

Enthalpies of Dissociation of Pure Methane and Carbon Dioxide Gas Hydrate

Qazi Nasir, K. K. Lau, Bhajan Lal

Abstract—In this study the enthalpies of dissociation for pure methane and pure carbon dioxide was calculated using a hydrate equilibrium data obtained in this study. The enthalpy of dissociation was determined using Clausius-Clapeyron equation. The results were compared with the values reported in literature obtained using various techniques.

Keywords—Enthalpies of dissociation, methane, carbon dioxide, gas hydrate, natural gas.

I. INTRODUCTION

GAS hydrate plays a significant part in the natural gas production; formation of gas hydrate could prompt to safety hazards to both production and transportation which ultimately leads to economic jeopardy. Hammerschmidt in 1934 [1] discovered that the cause of plugging in the natural gas pipelines was due to the formation of gas hydrate. Since then numerous investigation has been carried out on three phase equilibria of hydrate-liquid water-vapor (H-L_w-V).

In contrast vast deposit of natural gas hydrate under the ocean bed and in the permafrost region has exhilarated interest to recover gas from these deposits. However interest in the gas hydrate of CO₂ and CH₄ has been increasing recently with the exploration of high CO₂ content fields. One of major concerns for the production of natural gas from CO₂-riched gas and transportation is the susceptibility of the process to form hydrate. Since CO₂ is more prone to form hydrate as compare to methane, this means increase in concentration of CO₂ as high as 70 mole % is more vulnerable to form hydrate especially in transportation and separation process.

To prevent hydrate formation, methods are adopted to ensure the operating condition in the pipeline and separation processes are set above the hydrate forming region. It is for this reason precise hydrate equilibrium data and thermal properties of the gas hydrate are required. Enthalpy of dissociation for instance in the past have normally been calculated from phase equilibria using Clapeyron-equation and measured calorimetrically. Such methods produce large discrepancies of result in enthalpy of dissociation. In this work, hydrate equilibrium data comprises of (H-L_w-V) were reported for pure CO₂ and pure CH₄. Moreover, Clausius-Clapeyron equation is used by utilizing the previous reported data to calculate the enthalpy of dissociation.

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II. MATERIALS AND METHODOLOGY

A. Materials

In this work, CH₄ (≥99.9%), CO₂ (≥99.9%) were purchased from Gas walkers SDN BHD. Both gases are used without any further purification, whereas de-ionized water was used in all experiments.

B. Apparatus

Hydreval, a PVT apparatus specifically design to study the gas hydrate formation/dissociation was used in this work. The Schematic of the experimental apparatus is shown in Fig. 1. The apparatus consist of equilibrium cell with a capacity of 80 cm³, operating with maximum pressure of 20 MPa and temperature ranges from (253 – 523) K. Conditions such as pressure, temperature and volume are recorded in every two sec with an accuracy of ±0.1K, ±0.01 MPa and ±0.001 cm³ respectively. The apparatus is equipped with magnetic stirrer to provide homogeneous mixing of sample under test. Furthermore, a camera with image enlargement option was used to visually monitor any changes to the sample placed in the equilibrium cell.

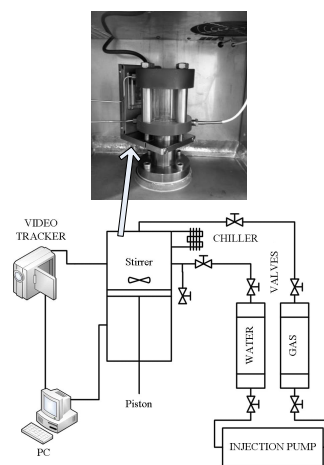


Fig. 1 Schematic diagram of apparatus

C. Procedure

A traditional T-cycle method with isochoric step heating technique was employed in this work [2]. Sapphire cell was washed thoroughly with distilled water and subsequently vacuumed to ensure the cell is air free. Then the cell was charged first with 25 ml de-ionized water followed by gas sample. Once the pressure-temperature condition stabilized, the stirrer was set at 600 rpm. Then the temperature of the system was reduced step-wise with a rate of 0.01 K/min. The

length of each step varies from 2 to 4 hours maximum. Hydrate formation was observed both visually along with sudden pressure drops. Once the hydrate is fully formed with no further pressure drop, the cell was heated slowly for complete dissociation.

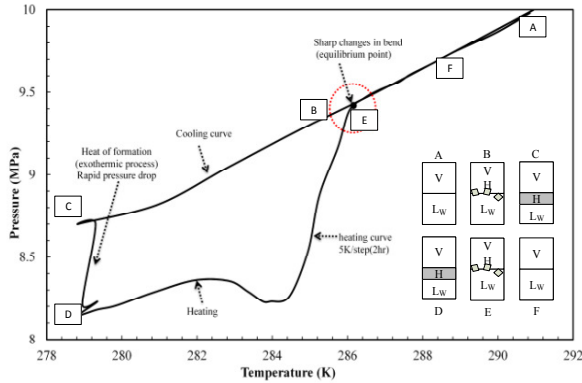


Fig. 2 Temperature-pressure trace to located hydrate dissociation point

Pressure-temperature trace was then plotted as shown in Fig. 2. The hydrate equilibrium point was taken as the first point where heating curve meets with the cooling curve. In addition to the pressure and temperature data, visual observation was carried out by using the attach camera. A series of pictures were taken during the formation and dissociation of the gas hydrate in the equilibrium cell is shown in Fig. 3.

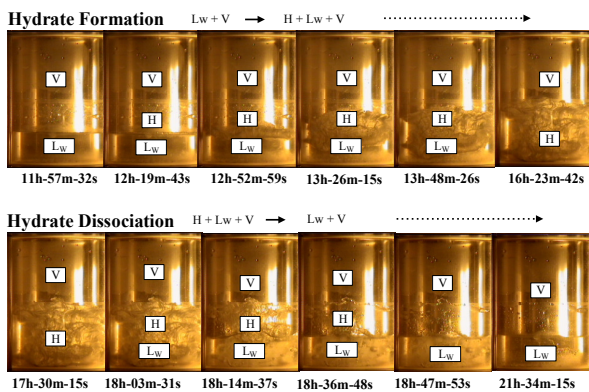


Fig. 3 Methane hydrate formation and dissociation pictures

D. Enthalpy of Dissociation

Clausius-Clapeyron equation was used in this study to calculate the enthalpy of dissociation. The equation is stated as:

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

where P is the pressure, T is temperature; ΔH_d is the enthalpy of dissociation, z is the compressibility factor and R is universal gas constant. The method was adopted by plotting

$\ln Pvs 1/T$ of H-Lw-V data. An arbitrarily line imposed on these data points showing a best straight line fit with constant slope. It is shown clearly that with in all experimental error, data points are appear to fall in line with same slope representing constant enthalpy of dissociation. As stated in (1) the ΔH_d also depends on the compressibility factor. Since z depends changes with temperature and pressure so the value of ΔH_d changes accordingly which support Skovborg and Rasmussen [3] that ΔH_d must show the change of same order of magnitude as the compressibility factor if the slope of $\ln Pvs 1/T$ is constant.

III. RESULT AND DISCUSSION

A. H-L_w-V Equilibrium Line

Hydrate dissociation condition of pure CH₄ and CO₂ were carried out at temperature and pressure range from (281 - 289) K and (5.55 - 13.32) MPa, (272 - 281) K and (1.34 - 4.03) MPa respectively. Experimental data obtained were plotted in Figs. 4 and 5 along with previously reported literature data [4]-[9].

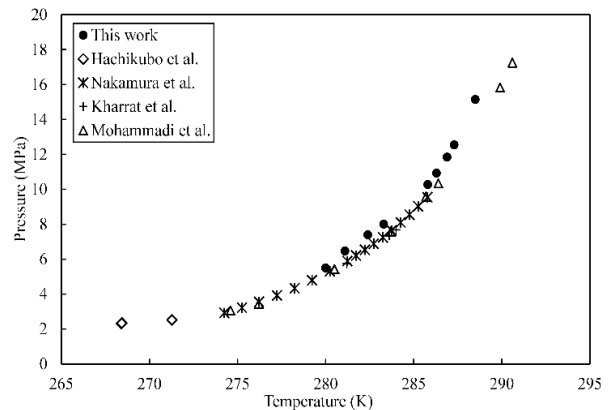


Fig. 4 Pure methane H-L_w-V data

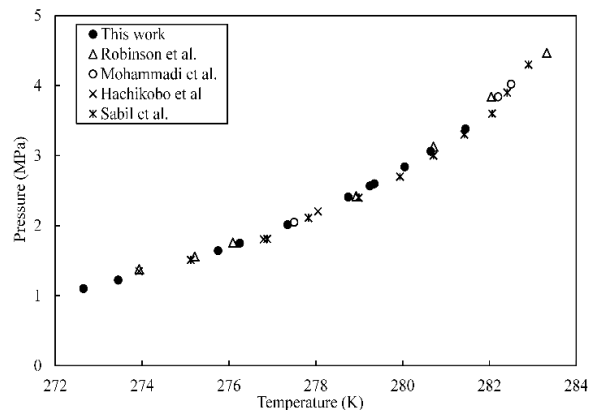


Fig. 5 Pure carbon dioxide H-L_w-V data

B. Enthalpy of Dissociation

For pure CH₄ and CO₂, plot was constructed as illustrated in Figs. 6 and 7. As previously mentioned, an arbitrarily line is

imposed on H-Lw-V data point representing a best straight line with constant slope. Enthalpy of dissociation was estimated from the slope of these H-Lw-V data point while substituting in (1). Compressibility factor z in (1) is calculated using SRK-EoS [10].

The result of enthalpy of dissociation ΔH_d and compressibility z was calculated for CH_4 and CO_2 at different three phases (H-Lw-V) equilibrium condition are illustrated in Figs. 8 and 9. As shown both the compressibility factor and enthalpy of dissociation change with the same order of magnitude.

Many authors reported the enthalpy of dissociation for pure CH_4 and CO_2 in literature using different techniques. The results are presented in Tables I and II for comparison. Reported result of methane hydrate show minor variation in enthalpy of dissociation, however considerable variation are observed among the reported result of enthalpy of dissociation for CO_2 hydrates

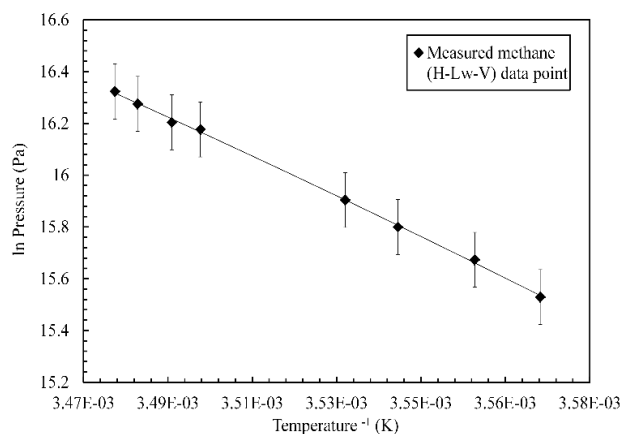


Fig. 6 Methane H-Lw-V data represented in log Pressure vs Temperature^{-1}

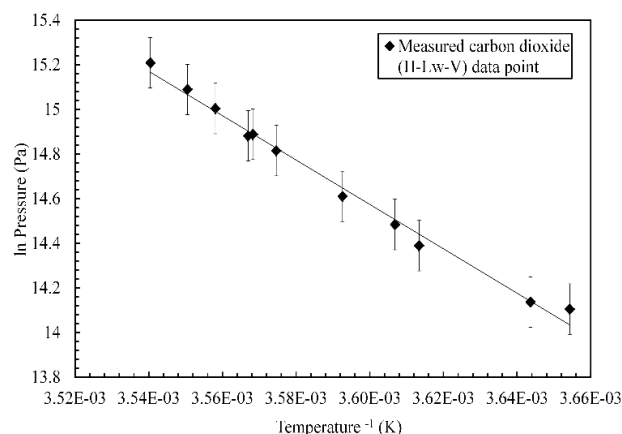


Fig. 7 CO_2 H-Lw-V data represented in log Pressure vs Temperature^{-1}

At high temperature our results matches more closely with Yoon et al. [11] and Anderson [12]; however, at low temperature, calculated enthalpies of dissociation suffer with

error as reported by Kamath [13] and Kang et al. [14].

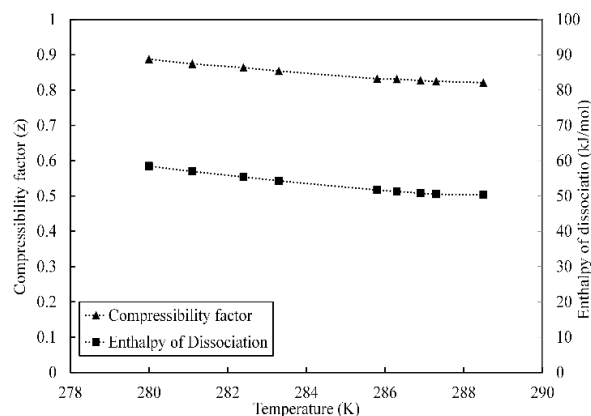


Fig. 8 ΔH_d and z for CH_4 hydrate vs temperature

Anderson [12] point out that error in values calculated using Clausius-Clapeyron equation were because of factor such as change in volume, CO_2 solubility in water and non-ideality of vapor phase.

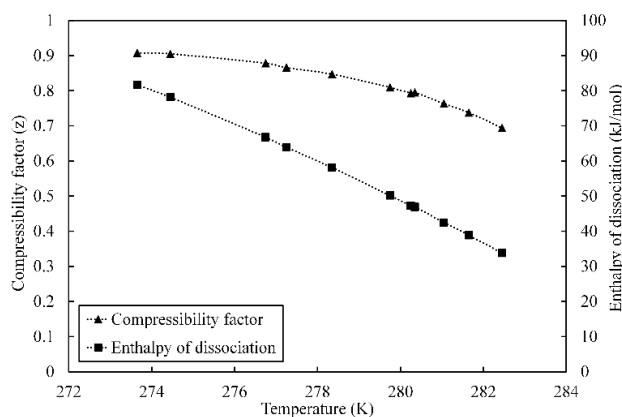


Fig. 9 ΔH_d and z for CO_2 hydrate vs temperature

However Uchida et al. [15] in contrast utilizes direct method techniques such as NMR and X-ray diffraction to measure the hydration number and he face difficulties in sample preparation supposition in analysis. Based on the above uncertainties of which method is more accurate to produce results of enthalpy of dissociation, comparison presented in Table II, and simplicity of Clausius Clapeyron equation, it is found that the enthalpy of dissociation obtained using Clausius-Clapeyron produce results with reasonable errors.

TABLE I
REPORTED VALUES OF THE ENTHALPIES OF DISSOCIATION FOR PURE CH₄
HYDRATE

Reference	$\Delta H(\text{kJ/mol})$	T(K)	Method
Yoon et al.[11]	53.81	273.15	Clausius–Clapeyron equation
Handa[16]	54.19	273.15	Calorimeter
Rueff et al.[17]	54.67	285.00	Calorimeter
Lievois et al.[18]	57.65	278.15	Calorimeter
Kang et al.[14]	56.84	274.15	Micro-calorimeter
Anderson[12]	53.50	273.15	Clapeyron equation
This Work	55.26	Q1	Clausius–Clapeyron equation

As shown in Table I, average of enthalpies of dissociation obtained for CH₄ in our work match very closely with previous results; however, in Table II for CO₂ as results deviates considerably among literature values, whereas based on comparison with some literature presented in Table II, our result are with close agreement with the reported data with reasonable error.

TABLE II
REPORTED VALUES OF THE ENTHALPIES OF DISSOCIATION FOR PURE CO₂
HYDRATE

Reference	$\Delta H(\text{kJ/mol})$	T(K)	Method
Kamath[13]	80.10	-	Clausius–Clapeyron equation
Long[19]	73.00	-	Clausius–Clapeyron equation
Kang et al. [14]	65.22	273.65	Calorimeter
Yoon et al. [11]	57.66	Q1	Clausius–Clapeyron equation
Anderson[12]	58.2-62.5	282.15- 274.15	Clapeyron equation
Delahaye et al. [20]	65.22	280.3	DSC
This Work	53.29	Q1	Clausius–Clapeyron equation

IV. CONCLUSION

In this work H-L_w-V equilibrium data of pure methane and carbon dioxide were measured along with the enthalpy of dissociation was calculated using Clausius-Clapeyron equation. Result obtained in compared against literature data. Acceptable agreement for both measure H-L_w-V data and enthalpy of dissociation was obtained for pure methane and carbon dioxide water system.

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