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Abstract:

The swapping of methane with carbon dioxide in hydrate has been proposed as a potential strategy for geologic sequestration of carbon dioxide and production of methane from natural hydrate deposits. However, this strategy requires a better understanding of the thermodynamic characteristics of CH_4 and CO_2 hydrate as well as (CH_4+CO_2) or $(CH_4+CO_2+N_2)$ mixed hydrates

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(since (CO_2+N_2) gas mixture is often used as the swapping gas), along with the thermal physics property changes during gas exchange. In this study, a high pressure micro-differential scanning calorimetry (HP μ-DSC) was performed on synthesized gas hydrates to investigate the dissociation behavior of various hydrates. The hydrate dissociation enthalpies were determined by both μ-DSC measurement and Clapeyron equation. For the single guest molecule hydrate system, the average dissociation enthalpies of CH_4 hydrate and CO_2 hydrate measured by integrating the endothermic peak area are 55.04 kJ·mol^{-1} and 58.95 kJ·mol^{-1}, respectively, which are very close to the values calculated by Clapeyron equation. However, in the multicomponent guest hydrates system, the μ-DSC measured dissociation enthalpies of the (CH_4+CO_2) binary hydrates and ($CH_4+CO_2+N_2$) ternary hydrates are a little higher than that of Clapeyron equation, it was found that their dissociation enthalpies locate between the limiting values of pure CH_4 hydrate and CO_2 hydrate, increasing with the mole fraction of CO_2 in hydrate phase. By monitoring the heat flow changes with the μ-DSC apparatus, it showed that there was no noticeable dissociation or formation process of hydrate occurring in the CH_4-CO_2/(CO_2+N_2) swapping, which indicates that most CH_4 hydrate forms (CH_4+CO_2) or ($CH_4+CO_2+N_2$) mixed hydrates directly instead of dissociating into liquid water or ice first. The dissociation equilibrium data obtained from the endothermic thermograms of the mixed hydrates after CO_2 and (CO_2+N_2) swapping demonstrates that about 66% and 85% of CH_4 in hydrate phase are replaced, respectively.

1. Introduction

Gas hydrates are ice-like crystalline compounds composed of cages formed by hydrogen-bonded water molecules which encapsulate small guest molecules, such as light hydrocarbons and carbon dioxide, under high pressure and low temperature conditions [1]. Depending on the size and

shape of guest molecules, there are three different structures of clathrate hydrates: structure I (sI),

structure II (sII) and structure H (sH). Gas hydrates are non-stoichiometric compounds and on a

mole basis, methane hydrate consists of 85.69($\pm$ 0.14)% water and 14.31($\pm$ 0.14)% methane [2].

This results in the physical and thermal properties of hydrates are similar to that of ice with some

exceptions. For instance, William et al. [3] found that methane hydrate is over twenty times stronger

than ice at the same conditions of temperature and strain rate, and John et al. [4] believed that the

thermal conductivity of hydrate is about four times lower than that of ice.

Large quantities of natural gas hydrates, which are primarily composed of CH_4, are found in

permafrost regions and deep ocean sediments, and they are regarded as a promising energy resource

in the future [5-10]. Recent years, the CH_4-CO_2 swapping in naturally occurring gas hydrates has

been suggested as an attractive method of both CH_4 recovery and CO_2 sequestration [11-18]. The

swapping of CH_4 with CO_2 from its hydrate phase is a thermodynamically spontaneous reaction [19]

and does not accompany the potential geo-mechanical hazards that might occur during hydrate

exploitation process [20]. Using swapping technology for the purpose of methane gas recovery and

CO_2 geologic storage requires a better understanding of the thermodynamic properties of CH_4 and

CO_2 hydrates. The dissociation enthalpy of (CH_4+CO_2) binary hydrate is a key parameter in

predicting the process on a reservoir scale because considerable latent heat might be generated or

absorbed in swapping. Some dissociation equilibrium data for gas hydrates have been reported in

the literature and are well summarized by Sloan [1]. Kwon et al [21] investigated the thermal

dissociation behavior of (CH_4+CO_2) binary mixed hydrates in a rigid-walled high-pressure reaction

vessel. They analyzed the compositions changes in vapor phase and hydrate phase during

dissociation based on gas chromatography measurements, calculated the dissociation enthalpy of

(CH_4+CO_2) mixed hydrate by fitting Clausius-Clapeyron equation to the pressure-temperature trace

of a dissociation test. Since the classical thermodynamic methods of phase equilibrium require a

considerable time for accurate experimental results, some researchers explored other measurement techniques. In 1980s, Handa [22-24] measured the compositions, dissociation enthalpies and heat capacities of hydrates of methane, propane, ethane, isobutene and natural gas hydrates over a wide range of temperatures (85-270 K) using a Calvet calorimeter. Recent years, differential scanning calorimetry (DSC) is broadly used for the characterization of phase change as a rapid and sensitive technique. Some researchers [25-27] compared DSC results of hydrates with phase equilibrium data obtained using a more classical technique, such as measurements of pressure variation vs. temperature at constant volume (PVT), demonstrating the validity of this application. Gupta et al [28] measured methane hydrate dissociation heat from 5.5 to 19.3 MPa using a DSC apparatus. They formed methane hydrate sample ex-situ using granular ice particles and transferred it into the DSC cell under liquid nitrogen, subsequently the sample was dissociated by raising the temperature above the hydrate equilibrium temperature at a constant pressure. They believed that the measured dissociation enthalpy of CH_4 hydrate is in agreement with the Clapeyron equation predictions at high pressures, while the Clausius-Clapeyron equation predictions have a high relative error. Lee et al [29] used a high pressure micro-differential scanning calorimeter (HP μ-DSC) to investigate the CH_4-CO_2 swapping process. Their hydrate dissociation equilibrium data obtained from the endothermic thermograms of the replaced gas hydrates indicate that at least 60% of CH_4 is recoverable after reaction with CO_2.

In this work, the changes of heat flow in various hydrates dissociation process were investigated using a high pressure micro-differential scanning calorimeter apparatus. Our study mainly focus on three points: 1, measure the dissociation enthalpies of various gas hydrates accurately, calculate them directly from the endothermic peak area integration and indirectly using the Clapeyron equation, since there is a significant difference among the published data about that, for instance, the dissociation enthalpy of CO_2 hydrate which Kamath [30] measured and reported is 80 kJ·mol^{-1},

while Qazi [31] believed that it is 53.29 kJ·mol^{-1}; 2, investigate if the CH$_4$ hydrate dissociates while the swapping reaction is proceeding, and reveal the influence of an additional guest on the thermal behavior of the CH$_4$ hydrate, because it is controversial according to the existing literature reports, some researchers believe the CH$_4$ hydrate would dissociate while others insist the hydrate structure would not be destroyed; 3, estimate the extent of CO$_2$ and (CO$_2$+N$_2$) swapping and exploring if all the CH$_4$ molecules can be recovered by swapping technology.

2. Experimental Section

2.1. Materials

Analytical grade methane (99.99%), carbon dioxide (99.99%), and nitrogen (99.99%) were obtained from AGA Gas Company. The gas mixtures were prepared by us and analyzed using a Agilent gas chromatograph (7890 A), the molar composition of each gas mixture is listed in Table 1. Gas mixture M$_1$ and M$_2$ are used to form binary and ternary hydrates and investigate their dissociation behavior, M$_3$ is used for swapping gas. Deionized water was used in the experiment.

Table 1. The molar compositions (mol%) of gas mixtures M$_1$-M$_3$ used in this work.

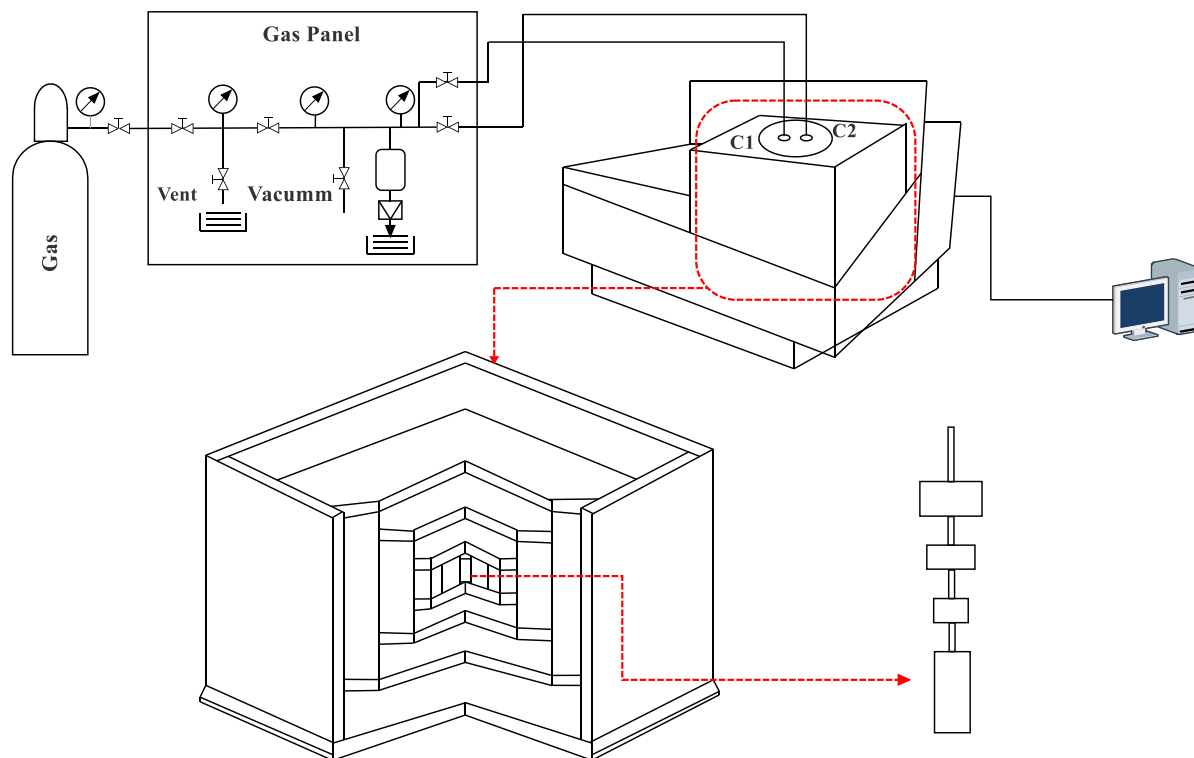| Component	M$_1$	M$_2$	M$_3$
CH$_4$	49.74	28.11	
CO$_2$	50.26	49.86	19.88
N$_2$		22.03	80.12

2.2. Experimental Apparatus

Figure 1. Schematic diagram of μ-DSC apparatus: C1, reference cell; C2, sample cell.

A high pressure micro-differential scanning calorimeter (HP μ-DSC VII Evo, Setaram Inc., France) was used to measure the dissociation temperature and enthalpies of gas hydrates. The μ-DSC apparatus can be operated in pressure range of 0.1 MPa to 40.0 MPa and at temperatures from 228.15 K to 393.15 K, it has a resolution of 0.02 μW. The schematic diagram of μ-DSC apparatus is shown in Figure 1. The sample cell is made of Hastelloy C276 material to eliminate corrosion or contamination, with an internal diameter of 6.4 mm and a useful height equivalent to 19.5 mm for the sample. The sample cell is connected to the gas panel where the pressure can be preset to the desired value and measured using a pressure transducer with an accuracy of ±0.25% (range: 0 to 20.0 MPa). Both the reference cell and sample cell are completely surrounded by a calorimetric furnace that can be heated or cooled from 0.001 to 1.2 K·min⁻¹ using Peltier cooling/heating. The μ-DSC setup was calibrated before performing experiments, and its accuracy can be checked against

reference standard of the calibration substances, i.e, water, naphthalene and *n*-decane. Table 2 shows the comparison between the NIST data and the results of temperature and enthalpy calibration values, the maximum deviation in the transition temperature and the latent heat from the NIST data was 0.18 K and 0.15 J·g^{-1}, respectively.

Table 2 The temperature and enthalpy calibration of μ-DSC apparatus.

Material	NIST transition temperature (K)	NIST enthalphy (J·g^{-1})	DSC transition temperature (K)	DSC enthalphy (J·g^{-1})
Water	273.15	333.33	273.15	333.31
Naphthalene	353.38	147.6	353.41	147.45
N-Decane	244.15		244.33	

*NIST stands for National Institute of Standards and Technology.

2.3. Experimental Procedures

In the μ-DSC experiment, hydrate nucleation and growth in static system of pure water is restricted due to mass transfer limitations and requires a high sub-cooling degree, which would lead to ice formation. In order to reduce the mass transfer resistance and achieve a high conversion of water to hydrate, the pure water was injected into three capillary tubes (2.3 mm diameter and 0.8 cm length) with a micro-syringe. These tubes loaded water were then placed inside the sample cell, while the reference cell was empty for the heat flow measurements. Then, the μ-DSC cells and all tubes were flushed with the test gas at least three times to remove any residual air. After that, methane was injected in the sample and reference cell through the gas panel until the desired experimental pressure was reached and temperature program was started. The experiments were performed under a constant temperature ramping program as shown in Figure 2, that is, the temperature decreased from 293.15 K to 243.15 K at the rate of 0.5 K·min^{-1}, after keeping constant for a certain time at 243.15 K, it increased from 243.15 K to 293.15 K at the rate of 0.25 K·min^{-1}. A

typical thermogram of CH_4 hydrate during an experiment is shown in Figure 3. The hydrate or ice formation is identified by the exothermic peaks during the cooling cycle of a ramping experiment. More than one exothermic peak was observed due to hydrate or ice formation in the three capillaries, since the test capillary tubes are separated, a nucleation in one of the tubes will not affect the remaining. Subsequently during heating, two endothermic peaks are observed, the first one at 273.15 K indicates ice melting and the second at 286.15 K represents hydrate dissociation. The amount of heat required to dissociate the hydrate sample can be calculated by integrating the endothermic peak area. In the investigation of CH_4-CO_2/(CO_2+N_2) swapping experiment, CH_4 hydrate sample preparation procedure and temperature decreasing process is the same as above, after that the experimental temperature increased to a specified value which keep the hydrate and ice in the sample cannot melt and dissociate (at 263.15 K in this study), then the outlet valve was opened and free CH_4 gas was released until the pressure reached the equilibrium pressure of CH_4 hydrate at the experimental temperature (1.844 MPa at 263.15 K). Subsequently the CO_2 or (CO_2+N_2) was injected into the reactor continually, the free gaseous CH_4 in the tubes and cells was therefore brought out by CO_2 or (CO_2+N_2), it should be noted that the pressure in the reactor was maintained at the equilibrium pressure of methane hydrate to make sure that methane hydrate did not dissociate during the sweep process. When the composition of CH_4 in the reactor was lower than 2%, the outlet valve was closed and CO_2 or (CO_2+N_2) gas mixture was injected into the cells until the pressure attained a predefined value which is lower than the CO_2 or (CO_2+N_2) liquefaction pressures at experimental temperature. Thereafter, the swapping process was assumed to have started. Keeping the experimental temperature constant for a long time (at least 24 h) to make sure the swapping reaction proceed completely, increasing the temperature to 293.15 K at the rate of 0.25 K·min^{-1} to investigate the dissociation behavior of mixed hydrates after swapping.
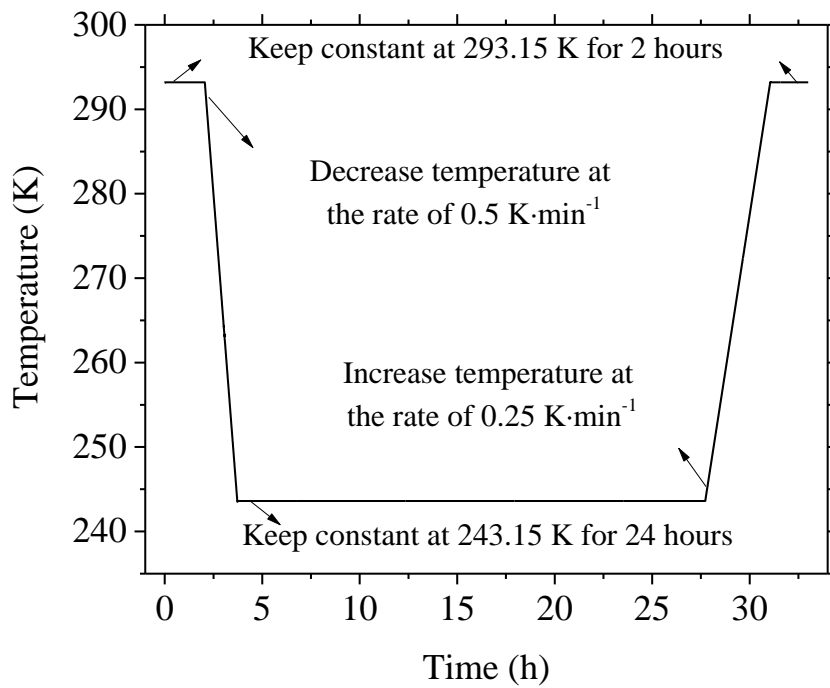
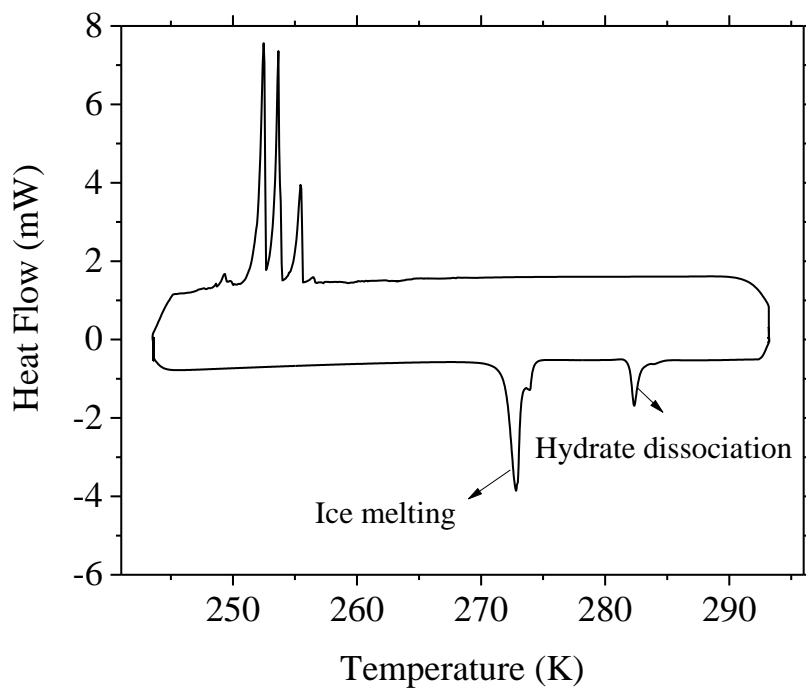**Figure 2.** Changes of temperature during the whole cooling-heating cycles.

Figure 3. Changes of heat flow during the whole cooling-heating cycles.

2.4. Data processing

In this work, we used two methods to calculate the dissociation enthalpies of hydrates, the first is integrating the endothermic peak area through μ-DSC measurement results, and the second is calculating them by Clapeyron equation. The following two equations represent the dissociation reaction of hydrates to gas and water or ice, respectively:

$$M \cdot nH_2O(s) \rightarrow M(g) + nH_2O(l) \tag{1}$$

$$M \cdot nH_2O(s) \rightarrow M(g) + nH_2O(s) \tag{2}$$
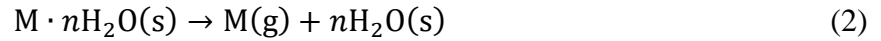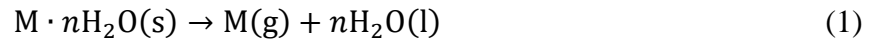
Where M is a hydrate forming gas (or hydrate-forming gas mixture), n is the hydration number. The difference in enthalpy between the two reactions is equal to the fusion enthalpy of ice, hence, we mainly focus on the dissociation enthalpy based on the reaction of hydrates to gas and liquid water in this work. The most sensitive parameter in calculating the enthalpy of hydrate dissociation is the mass of reaction water associated with the hydrate and the mass of free water or ice in the sample. The accurate amount of free water, m_i, can be calculated and confirmed from the endothermic peak area of ice melting using an ice melting enthalpy of 333.33 J·g^{-1}:

$$m_i = \frac{Q_i}{333.33} \tag{3}$$

Where Q_i is the amount of heat which ice melting released, and it can be calculated by integrating the endothermic peak area of ice melting. Then the enthalpy of hydrate dissociation per mole of producing gas, ΔH_d, can be calculated by:

$$\Delta H_d = \frac{Q_h}{m_t - m_i} \times M_W \times n \tag{4}$$

Where Q_h is the amount of heat absorbed in hydrate dissociation process, and also it can be calculated by integrating the endothermic peak area of hydrate dissociation correspondingly, m_t is

the total mass of water in the sample cell, M_W is the molar mass of water. Circone et al. [2] showed that the hydration number for methane hydrate does not change within the pressure and temperature conditions ranged from 1.9 to 9.7 MPa and 263 to 285 K, the average hydrate composition is found to be $CH_4\cdot 5.99(\pm 0.07)H_2O$, therefore, a hydration number of 6.0 is used here. As for the hydration number of the CO_2 hydrate and other mixed hydrates, it takes 6.0 in this work according to some researchers' reports [32-34].

Clapeyron equation is widely used to obtain enthalpy changes involved in the pure component phase transition process. It was suggested by van der Waals and Platteeuw [35] that Clapeyron equation could be applied to calculate the dissociation enthalpy of the clathrate hydrate along the three phase equilibrium line. The dissociation enthalpy can be calculated from the slope of the three phase line and the change in molar volume using the Clapeyron equation for hydrate to water and gas reaction by:

$$\frac{dP}{dT} = \frac{\Delta H_d}{T\Delta V} \tag{5}$$

Where, P and T are the absolute pressure and temperature, ΔV is the molar volume change due to the phase transition from hydrate to water and gas, can be calculated by:

$$\Delta V = V_G + nV_W - V_H \tag{6}$$

Where, V_G, V_W, V_H are the molar volume of gas, water and hydrate, respectively. The water and gas molar volume can be obtained using national institute of standard and technology (NIST) program, and V_H, $\frac{dP}{dT}$ can be calculated with Anderson's method [36,37]. Substituting Equation (6) into the Clapeyron equation, the expression for hydrate dissociation enthalpy is obtained,

$$\Delta H_d = T \times (V_G + nV_W - V_H) \times \frac{dP}{dT} \tag{7}$$

3. Results and disscusion

3.1. Onset temperature and enthalpies of hydrate dissociation by μ-DSC measurements

A series of μ-DSC measurements were conducted to investigate the dissociation behavior of various hydrates. Figure 4, 5, 6 and 7 showed the dissociation thermograms of CH_4 hydrate, CO_2 hydrate, M_1 binary hydrates and M_2 ternary hydrates at different experimental conditions. Since the endothermic peak from ice melting is detected at 273.15 K in each experimental run, it hasn't been present in these figures to make sure the peak caused by hydrate dissociation is more clearly. At a certain pressure condition, the onset temperature of endothermic peak which is marked in each dissociation thermogram, is taken as the hydrate initial dissociation temperature in three phase transition process. The heat flow decreases remarkably from the onset temperature point, and it consists of water-hydrate-gas three phase until the offset temperature point at which the heat flow return its baseline. As we can see from the figures, most dissociation thermograms of pure CH_4 or CO_2 hydrate are smooth and have a single peak detected in each experimental run, however, some of the dissociation thermograms of binary or ternary hydrates present a small peak which followed close behind the main peak, especially in ternary hydrates system at the higher pressure conditions. The reason might be there are more than one guest molecule in binary or ternary hydrates structure and the dissociation conditions of hydrate formed by each guest molecule are different, a kind of guest molecule escape from the hydrate clathrate would lead to the cage become unstable or destroyed and release the other guest molecules.

In Figure 8, the hydrate dissociation equilibrium data obtained from the μ-DSC measurements are compared with the calculated values by CSMGem model [1]. The CSMGem model results are actually the H-L-V three phase equilibrium boundaries in hydrate formation process, and they are basically the same as that of the dissociation process [38]. In this study, the CSMGem model results are used for dissociation equilibrium boundaries, since we can calculate the hydrate composition for binary and ternary hydrates with it. As we can see from Figure 8, the μ-DSC measurements have a good agreement with CSMGem model calculations. In addition, it also demonstrated and confirmed

that the μ-DSC can provide accurate H-L-V equilibrium data for the single or multi guest molecules hydrates system. By integrating the endothermic peaks and calculating according to equation (4), the dissociation enthalpies of hydrates are obtained and list in Table 3 and 4. The average dissociation enthalpy of CH_4 hydrate is 55.04 kJ·mol^{-1} in the range of temperature 275.54-286.35 K and pressure 3.163-10.143 MPa, while that of CO_2 hydrate is 58.95 kJ·mol^{-1} in the range of temperature 273.54-277.57 K and pressure 1.290-2.114 MPa, which is a litter higher than that of CH_4 hydrate. As we can see from the results, the dissociation enthalpies of hydrates did not show any temperature and pressure dependence in experimental condition. The dissociation enthalpies of M_1 binary and M_2 ternary hydrates are between that of the pure CH_4 hydrate and that of the pure CO_2 hydrate. In addition, it was observed that the dissociation enthalpy of M_1 binary hydrates increased with the mole fraction of CO_2 in hydrate phase, as shown in Figure 9, and this result is consistent with Kwon's [21] investigation and Lee's [29] study. It has the similar tendency as well in the M_2 ternary hydrates system, since the mole fraction of N_2 in hydrate phase is much lower and the dissociation enthalpy is mainly depending on the concentration of CO_2 and CH_4 in hydrate phase.
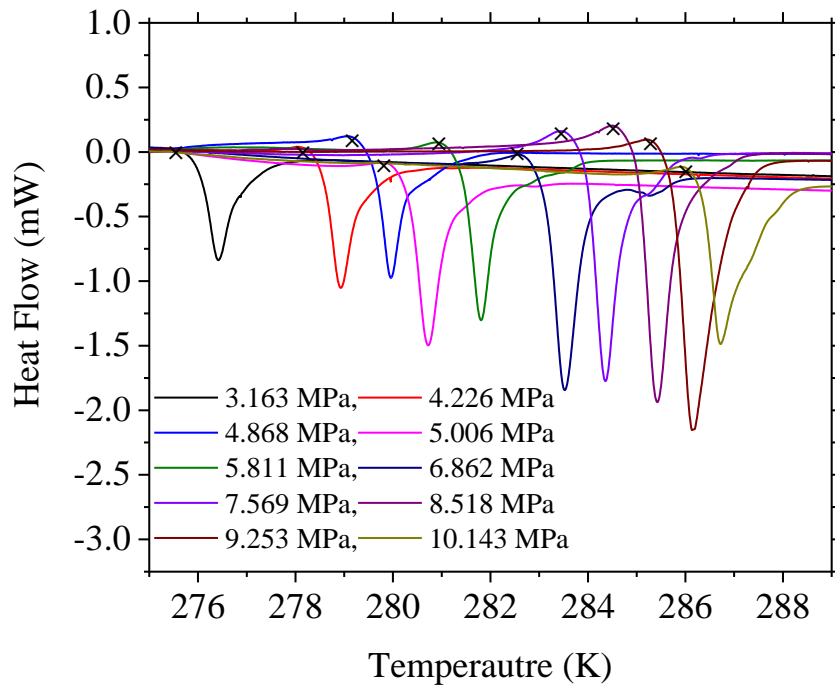
Figure 4. The dissociation thermograms of CH_4 hydrate at different pressure conditions.
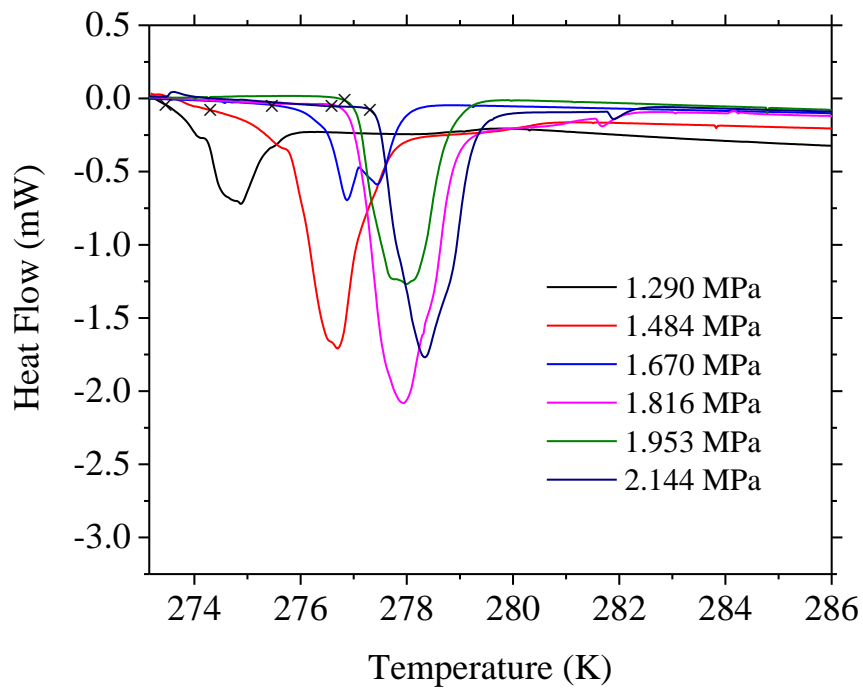
Figure 5. The dissociation thermograms of CO_2 hydrate at different pressures.
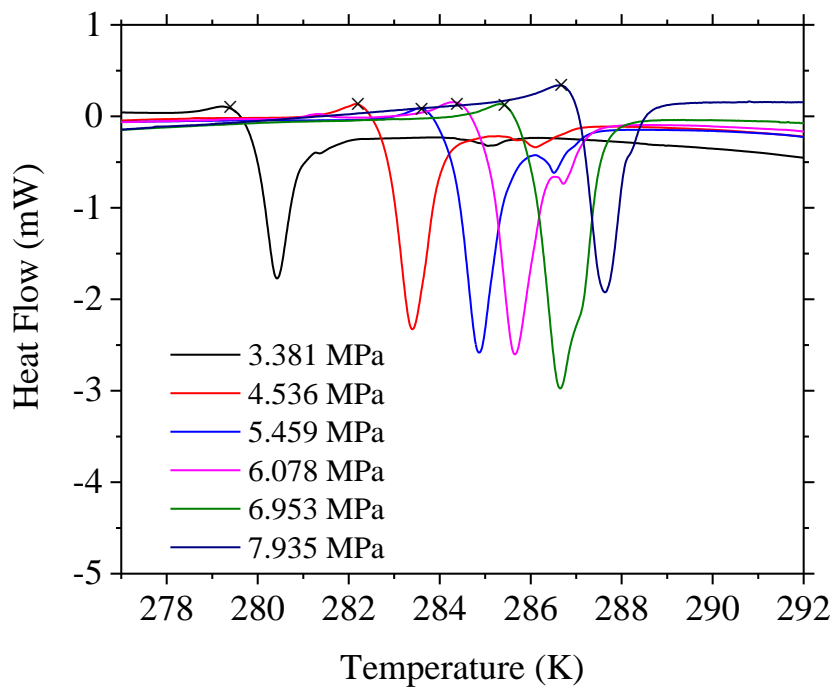
Figure 6. The dissociation thermograms of M_1 binary hydrate at different pressures.
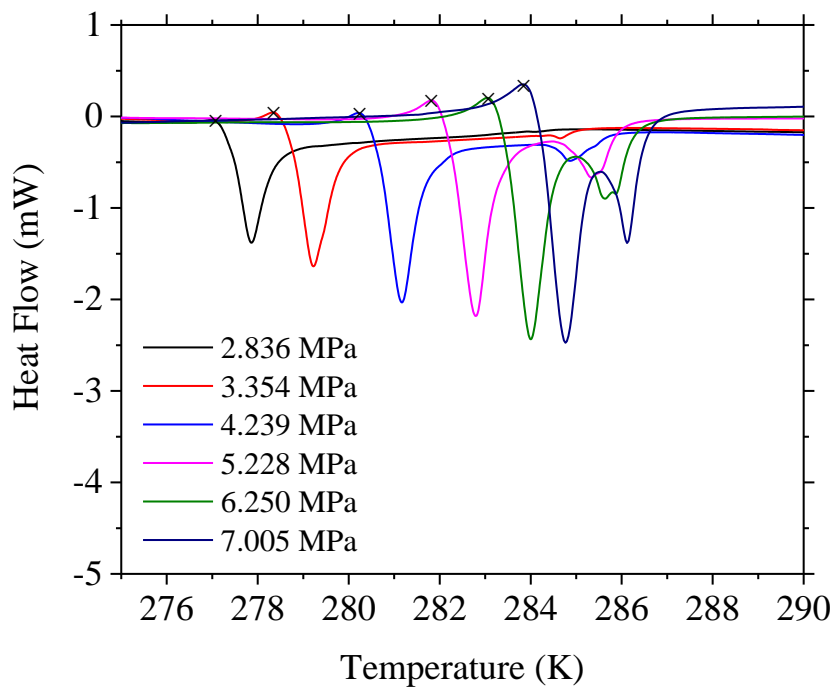
Figure 7. The dissociation thermograms of M_2 ternary hydrate at different pressures.
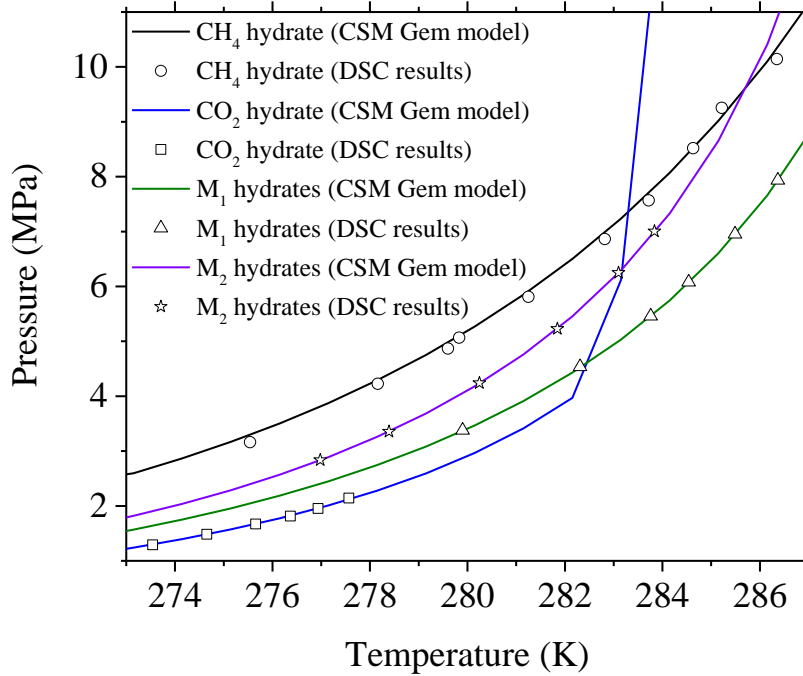
Figure 8. Comparison of hydrate dissociation equilibrium data from the μ-DSC measurements and CSMGem model calculation.

Table 3 The μ-DSC measurement results and dissociation enthalpies of pure CH_4 and CO_2 hydrate.

Run	T_{onset} (K)	P (MPa)	m_W (mg)	x_I (wt%)	x_H (wt%)	ΔH_d (kJ·mol^{-1})
			CH_4 hydrate			
1	275.54	3.163	2.8	89.36	10.64	55.09
2	278.16	4.226	2.1	82.60	17.40	54.98
3	279.60	4.868	2.8	85.93	14.07	55.10
4	279.83	5.066	2.0	74.76	25.24	54.99
5	281.25	5.811	2.7	81.61	18.39	55.02
6	282.82	6.862	3.7	77.88	22.12	55.02
7	283.72	7.569	3.0	72.70	27.30	54.99
8	284.63	8.518	2.9	75.39	24.61	54.92
9	285.22	9.253	2.9	61.66	38.34	54.97
10	286.35	10.143	2.7	77.97	22.03	55.01
			CO_2 hydrate			
11	273.54	1.290	2.1	60.57	39.43	58.96
12	274.65	1.484	2.7	77.22	22.78	59.01

13	275.66	1.670	2.3	87.57	12.43	58.76
14	276.37	1.816	3.4	59.12	40.88	58.97
15	276.94	1.953	2.0	34.50	65.50	58.95
16	277.57	2.144	2.1	66.57	33.43	59.08

* x_I, x_H are the mass fraction of ice and hydrate phase, respectively, similarly hereinafter.

Table 4 The μ-DSC measurement results and dissociation enthalpies of binary and ternary hydrates.

Run	T_{onset} (K)	P (MPa)	m_W (mg)	x_I (wt%)	x_H (wt%)	$C_{CH_4}^H$ (mol%)	$C_{CO_2}^H$ (mol%)	$C_{N_2}^H$ (mol%)	ΔH_d (kJ·mol^{-1})
				M_1 binary hydrates					
17	279.90	3.381	2.5	68.28	31.72	35.71	64.29	-	57.47
18	282.31	4.536	3.0	59.60	40.40	37.22	62.78	-	57.30
19	283.76	5.459	2.4	46.63	53.37	38.41	61.59	-	57.25
20	284.54	6.078	2.4	45.00	55.00	39.21	60.79	-	57.19
21	285.49	6.953	2.3	35.74	64.26	40.38	59.62	-	57.14
22	286.37	7.935	2.4	42.50	57.50	41.75	58.25	-	57.05
				M_2 ternary hydrates					
23	276.98	2.836	3.7	76.95	23.05	22.69	73.59	3.72	57.61
24	278.39	3.354	3.8	72.62	27.38	23.20	72.91	3.89	57.50
25	280.25	4.239	4.0	68.70	31.30	24.01	71.83	4.16	57.38
26	281.84	5.228	4.1	66.15	33.85	24.88	70.66	4.47	57.35
27	283.10	6.250	4.1	64.03	35.97	25.77	69.44	4.79	57.26
28	283.84	7.005	4.4	63.61	36.39	26.43	68.54	5.03	57.14

*$C_{CH_4}^H$,$C_{CO_2}^H$,$C_{N_2}^H$ are the mole fraction of CH$_4$, CO$_2$, N$_2$ in hydrate phase, respectively, which were calculated with CSMGem model, similarly hereinafter.
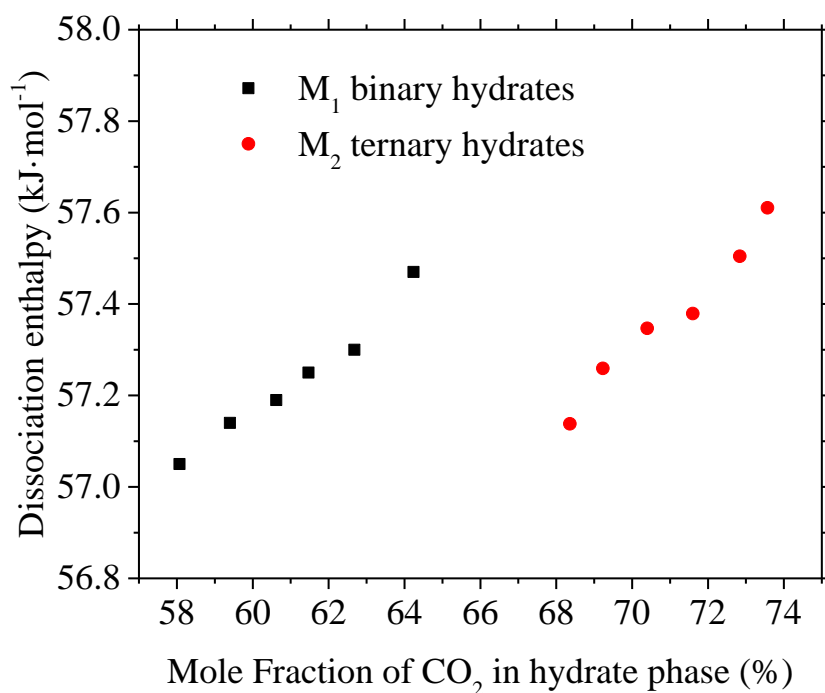
Figure 9. Dissociation enthalpies of the M_2 binary and M_3 ternary hydrates with respect to the CO_2 composition in hydrate phase.

3.2. Dissociation enthalpies of various hydrates calculated with Clapeyron equation.

Clapeyron equation relates the enthalpy change of a phase equilibrium reaction to the volumetric properties of the reactants and products along the phase boundary, van der Waals [39] pointed out that the validity of Clapeyron equation depends on the fact that the reaction in either of Equation (1) or (2) is univariant. According to Gibbs phase rule, the number of components and phases in the single guest molecule hydrate system are 2 and 3, it is univariant at the three-phase equilibrium conditions. Strictly speaking, it is not univariant for the dissociation process of the (CH_4+CO_2) binary and $(CH_4+CO_2+N_2)$ ternary hydrates. However, many researchers calculated the dissociation enthalpies of some binary and ternary hydrates using Clausius-Clapeyron equation [40-43], which is derived from Clapeyron equation, by treating the multicomponent guest molecules as a single. Besides, in their study, they simply assumed that the volume change in hydrate dissociation phase

transition process is equal to the gas volume, and supposed that the slope of the three-phase equilibrium curve is not changing with pressure and temperature. These assumptions lead to a large relative error in the predictions even for univariant system, and Gupta et al. [28] has investigated and validated it in their research. Hence, here we present the calculation of dissociation enthalpy for the single guest hydrate using Clapeyron equations, and tried to estimate the dissociation enthalpy of binary and ternary hydrates, they are list in Table 5 and 6, respectively. Table 5 showed the predictions of dissociation enthalpy depending on the phase equilibrium data obtained from μ-DSC measurements. In this study, the dissociation enthalpy was calculated according to Anderson's method [36,37]. The slope of the three-phase equilibrium curve at any temperature, $\frac{dP}{dT}$, was determined by first developing a polynomial equation, and then differentiating with temperature. The volume change from hydrate to gas and water, ΔV, was calculated using $\Delta V = V_G + nV_W - V_H$ instead of assuming $\Delta V = V_G$. This method takes into account the finite volumes of the condensed phases, the non-ideality of the vapor phase, and the solubility of carbon dioxide and methane in water. As shown in Table 5, the dissociation enthalpies of CH_4 hydrate and CO_2 hydrate at different temperature are very close to μ-DSC measurement results. It also demonstrated that the dissociation enthalpies calculation in μ-DSC measurements was accurate. As far as the dissociation enthalpies of binary or ternary hydrates system, we calculated them using Clapeyron equation and list in Table 6, most of the calculation results are close to μ-DSC measurements with some exceptions, for example, the endpoint data have a relative error might because of differentiating in the calculation process, we believe the most accurate way is to measure it calorimetrically.

Table 5 The dissociation enthalpy calculation of CH_4 and CO_2 hydrate with Clapeyron equation.

Run	T_{onset} (K)	P (MPa)	dP/dT (MPa·K^{-1})	V_G (m^3·mol^{-1})	V_W (m^3·mol^{-1})	V_H (m^3·mol^{-1})	ΔV (m^3·mol^{-1})	ΔH_d (kJ·mol^{-1})
				CH_4 hydrate				

Run	T_{onset} (K)	P (MPa)	dP/dT (MPa·K^{-1})	V_G (m^3·mol^{-1})	V_w (m^3·mol^{-1})	V_H (m^3·mol^{-1})	ΔV (m^3·mol^{-1})	ΔH_d (kJ·mol^{-1})
1	275.54	3.163	0.316	6.704E-04	1.797E-05	1.343E-04	6.393E-04	55.64
2	278.16	4.226	0.419	4.954E-04	1.796E-05	1.343E-04	4.646E-04	55.42
3	279.60	4.868	0.480	4.269E-04	1.796E-05	1.343E-04	3.966E-04	55.48
4	279.83	5.066	0.522	4.088E-04	1.796E-05	1.343E-04	3.787E-04	55.31
5	281.25	5.811	0.598	3.532E-04	1.795E-05	1.344E-04	3.235E-04	55.39
6	282.82	6.862	0.735	2.951E-04	1.795E-05	1.344E-04	2.652E-04	55.16
7	283.72	7.569	0.823	2.652E-04	1.794E-05	1.344E-04	2.356E-04	55.03
8	284.63	8.518	0.942	2.328E-04	1.794E-05	1.344E-04	2.034E-04	54.56
9	285.22	9.253	1.047	2.123E-04	1.793E-05	1.344E-04	1.832E-04	54.11
10	286.35	10.143	1.152	1.924E-04	1.793E-05	1.344E-04	1.629E-04	54.25
				CO_2 hydrate				
11	273.54	1.290	0.153	1.601E-03	1.833E-05	1.389E-04	1.414E-03	59.25
12	274.65	1.484	0.177	1.377E-03	1.833E-05	1.389E-04	1.212E-03	59.04
13	275.66	1.670	0.203	1.210E-03	1.835E-05	1.389E-04	1.053E-03	58.79
14	276.37	1.816	0.223	1.103E-03	1.838E-05	1.389E-04	9.478E-04	58.51
15	276.94	1.953	0.242	1.027E-03	1.838E-05	1.389E-04	8.808E-04	59.09
16	277.57	2.144	0.266	9.118E-04	1.838E-05	1.389E-04	7.862E-04	57.50

Table 6 The dissociation enthalpy calculation of binary and ternary hydrates with Clapeyron equation.

Run	T_{onset} (K)	P (MPa)	dP/dT (MPa·K^{-1})	V_G (m^3·mol^{-1})	V_w (m^3·mol^{-1})	V_H (m^3·mol^{-1})	ΔV (m^3·mol^{-1})	ΔH_d (kJ·mol^{-1})
				M_1 binary hydrates				
17	279.90	3.381	0.398	5.788E-04	1.835E-05	1.389E-04	4.885E-04	54.36
18	282.31	4.536	0.570	4.090E-04	2.265E-05	1.389E-04	3.487E-04	56.15
19	283.76	5.459	0.727	3.231E-04	2.265E-05	1.389E-04	2.749E-04	56.68
20	284.54	6.078	0.840	2.814E-04	2.265E-05	1.389E-04	2.390E-04	57.16
21	285.49	6.953	1.016	2.344E-04	2.265E-05	1.389E-04	1.986E-04	57.60
22	286.37	7.935	1.220	1.944E-04	2.265E-05	1.389E-04	1.642E-04	57.40
				M_2 ternary hydrates				
23	276.98	2.836	0.343	6.892E-04	1.820E-05	1.389E-04	6.178E-04	58.68
24	278.39	3.354	0.405	5.666E-04	1.820E-05	1.389E-04	5.026E-04	56.67
25	280.25	4.239	0.533	4.278E-04	1.820E-05	1.389E-04	3.722E-04	55.60
26	281.84	5.228	0.718	3.253E-04	1.820E-05	1.389E-04	2.759E-04	55.84
27	283.10	6.250	0.933	2.526E-04	1.820E-05	1.389E-04	2.076E-04	54.81
28	283.84	7.005	1.094	2.131E-04	1.861E-05	1.389E-04	1.730E-04	53.71

3.3. Comparison with the dissociation enthalpies in literature.

The dissociation enthalpies of various gas hydrates in literature are listed in Table 7. The hydrate dissociation enthalpies reflect the magnitude of stabilization due to the interactions between guest and host molecules. The guest molecules prevent interaction between opposite water molecules and thereby keep the lattice from collapsing, the empty hydrate lattices are thermodynamically unstable. In this work, by using of μ-DSC method and Clapeyron equation calculation, the average values of CH_4 hydrate dissociation enthalpies in the range of temperature 275.54-286.35 K and pressure 3.163-10.173 MPa are 55.04 and 55.12 kJ·mol^{-1}, respectively, they are very close to the previous research results. However, the average value of CO_2 hydrate dissociation enthalpies in the range of temperature 273.54-277.57 K and pressure 1.290-2.144 MPa, whether the value obtained from μ-DSC measurements or calculated by Clapeyron equation, are a little higher than Kang's investigation [46], our results are more consistent with Lee's work [29] and Yoon's study [45]. For (CH_4+CO_2) binary hydrates system, the dissociation enthalpy is 57.23 kJ·mol^{-1} which is a little lower than the results investigated by Kwon [21] who performed their experiment using a PVT method and calculated the dissociation enthalpies from Clausius-Clapeyron equation. As for as the dissociation enthalpy of $(CH_4+CO_2+N_2)$ ternary hydrates, there is no relevant data published in literature, but it is reasonable that the dissociation enthalpy of 57.37 kJ·mol^{-1} obtained here, because the mole fraction of N_2 in hydrate phase are much lower and they basically have the same dissociation enthalpies with (CH_4+CO_2) binary hydrates.

Table 7 The dissociation enthalpies of various gas hydrates in literature.

Guest Molecule	ΔH_d (kJ·mol^{-1})	Temperature (K)	Pressure (MPa)	Hydration Number	Reference	Method
CH_4	54.44±1.45	280.60-291.65	5.5-19.3	6.00	Gupta et al. [28]	DSC
	54.19±0.28	85-270.0	3.40±0.10	6.00	Handa [23]	Calorimeter
	56.9	273-286.0	2.0-20.0	-	Sloan et al. [47]	Clausius-Clapeyron
	56.84±0.89	273.15	0.1	6.38	Kang et al. [46]	DSC

	51.6	200.78	-	6.00	Rydzy et al. [44]	Calorimeter
	52.9±1.3	274-318	2.85-311.12	5.90±0.3	Anderson [37]	Clapeyron
	53.81	273.15	-	6.07	Yoon et al. [45]	Clausius-Clapeyron
	54.1±0.2	-	-	6.00	Lee et al. [29]	DSC
	$55.04^a, 55.12^b$	275.54-286.35	3.163-10.073	6.00	This work	DSC+Clapeyron
CO_2	57.7±1.8-63.6±1.8	274.15-282.15	1.377-3.858	6.6±0.3-5.6±0.3	Anderson [36]	Clapeyron
	65.22±1.03	273.15	0.1	7.23	Kang et al. [46]	DSC
	57.66	273.15	-	6.21	Yoon et al. [45]	Clausius-Clapeyron
	57.1±0.1	-	-	6.30	Lee et al. [29]	DSC
	$58.95^a, 58.70^b$	273.54-277.57	1.290-2.144	6.00	This work	DSC+Clapeyron
CH_4/CO_2 (0.85:0.15)	53.4	205.20	-	6.00	Rydzy et al. [44]	Calorimeter
CH_4/CO_2 (0.29:0.71)	62.82	275.15-279.15	1.5-2.8	6.00	Kwon et al. [21]	Clausius-Clapeyron
CH_4/CO_2 (0.12:0.88)	56.1±0.1	-	-	6.23	Lee et al. [29]	DSC
CH_4/CO_2 (0.39:0.61)	$57.23^a, 56.56^b$	279.90-287.07	3.381-7.935	6.00	This work	DSC
$CH_4/CO_2/N_2$ (0.25:0.71:0.04)	$57.37^a, 55.89^b$	276.98-283.34	2.836-7.005	6.00	This work	DSC

* $CH_4/CO_2/N_2$ indicates the mole ratio of CH_4 to CO_2 to N_2 in hydrate phase, a is the DSC measurement value and b is the calculation value by Clapeyron equation.

3.4. The swapping process of CH_4 hydrate by CO_2 and (CO_2+N_2)

In this work, in order to investigate if the CH_4 hydrate would dissociate while the swapping reaction is proceeding, we used μ-DSC apparatus to monitor the whole CH_4-$CO_2/(CO_2+N_2)$ swapping process in gas hydrates, because the μ-DSC has a high resolution and any tiny heat changes caused by hydrate formation or dissociation can be detected. For an accurate experimental results of the CH_4-$CO_2/(CO_2+N_2)$ swapping, it should be keep the sample cell pressure no less than the equilibrium pressure at experimental temperature while releasing the free CH_4 gas and blowing with CO_2 or M_3, make sure any possible CH_4 hydrate dissociation during this process could be

avoided. Figure 10 shows the heat flow changes in the process of CH_4 release and swapping gas injection at 263.15 K, it fluctuates and returns to the baseline quickly. Some researchers [15,48] reported the CH_4-CO_2 swapping process in gas hydrates undergoes a solid-liquid-solid transition and believed the CH_4 hydrate would dissociate and reform. In this study, the swapping reaction process last for 24 hours and then increasing experimental temperature to dissociate the hydrate sample. Figure 11 shows the thermograms of CH_4-CO_2/M_3 swapping at 263.15 K, as we can see from that, there is no noticeable exothermic and endothermic peaks detected within the high resolution and sensitivity of μ-DSC, it indicates that the swapping reaction occurs without significant hydrate dissociation or formation. This result is consistent with Ersland's [16] and Baldwin's [49] magnetic resonance imaging (MRI) experiments, in their investigation the free water phase was not detected during the CH_4-CO_2 swapping process. Figure 12 shows the dissociation thermograms of CH_4 hydrate before swapping and the mixed hydrate after swapping, the endothermic peaks from the mixed hydrates have a significant shift with respect to the peak formed by pure CH_4 hydrate dissociation, it indicates the hydrate composition has a dramatically change after swapping.
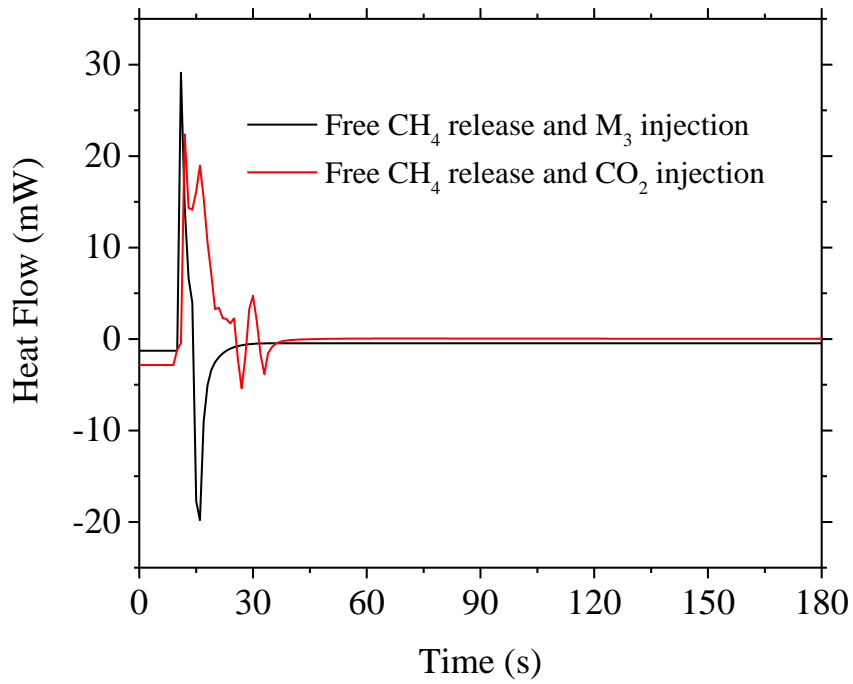
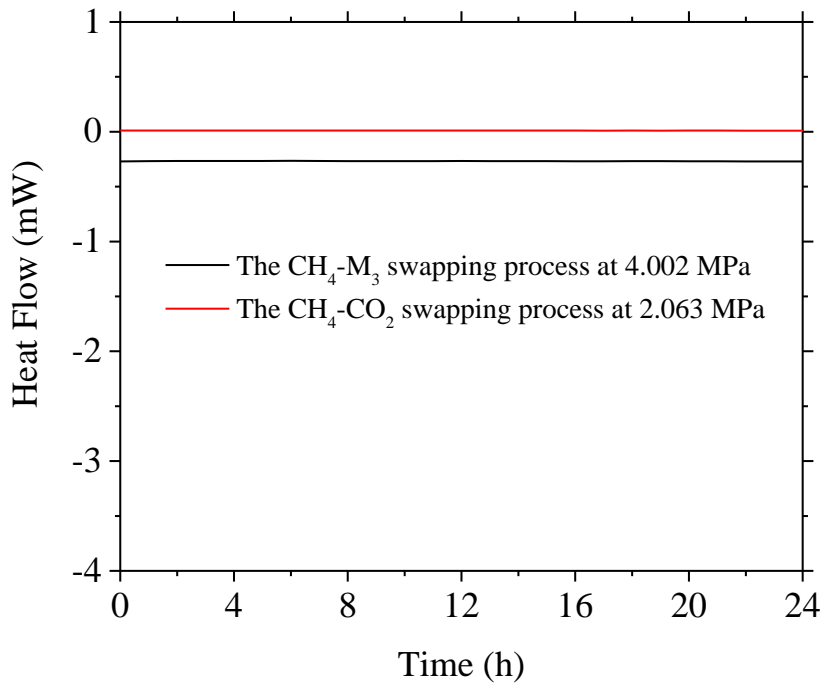**Figure 10**. The changes of heat flow in the process of CH_4 release and swapping gas injection at 263.15 K.

Figure 11. Thermograms of CH_4-CO_2/M_3 swapping process at 263.15 K.
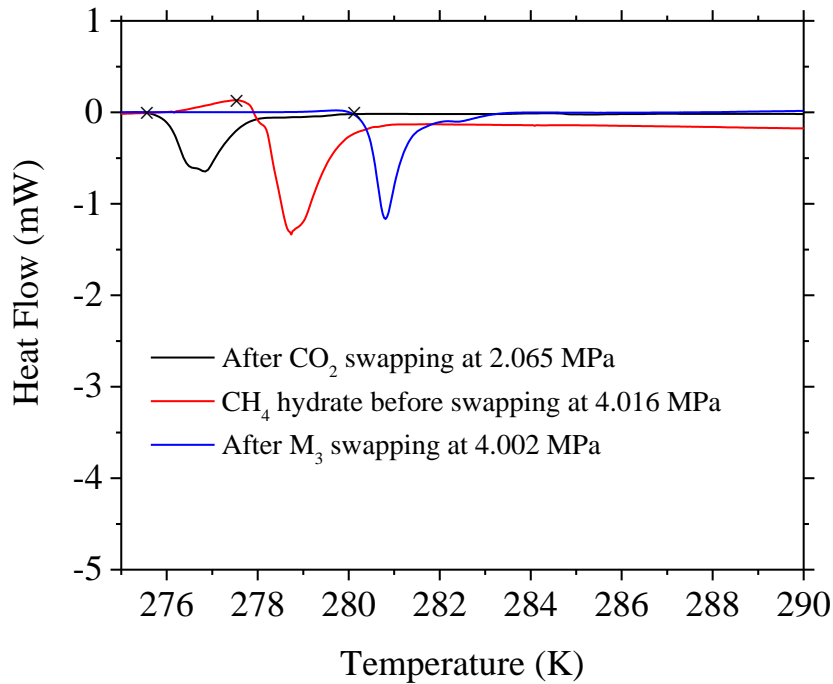
Figure 12. Dissociation thermograms of the pure CH_4 hydrate before swapping and the mixed hydrates after CO_2/M_3 swapping.

3.5. The estimation of the extent of swapping reaction in the CH_4 gas hydrate

The phase boundary and dissociation enthalpies of (CH_4+CO_2) binary hydrates are located between that of the pure CH_4 hydrate and that of the pure CO_2 hydrate, hence it can provide an approximate estimation of the CH_4-CO_2 swapping reaction extent, because the composition of mixed hydrates after swapping can be calculated by fitting their dissociation equilibrium data with CSMGem model. As for as the mixed hydrates after (CO_2+N_2) swapping, since the mole fraction of N_2 in hydrate phase is much lower than that of CO_2 and CH_4, the extent of swapping can also be estimated like that. In this study, the dissociation equilibrium data of mixed hydrates after CO_2/M_3 swapping at different pressure was obtained through μ-DSC measurements. As we can see from Figure 12, the measured dissociation equilibrium data of mixed hydrates after CO_2 swapping have a

good agreement with the phase boundary which formed by M_1 binary hydrates. The composition of hydrate phase at different pressure are listed in Table 8, it is found that only about 66% of CH_4 in hydrate phase has been replaced by CO_2 in the swapping reaction, since the CO_2 molecules prefer to replace CH_4 in large cages in hydrate, leaving CH_4 in small cages almost intact. This result is in accord with Lee's research [12,17], they estimated the extent of CH_4-CO_2 swapping is approximately 67% from batch type reactions through thermodynamic equilibrium studies and ^{13}C NMR spectroscopic analysis. The measured dissociation equilibrium data of mixed hydrate after M_3 swapping at different pressure match well with the hydrate phase boundary which formed by (CO_2 60 mol% + CH_4 20 mol% + N_2 20 mol%) gas mixture, and it is estimated that about 85% of CH_4 in hydrate phase has been replaced by M_3 in the swapping reaction. This result is pretty close to Lee's [13] investigation of CH_4-(CO_2+N_2) exchange with microscopic experiments, they reported that the maximum swapping extent achieved is 84% for sI gas hydrate and confirmed that the preferential enclathration of N_2 molecules in small 5^{12} cages of structure I hydrates improved the extent of the CH_4 recovery by ^{13}C NMR and gas composition analyses [50,51]. In addition, the dissociation enthalpies of mixed hydrates after CO_2/M_3 swapping, which are measured by μ-DSC and list in Table 8, are a little lower than that of the pure CO_2 hydrate and higher than that of the CH_4 hydrate.
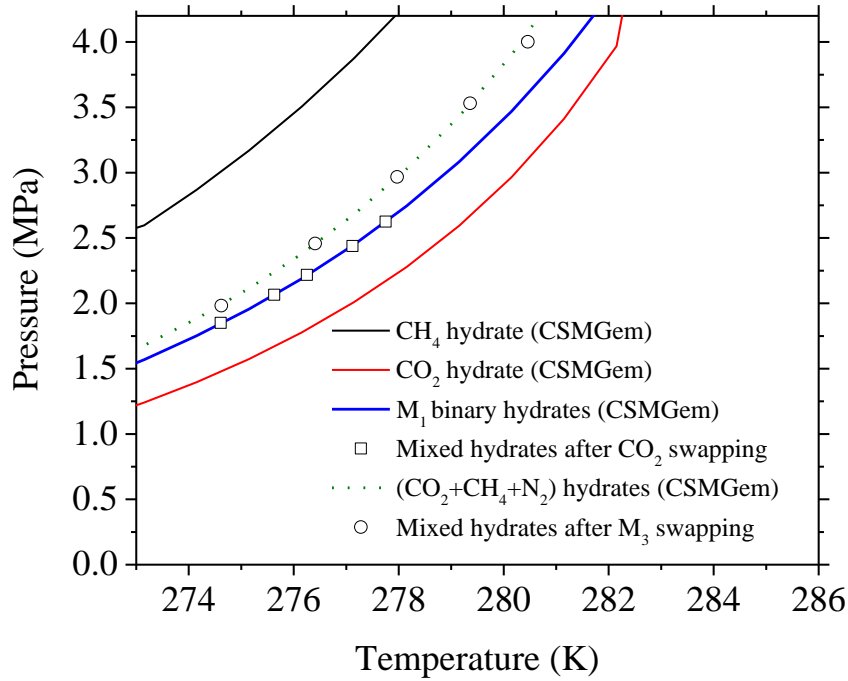
Figure 13. Dissociation equilibrium data of mixed hydrates after CO_2 and M_3 swapping at different pressure.

Table 8 The dissociation equilibrium data of mixed hydrates after CO_2 and M_3 swapping.

T_{onset} (K)	P (MPa)	m_W (mg)	x_I (wt%)	x_H (wt%)	$C_{CH_4}^H$ (mol%)	$C_{CO_2}^H$ (mol%)	$C_{N_2}^H$ (mol%)	ΔH_d (kJ·mol^{-1})
			Mixed hydrates after CO_2 swapping					
274.61	1.851	3.9	47.46	52.54	33.39	66.61	-	57.45
275.63	2.065	3.8	67.63	32.37	33.76	66.24	-	57.43
276.25	2.218	4.2	64.07	35.93	34.01	65.99	-	57.40
277.12	2.439	4.2	57.96	42.04	34.36	65.64	-	57.38
277.75	2.625	3.5	52.46	47.54	34.64	65.36	-	57.31
			Mixed hydrates after M_3 swapping					
274.62	1.982	3.5	57.26	42.74	14.97	81.99	3.04	57.83
276.41	2.458	2.9	52.14	47.86	15.42	81.37	3.21	57.76
277.97	2.968	2.8	49.14	50.86	15.86	80.76	3.38	57.56
279.36	3.531	3.2	47.44	52.56	16.32	80.12	3.56	57.47
280.31	4.002	2.2	52.46	47.54	16.69	79.60	3.71	57.35

4. Conclusion

The CH$_4$-CO$_2$ swapping in naturally occurring gas hydrates is regarded as an attractive method of CH$_4$ recovery and CO$_2$ sequestration. In this study, a μ-DSC apparatus was used to investigate the dissociation behavior of various gas hydrates, and it provided reliable measurements of hydrate dissociation equilibrium data and enthalpies for the pure and mixed gas hydrates. The μ-DSC measured dissociation enthalpies of CH$_4$ hydrate and CO$_2$ hydrate are 55.04 kJ·mol^{-1} and 58.95 kJ·mol^{-1}, respectively, which are very close to the calculation results by Clapeyron equation and literature values. The dissociation enthalpies of the (CH$_4$+CO$_2$) binary hydrates and (CH$_4$+CO$_2$+N$_2$) ternary hydrates were between that of the pure CH$_4$ hydrate and that of the pure CO$_2$ hydrate, increasing with the mole fraction of CO$_2$ in hydrate phase. It was found that there was no significant dissociation or formation phenomenon of hydrate occurring in the CH$_4$-CO$_2$/(CO$_2$+N$_2$) swapping process by investigating the heat flow changes with the μ-DSC apparatus. It indicates that most CH$_4$ hydrate forms (CH$_4$+CO$_2$) or (CH$_4$+CO$_2$+N$_2$) hydrate directly instead of dissociating into liquid water or ice first. The hydrate dissociation equilibrium data obtained from the endothermic thermograms of the mixed hydrates indicate that about 66% and 85% of CH$_4$ is replaced after reaction with CO$_2$ and (CO$_2$+N$_2$), respectively.

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