produced, which contain $\frac{n x_{\text{CH}_4}}{1 - x_{\text{CH}_4}}$ moles of dissolved methane gas. At H-L_W-V equilibrium, the process can be expressed as equation (1) [35]. The term $\text{H}_2\text{O}(1, \text{CH}_4 \text{ sat})$ refers to a mole of liquid water that is saturated with respect to CH₄. n is hydration number.



The dissociation enthalpy ΔH of methane hydrate in salt solution consists of two parts that can be expressed as equation (2). One is the enthalpy change ΔH_1 of hydrate into free gas and saturated solution, and the other is the enthalpy change ΔH_2 of gas dissolving in solution.

$$\Delta H = \Delta H_1 + \Delta H_2 \quad (2)$$

The term ΔH_1 can be calculated using the Clapeyron equation (3) [21,22]. T and p represent the temperature and pressure at H-L_W-V equilibrium. The (p, T) data are fitted to an analytical function, which is then differentiated to find (dp/dT) . ΔV is the volume change caused by methane hydrate dissociation, which can be calculated employing equation (4) [22]. The term V_{CH_4} refers to the molar volume of pure CH₄ gas that can be found at each (p, T) in the NIST WebBook [36]. V_{liq} is the volume of the liquid containing 1 mol of solution and the corresponding dissolved methane gas. V_{hyd} is the volume of hydrate containing 1 mol of methane gas. $V_{\text{H}_2\text{O}, \text{CH}_4}$ is the partial molar volume of solution, which is taken to be the molar volume of solution at (T, p) and can be found in the NIST Webbook [36]. $V_{\text{CH}_4, \text{H}_2\text{O}}$ is the partial volume of methane, which is taken as constant and equal to the infinite dilution value since the solubility of methane in solution is so low.

$$\Delta H_1 = T \Delta V (dp/dT) \quad (3)$$

$$\begin{aligned} \Delta V &= \left(1 - \frac{n x_{\text{CH}_4}}{1 - x_{\text{CH}_4}}\right) V_{\text{CH}_4} + n V_{\text{liq}} - V_{\text{hyd}} \\ &= \left(1 - \frac{n x_{\text{CH}_4}}{1 - x_{\text{CH}_4}}\right) V_{\text{CH}_4} \\ &\quad + n \left(V_{\text{H}_2\text{O}, \text{CH}_4}(T, p) + \frac{x_{\text{CH}_4}}{1 - x_{\text{CH}_4}} V_{\text{CH}_4, \text{H}_2\text{O}}(T, p) \right) \\ &\quad - \left(2.2369 \cdot 10^{-5} \right) \cdot \left(1 - 1.098 \cdot 10^{-4} \cdot p \right) \\ &\quad \cdot \left(1 + 1.78 \cdot 10^{-4} (T - 271.15) \right) \cdot n \end{aligned} \quad (4)$$

The dissolved methane gas in solution is taken into account during the calculation by the Clapeyron equation, i.e. the enthalpy change ΔH_2 of methane gas dissolving in solution is calculated, which can be calculated using equation (5) [22]. The term $\Delta H_{\text{CH}_4, \text{H}_2\text{O}}^\infty$ is the partial molar enthalpy of solution per mole of methane in the infinite dilution.

$$\Delta H_2 = -\frac{n x_{\text{CH}_4}}{1 - x_{\text{CH}_4}} \Delta H_{\text{CH}_4, \text{H}_2\text{O}}^\infty \quad (5)$$

3.2. The Clausius-Clapeyron equation

The Clausius-Clapeyron equation is the simplified Clapeyron

Table 1
Experimental materials.

Material	Component	Purity	Supplier
CH ₄	CH ₄	0.9999 (molar fraction)	Qingdao Ruifeng Gas Co., Ltd
NaCl	NaCl	0.995 (mass fraction)	Sinopharm Chemical Reagent Co., Ltd
MgCl ₂	MgCl ₂ · 6H ₂ O	0.995 (mass fraction)	
CaCl ₂	CaCl ₂	0.990 (mass fraction)	
Deionized water			Laboratory-made

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