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 CO$_2$ and CH$_4$ has been increasing recently with the exploration of high CO$_2$ content fields. One of major concerns for the production of natural gas from CO$_2$-riched gas and transportation is the susceptibility of the process to form hydrate. Since CO$_2$ is more prone to form hydrate as compare to methane, this means increase in concentration of CO$_2$ 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. Enthalphy 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 CO$_2$ and pure CH$_4$. Moreover, Clausius-Clapeyron equation is used by utilizing the previous reported data to calculate the enthalpy of dissociation.

II. MATERIALS AND METHODOLOGY

A. Materials

In this work, CH$_4$ (≥99.9%), CO$_2$ (≥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 cm$^3$, 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 cm$^3$ 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.

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

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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.

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.

**III. RESULT AND DISCUSSION**

**A. H-Lw-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].

**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 \( \Delta H_d \) and compressibility \( z \) was calculated for \( \text{CH}_4 \) and \( \text{CO}_2 \) 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 \( \text{CH}_4 \) and \( \text{CO}_2 \) 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 \( \text{CO}_2 \) hydrates.

Fig. 6 Methane H-Lw-V data represented in log Pressure vs Temperature

Fig. 7 \( \text{CO}_2 \) H-Lw-V data represented in log Pressure vs Temperature

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].

Anderson [12] point out that error in values calculated using Clausius-Clapeyron equation were because of factor such as change in volume, \( \text{CO}_2 \) solubility in water and non-ideality of vapor phase.

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.
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 I

<table>
<thead>
<tr>
<th>Reference</th>
<th>ΔH (kJ/mol)</th>
<th>T (K)</th>
<th>Method</th>
</tr>
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<tbody>
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<td>[1] Yoon et al.</td>
<td>53.81</td>
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<td>[2] Handal</td>
<td>54.19</td>
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<td>[3] Rueff et al.</td>
<td>54.67</td>
<td>285.00</td>
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<td>[4] Lievois et al.</td>
<td>57.65</td>
<td>278.15</td>
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<tr>
<td>[5] Kang et al.</td>
<td>56.84</td>
<td>274.15</td>
<td>Micro-calorimeter</td>
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<td>[6] Anderson</td>
<td>53.50</td>
<td>273.15</td>
<td>Clapeyron equation</td>
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<td>This Work</td>
<td>55.26</td>
<td>Q1</td>
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### Table II

<table>
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<th>ΔH (kJ/mol)</th>
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<tbody>
<tr>
<td>[1] Kamath</td>
<td>80.10</td>
<td>-</td>
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<tr>
<td>[2] Long</td>
<td>73.00</td>
<td>-</td>
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<td>[3] Kang et al.</td>
<td>65.22</td>
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<td>[4] Yoon et al.</td>
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<td>Clausius–Clapeyron equation</td>
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<tr>
<td>[5] Anderson</td>
<td>58.2-62.5</td>
<td>282.15-274.15</td>
<td>Clapeyron equation</td>
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<tr>
<td>[6] Delahaye et al.</td>
<td>65.22</td>
<td>280.3</td>
<td>DSC</td>
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<td>This Work</td>
<td>53.29</td>
<td>Q1</td>
<td>Clausius–Clapeyron equation</td>
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</table>

### IV. CONCLUSION

In this work H₅-L₅-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 H₅-L₅-V data and enthalpy of dissociation was obtained for pure methane and carbon dioxide water system.

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### REFERENCES