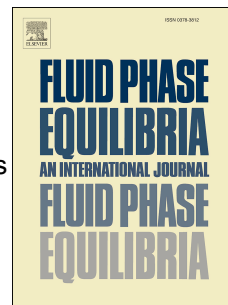


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Impact of acetone on phase boundary of methane and carbon dioxide mixed hydrates

Behzad Partoon, Khalik M. Sabil, Hariz Roslan, Bhajan Lal, Lau Kok Keong



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5 **Impact of acetone on phase boundary of methane and carbon**
6 **dioxide mixed hydrates**
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12 **Behzad Partoon^a, Khalik M. Sabil^{b*}, Hariz Roslan^a, Bhajan Lal^a,**
13 **Lau Kok Keong^a,**

14
15 ^aChemical Engineering Department, Universiti Teknologi PETRONAS, 32610 Bandar
16 Seri Iskandar, Perak Darul Ridzuan, Malaysia

17
18 ^bInstitute of Petroleum Engineering, School of Energy, Geoscience, Infrastructure and
19 Society, Heriot-Watt University Malaysia, No 1 Jalan Venna P5/2, Precinct 5, 62200
20 Putrajaya, Federal Territory of Putrajaya Malaysia

21
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23
24
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29
30 *corresponding author: k.msabil@hw.ac.uk, tel: +60124211974
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34 **Abstract**

35 In this work, the hydrate phase boundary of a gas mixture consisted of 29.9 mol% CH₄ and 70.1 mol%
36 CO₂ is experimentally studied in the presence of 1 to 7 mol% of an aqueous acetone solution. Results
37 indicated that acetone acts as a weak inhibitor on this gas mixture. In addition, enthalpy of hydrate
38 dissociation for this system is reported. Based on the results, the inhibition effect of acetone is found
39 to be decreasing with the increase of acetone concentration while the enthalpy of hydrate dissociation
40 is increasing with the increase of acetone concentration within the studied range.

41 **Keywords:** Hydrate phase boundary; Acetone; Carbon dioxide-Methane Mixed Gas; Inhibitor; Enthalpy of
42 dissociation

43 **1. Introduction**

44 Gas hydrates are crystalline complex structures consist of hydrated polyhedron lattice, which
45 acts as a host and entrapped guest molecules. Guest molecules, generally, may carry strong
46 hydrophobic characteristics and none or weak polarity, which leading to immiscibility with water [1].
47 Still, some water soluble hydrocarbon can form clathrate hydrate due to minimization of Gibbs free
48 energy of the guest and host molecules at high pressure and relatively low temperatures [2].

49 Increasing energy demand across the globe in the 21st century makes non-conventional fuel
50 resources to become economically interesting. This includes the development of high carbon dioxide
51 (CO₂) gas reservoir where CO₂ content can be more than 50 mol% of the gas originally in place. For
52 example, K5 field located offshore of Sarawak, Malaysia with 25.65 trillion SCF gas reserve, shows
53 evidence of bearing more than 70 mol% CO₂. [3] In addition, biogas and landfill gas that can be
54 classified as renewable energy resources, mostly consist of 45 to 60 vol% methane (CH₄) and 40-60
55 vol% CO₂ with traces of some other gases [4, 5]. Economically, the high CO₂ gas requires an efficient
56 CO₂ separation module to make these resources marketable or even suitable as feedstock for
57 manufacturing processes [3]. On the other hand, international regulations, such as Kyoto Protocol,
58 emphasize on the reduction of greenhouse gases emission, particularly CO₂, to the atmosphere [6, 7].
59 Therefore, both economic and environmental aspects are pointing to a need for a clean CO₂
60 separation process prior to the utilization of these new resources.

61 The common gas separation technologies such as chemical absorption, adsorption, cryogenic
62 distillation and membrane separation, are incapable, both economically and technically, to capture
63 the large amounts of CO₂ from gas streams. Some critical problems are associated with large energy
64 consumption, corrosion, foaming, and low capacity. For example, estimations showed that the
65 deployment of absorption capturing technology in flue gas cleaning from a modern power plant can
66 reduce the thermal efficiency from approximately 45% to approximately 35%. [8]. Therefore,

67 development of new and existing capturing technologies should lower the energy requirements in
68 order to minimize the overall costs as well as environmental impacts [9].

69 Utilization of gas hydrate as a separation technology is one of the alternatives. Separation of CO₂
70 from N₂ by forming gas hydrate in the presence of tetrahydrofuran (THF) was reported by Kang and
71 Lee [10]. According to their investigation, utilization of hydrate technology is less energy intensive
72 compared to common capturing process due to the moderate temperature condition of 273 to 283 K.
73 In addition, using THF can decrease hydrate formation pressure and consequently decrease the
74 overall energy consumption for the process [10]. There are several publications in the open literature
75 that suggest hydrate formation process for separation of CO₂ from N₂, H₂ and some other gases.
76 Eslamimanesh et al. (2012) presented a comprehensive survey of experimental studies dealing with
77 separation of a gases by hydrate formation technology [11]. However, separation of CO₂ from CH₄
78 received less attention in these studies. Seo et al. at (2000) showed that separation of CO₂ from CH₄ is
79 possible through hydrate formation process [12]. Both CO₂ and CH₄ are good gas hydrate former and
80 their gas hydrate phase boundaries are relatively close to each other. This makes their separation
81 through hydrate formation process more challenging. A suitable promoter to enhance the separation
82 may be the key. THF as the most famous promoter is shown good promotion effects for both gases
83 [13, 14]. Consequently, it cannot be a good candidate to enhance their separation.

84 Acetone, as a common solvent, can be a good candidate for this purpose. Acetone has shown a
85 thermodynamic promotion effect on methane hydrate formation at low concentration [14, 15]. The
86 promotion effects of acetone on methane hydrate is first observed by Ng and Robinson when they
87 were looking for a new inhibitor for methane hydrate [16]. Acetone is a polar compound that is liquid
88 at room temperature. At first glance, acetone seems to be an inhibitor, as it has many characteristics in
89 common with alcohols. But, at low concentrations, it thermodynamically promotes the methane
90 hydrate formation condition. The maximum promotion effect was observed at around 6 mol%
91 concentration [17]. This promotion effect is converted to inhibition when acetone concentration is
92 higher than 30 mol% [15]. On the other hand, acetone showed thermodynamic inhibition effect for
93 carbon dioxide hydrate at all concentration [18]. Therefore, as acetone has different effects on pure
94 CH₄ and CO₂ hydrates at low concentrations, it may show some selectivity on separation of these
95 gases by hydrate formation process. Yet, prior to study the separation efficiency, the equilibrium
96 phase boundary for such system should be studied and analyzed first. Acetone and water are well
97 known for non-ideal behaviors and hence predictions of hydrate formation in such system through
98 thermodynamic modeling have a considerable error. Thus, in this work, the phase boundary of gas
99 hydrate for a system of water + acetone + CO₂ + CH₄ is experimentally measured and reported.

102

103 2. Experimental Section

104 2.1. Material

105 Acetone with purity of 99.8% was purchased from Merck Millipore. A pre-mixed CH₄ and CO₂
106 gas mixture was purchased from AirProduct Singapore Pte. Ltd. The gas mixture ratio as specified by
107 the supplier is 29.99 mole % CH₄ and 70.01 mol% CO₂. This CO₂ to CH₄ ratio is selected in order to
108 simulate the K5 field gas composition and the pre-mixed gas was used without any further
109 purification. Deionized water was used to prepare aqueous acetone solutions.

110

111 2.2. Apparatus

112 A high-pressure cell, manufactured by Dixon FA engineering Sdn. Bhd is used for the
113 measurement of gas hydrate phase boundary. The schematic of the experimental rig is depicted in
114 Figure 1. The equilibrium cell is made of stainless still and has an internal volume of 500 ml. The cell
115 is equipped with a PT-100 platinum thermometer with the accuracy of ± 0.15 °C. A GP-M250
116 Keyence pressure transducer with the accuracy of $\pm 1.0\%$ full span is used to measure the pressure
117 inside the cell. In addition, a magnetic stirring system consisted of a 2-bladed pitch impeller and a 400
118 rpm motor is used to agitate liquid in the cell. The cell is immersed inside a thermostatic bath. The
119 bath temperature is controlling by a PID controller with an accuracy of ± 0.3 °C. In addition, the bath
120 temperature set point is programmable through data acquisition system. Pressure and temperature
121 data is recorded every second.

122

122 INSERT FIGURE 1

123 **Figure 1.** Simplified schematic of experimental rig.

124

125 2.3. Procedure

126 The -hydrate equilibrium points were measured by employing an isochoric method. The cell was
127 washed using distilled water and dried. The extra air was removed from the cell using a vacuum
128 pump. 100 cm³ of aqueous acetone solution at the desired concentration was fed into the cell through
129 liquid injection point and gas was purged three times to ensure complete removal of air from the
130 system. Then, gas was introduced to the cell until the desired pressure is achieved at room
131 temperature. The stirring system was turned on and then the temperature was decreased to 273 K.
132 System was kept at this temperature for 4 hrs to ensure gas hydrate formation. After that, the system
133 was warmed stepwise to 293 K. At each step, the temperature was held constant for 30 min to 240
134 min, according to the set point temperature and expected equilibrium temperature. The hydrate
135 dissociation condition was determined through P-T diagram, as described by Tohidi et al.[19].

136 To produce the phase boundary for $\text{CO}_2 + \text{CH}_4 + \text{water} + \text{acetone}$ system, four different acetone
137 concentrations was studied at three different pressures. In addition, to validate the accuracy of the
138 experimental setup, methane hydrate phase boundary in the presence of deionized water at three
139 different pressures was measured and compared with literature data.

140 3. Results and Discussion

141 3.1. Validation of the new setup

142 The pressure-temperature profile for CH_4 -water system as a sample of the experimental
143 procedure followed in this work is depicted in Figure 2. The cooling step is set to be fast to shorten the
144 experimental time. The rapid pressure drop is due to the hydrate formation. The heating part consisted
145 of a fast heating step following by several slow steps. The location of the change in the P-T slope, as
146 shown in Figure 2, is taken as the hydrate equilibrium point. The methane hydrate equilibrium point
147 shown in Figure 2 is 5.808 MPa and 281.35 K. In Figure 3, CH_4 -water equilibrium data points are
148 included. As shown in this figure, the measured data coincides with pure methane hydrate data
149 reported by Nakamura et al. [20].

150 151 INSERT FIGURE 2

152 **Figure 2.** Pressure-Temperature profile measured during $\text{CH}_4 + \text{water}$ experiment.

153 154 155 3.2. $\text{CH}_4 + \text{CO}_2 + \text{acetone} + \text{water}$ hydrates Equilibrium data

156 The equilibrium points of $\text{CH}_4 + \text{CO}_2 + \text{acetone} + \text{water}$ hydrates are tabulated in Table 1. Four
157 different aqueous solutions of 1, 3, 5 and 7 mol% of acetone are studied in this work. In addition,
158 blank deionized water is studied as reference condition. For each solution, the hydrate dissociation
159 condition is reported for three to four different pressures between 2.68 to 5.36 MPa. In each
160 experiment, the pre-mixed gas mixture of 29.9 mol% CH_4 and 70.1 mol% CO_2 is used as the feed gas.
161 In each experiment, based on starting pressure and temperature condition the final concentration of
162 gas and liquid phase composition is changed. In Table 1, the CO_2 and CH_4 concentration in gas phase
163 is calculated by vapor-liquid equilibrium (VLE) calculations at equilibrium pressure and temperature
164 with utilization of a ϕ - ϕ approach, using Peng-Robinson equation of state [21] with modified
165 Huron-Vidal (MHV1) mixing rule [22] and UNIFAC activity coefficient model [23] to calculate the
166 non-ideality of system.

167 As previously mentioned, the presence of acetone promotes CH_4 hydrate formation at
168 concentrations lower than 7 mol%, while for CO_2 hydrate it acts as an inhibitor at all concentrations.
169 Therefore, for a mixture of CO_2 and CH_4 , its impact is more complicated. The gas hydrate phase
170 boundaries of CH_4 , CO_2 and mixed CO_2/CH_4 in the presence of 1 mol% acetone aqueous solution is

171 depicted in Figure 3. The data for CH₄ + acetone in Figure 3 to 6 are taken from Seo et al. [14] and
 172 Partoon et al.[15] while those for CO₂ + acetone data are taken from Maekawa work [18]. In addition,
 173 HLV equilibrium data of CH₄ hydrate and CO₂ hydrate in pure water are also illustrated in Figure 3 to
 174 provide better observation of acetone impact on gas hydrate phase boundary. The CH₄ and CO₂
 175 hydrate data are taken from Nakamura et al. [20] and Sabil et al. [24], respectively.

176

177 **Table 1.** Gas hydrate equilibrium condition for CO₂ + CH₄ + acetone + water system. The feed gas consisted of 29.9
 178 mol% CH₄ and 70.1 mol% CO₂.

Acetone concentration in solution (mol%)	Equilibrium condition				Acetone concentration in solution (mol%)	Equilibrium condition			
	y ¹ CO ₂ (mol%)	y ¹ CH ₄ (mol%)	T ² (K)	P ² (MPa)		yCO ₂ (mol%)	yCH ₄ (mol%)	T (K)	P (MPa)
0	69.95	34.16	281.35	3.25	3	63.66	35.84	281.65	4.17
	69.97	33.36	283.05	4.35		64.13	35.22	282.85	5.13
	69.98	32.75	284.65	5.32		64.92	34.37	283.15	5.36
1	64.84	34.95	279.35	3.22	5	60.70	38.77	280.65	3.32
	65.54	34.22	281.1	4.16		61.84	37.54	282.05	4.18
	66.31	33.35	282.85	5.28		62.74	36.48	282.95	5.05
3	62.16	37.44	279.25	2.68	7	57.83	41.57	281.2	3.36
	62.78	36.81	279.85	3.19		59.48	39.85	282.25	4.22
	63.02	36.54	280.75	3.71		60.65	38.52	283.35	5.03

179 ¹ Calculated value

180 ² Standard combined uncertainties: $u_c(P) = 0.07$ MPa and $u_c(T) = 0.1$ K.

181

182

183

INSERT FIGURE 3

184 **Figure 3.** HLV phase boundary of CH₄, CO₂ and their mixture in the presence of 1 mol% acetone solution.

185

186 As shown in Figure 3, the presence of 1 mol% acetone in the solution shifts CO₂ hydrate phase
 187 boundary to lower temperature, while it moves CH₄ phase boundary to the higher temperature
 188 condition. This resulted in almost the same equilibrium hydrate boundary for CO₂, CH₄ and
 189 consequently their mixture, as it shown in this figure. By increasing acetone concentration to 3 mol%,
 190 its promotional effect on CH₄ hydrate and its inhibition effect on CO₂ hydrate is increasing and thus
 191 creating a distinct separation between the two equilibrium lines as depicted in Figure 4.

192

INSERT FIGURE 4

193 **Figure 4.** HLV phase boundary of CH₄, CO₂ and their mixture in the presence of 3 mol% acetone solution.

194

195 As shown in Figure 4, methane hydrate phase boundary is shifting to a higher temperature in the
 196 presence of 3 mol% acetone. In contrast, the inhibition effect of acetone significantly reduced the

197 phase boundary of CO₂ hydrate. Therefore, in the presence of 3 mol% of acetone in the aqueous
198 solution, CH₄ hydrate is forming at higher pressure and temperature than that of CO₂ hydrate. For the
199 mixed gas, as expected, the hydrate phase boundary is laying between that of pure gases
200 hydrate-liquid-vapor (HLV) equilibrium line. However, as the studied gas mixture is rich in CO₂, its
201 HLV line is tending toward CO₂ HLV line.

202 INSERT FIGURE 5

203 **Figure 5.** HLV phase boundary of CH₄, CO₂ and their mixture in the presence of 5 mol% acetone solution.

204
205 A similar trend is observed for a system with 5 mol% aqueous acetone solution as depicted in
206 Figure 5. Due to the increase in acetone concentration, the gap between methane and carbon dioxide
207 hydrate phase boundaries is increasing. This behavior can be attributed to cage occupancy
208 competition. First of all, because of acetone molecular size, the presence of acetone in the system
209 converts structure sI methane and carbon dioxide hydrate to structure sII, where acetone molecules
210 are occupying the large cavities of structure sII hydrates. For methane hydrate, sII provides lots of
211 small cages where methane molecules can best fit inside. In contrast, due to the diameter of
212 CO₂ molecules, the small cages are very tight and although CO₂ molecules can also occupy small
213 cages of both sI and sII, they tend to go into large cavities [1]. This creates a competition between
214 CO₂ and acetone molecules to occupy the larger cavities of sII hydrates. Therefore, for methane
215 hydrate at low concentrations, where acetone molecules occupy the large cavities and methane
216 occupies mostly small cavities, acetone promotes the hydrate formation condition while the similar
217 trend is not observed for the CO₂ system. It is interesting to notice that the maximum promotion effect
218 of acetone in such system is at 6 mol% where they can completely fill all large cavities of sII hydrate.
219 At higher concentrations, the polar properties of free acetone molecules start to inhibit the hydrate
220 formation. Thus, at 30 mol% acetone becomes inhibitor for CH₄ hydrate [15, 17]. For CO₂ hydrates,
221 the competition between acetone and CO₂ molecules along with polar properties of both compounds
222 convert acetone to an inhibitor at all concentrations.

224 INSERT FIGURE 6

225 **Figure 6.** HLV phase boundary of CH₄, CO₂ and their mixture in the presence of 7 mol% acetone solution.

226
227 Figure 6 depicts CH₄, CO₂ and CO₂-CH₄ mixture phase boundaries in the presence of 7 mol% of
228 acetone. At this concentration, the promotion effect of acetone on methane hydrate phase boundary is
229 started to decrease. This is, however, not directly affected the phase boundary of the CO₂/CH₄ system.

230 The impact of acetone on mixed gas hydrate HLV is inhibition for all acetone concentrations.
231 Figure 7 compares the gas hydrate equilibrium temperature of the mixed gas as a function of acetone
232 concentration at different pressures. As it shown in this figure, the presence of acetone in the solution

233 decreases the mixed gas hydrate equilibrium temperature at constant pressure. This thermodynamic
 234 inhibition effect is a weak function of acetone concentration. For example, at 5 MPa and 1 mol% of
 235 acetone the hydrate equilibrium temperature is decreased around 2 K. This shift in equilibrium
 236 temperature is 1.4 K at 7 mol% for the same pressure.

237

238

INSERT FIGURE 7

239

Figure 7. The impact of acetone on mixed gas hydrates equilibrium temperature at constant pressures.

240

3.3. Enthalpy of dissociation

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Another important parameter for industrial application of gas hydrate is enthalpy of dissociation, ΔH_d , which by definition is the amount of heat required for dissociating hydrate crystals to liquid and gas phases. Gas hydrate enthalpy of dissociation is quantitatively much higher than water enthalpy of melting. ΔH_d is equal to the amount of heat being released during hydrate formation and it is known as enthalpy of hydrate formation. This parameter plays essential roles in process design and optimization. To calculate ΔH_d , Clausius–Clapeyron type equation can be applied:

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

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Table 2. Average enthalpy of dissociation for studied systems.

Acetone concentration in solution (mol%)	ΔH_d (kJ/mol)
0	55.6
1	69.0
3	90.7
5	92.2
7	94.5

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As presented in this table, the ΔH_d in the absence of acetone is in the range of sI hydrates value such as methane and carbon dioxide [25, 26]. ΔH_d is increasing as a result of large cage occupation by acetone molecules. However, the values are less than common sII hydrate formers such as propane ($\Delta H_d = 129$ kJ/mol) [1]. This is shown that both small and large cavities of sII hydrate are filling with

263 gases. In addition, increasing the enthalpy of dissociation with acetone concentration indicates that
264 acetone is occupying large cavities of sII crystals more than CO₂ or even CH₄. This result is in line
265 with the impact of acetone on HLV of studied system, as discussed before.

266 4. Conclusion

267 The phase boundary of CO₂ and CH₄ gas mixture in the presence of acetone solution is
268 experimentally measured in this work. The results indicated that presence of acetone in the solution
269 has inhibition effects on mixed gas HLV phase boundary. However, this inhibition effects is
270 decreasing by increasing the acetone concentration in the studied range. In addition, the enthalpy of
271 dissociation for this system is presented in this work. Enthalpy analysis indicates that chance of
272 acetone for the occupation of large cavities of sII hydrate is increasing by an increase in acetone
273 concentration. These findings show that acetone has the potential to act as a selective additive for
274 separation of CO₂ and CH₄. The slight inhibition effect of acetone on the equilibrium condition does
275 not have a large impact on the operational condition of any proposed process for separation of these
276 gases. In such process, at a certain pressure, the operating temperature should be put well below the
277 equilibrium temperature to provide enough super-saturation. As a matter of fact, the reduction of
278 water freezing point as a result of acetone presence in the system can give this opportunity to reduce
279 the operational temperature to below ice point temperature. However, further study is required to
280 investigate this application for acetone. Especially, the amount and composition of captured gas by
281 hydrate at a certain temperature below the hydrate equilibrium temperature should be measured to
282 find out if acetone can work as a selective additive for separation of CO₂ from CH₄ or not

283 Acknowledgements

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286 Reference

- 287 [1] E.D. Sloan, C. Koh, Clathrate hydrates of natural gases, 3rd ed., CRC Press-Taylor & Francis
288 Group, New York, USA, 2008.
289 [2] Y. Saito, T. Kawasaki, T. Okui, T. Kondo, R. Hiraoka, Methane Storage in Hydrate Phase with
290 Water Soluble Guests, in: 2nd International Conference on Natural Gas Hydrate. Toulouse, France,
291 1996.
292 [3] K.M. Sabil, Q. Nasir, B. Partoon, A.A. Seman, J. Chem. Eng. Data, 59 (2014) 3502-3509.
293 [4] Q. Aguilar-Virgen, P. Taboada-González, S. Ojeda-Benítez, J. Clean. Prod., 79 (2014) 53-60.
294 [5] D.R. Reinhart, Beneficial Utilization of Landfill Gas, Report No.: 94-7, University of Central
295 Florida, 1994.
296 [6] Kyoto Protocol to United Nations Framework Convention on Climate Change, United Nations,
297 1998.

- 298 [7] L.C. Lau, K.T. Lee, A.R. Mohamed, *Renew. Sustainable Energy Rev.*, 16 (2012) 5280-5284.
299 [8] N. MacDowell, N. Florin, A. Buchard, J. Hallett, A. Galindo, G. Jackson, C.S. Adjiman, C.K.
300 Williams, N. Shah, P. Fennell, *Energy Environ. Sci.*, 3 (2010) 1645.
301 [9] K.M. Sabil, G.-J. Witkamp, C.J. Peters, *Fluid Phase Equilib.*, 290 (2010) 109-114.
302 [10] S.-P. Kang, H. Lee, *Environ. Sci. Technol.*, 34 (2000) 4397-4400.
303 [11] A. Eslamimanesh, A.H. Mohammadi, D. Richon, P. Naidoo, D. Ramjugernath, *J. Chem.*
304 *Thermodyn.*, 46 (2012) 62-71.
305 [12] Y.-T. Seo, S.-P. Kang, H. Lee, C.-S. Lee, W.-M. Sung, *Korean J. Chem. Eng.*, 17 (2000)
306 659-667.
307 [13] Y. Seo, S.-P. Kang, S. Lee, *J. Chem. Eng. Data*, 53 (2008) 2833-2837.
308 [14] Y.T. Seo, S.P. Kang, H. Lee, *Fluid Phase Equilib.*, 189 (2001) 99-110.
309 [15] B. Partoon, J. Javanmardi, *J. Chem. Eng. Data*, 58 (2013) 501-509.
310 [16] H.J. Ng, D.B. Robinson, *Ann N.Y. Acad. Sci.*, 715 (1994) 450-462.
311 [17] S. Mainusch, C.J. Peters, J. de Swaan Arons, J. Javanmardi, M. Moshfeghian, *J. Chem. Eng.*
312 *Data*, 42 (1997) 948-950.
313 [18] T. Maekawa, *Fluid Phase Equilib.*, 303 (2011) 76-79.
314 [19] B. Tohidi, R.W. Burgass, A. Danesh, K.K. ØStergaard, A.C. Todd, *Ann. N.Y. Acad. Sci.*, 912
315 (2000) 924-931.
316 [20] T. Nakamura, T. Makino, T. Sugahara, K. Ohgaki, *Chem. Eng. Sci.*, 58 (2003) 269-273.
317 [21] D.Y. Peng, D.B. Robinson, *Ind. Eng. Chem., Fundam.*, 15 (1976) 59-64.
318 [22] M.L. Michelsen, *Fluid Phase Equilib.*, 60 (1990) 213-219.
319 [23] D.S. Abrams, J.M. Prausnitz, *AIChE J.*, 21 (1975) 116-128.
320 [24] K.M. Sabil, G.-J. Witkamp, C.J. Peters, *Fluid Phase Equilib.*, 284 (2009) 38-43.
321 [25] Y. Lee, S. Lee, J. Lee, Y. Seo, *Chem. Eng. J.*, 246 (2014) 20-26.
322 [26] K.M. Sabil, O. Nashed, B. Lal, L. Ismail, A. Japper-Jaafar, *J. Chem. Thermodyn.*, 84 (2015)
323 7-13.

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- 327 **Figure 8.** Simplified schematic of experimental rig.
- 328 **Figure 9.** Pressure-Temperature profile measured during CH₄ + water experiment.
- 329 **Figure 10.** HLV phase boundary of CH₄, CO₂ and their mixture in the presence of 1 mol% acetone solution.
- 330 **Figure 11.** HLV phase boundary of CH₄, CO₂ and their mixture in the presence of 3 mol% acetone solution.
- 331 **Figure 12.** HLV phase boundary of CH₄, CO₂ and their mixture in the presence of 5 mol% acetone solution.
- 332 **Figure 13.** HLV phase boundary of CH₄, CO₂ and their mixture in the presence of 7 mol% acetone solution.
- 333 **Figure 14.** The impact of acetone on mixed gas hydrates equilibrium temperature at constant pressures.

AB: Alcoholic Bath
A/D: Analog to Digital module
C: High pressure cell
D: Data logging program
G: Gas Cylinder
LV: Liquid Valve
M: Magnetic Motor
PSV: Pressure Safety Valve
PT: Pressure Transmitter
PT-100: Temperature sensor
TCS: Temperature control system
TT: Temperature Transmitter
VP: Vacuum Pump

