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# Study of Gas Hydrate Formation in the Carbon Dioxide + Hydrogen + Water Systems: Compositional Analysis of the Gas Phase

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**ABSTRACT:** Molar compositions of carbon dioxide (and hydrogen) in the gas phase in equilibrium with gas hydrate and aqueous phases were measured for various ($H_2$ + $CO_2$) gas mixtures + water systems in the temperature range of 273.6−281.2 K at pressures up to ∼9 MPa. The compositions of the gas phase were measured using an isochoric technique, in combination with the ROLSI capillary gas-phase sampling and a gas chromatography technique. The compositional data generated in this work are compared with the literature data, and the agreement is found to be generally acceptable.

## 1. INTRODUCTION

Gas hydrate technology is a reversible approach in which pressurized gas such as $CO_2$, $N_2$, methane ($CH_4$), hydrogen ($H_2$), etc. and water are combined to form a crystalline solid, called gas hydrate or clathrate hydrate.[1] In gas hydrates, the gas molecules (called guest molecules) are trapped in special cavities that are composed of hydrogen-bonded water molecules (called host molecules).[1] Gas hydrates are known to have one of three typical hydrate crystal structures: structure I ($sI$), structure II ($sII$), and structure H ($sH$).[1] The type of crystal structure generally depends on the size of the guest molecule.[1]

Considerable research has been devoted in the past decades to examine potential industrial applications of gas hydrates.[1−13] Examples are natural gas storage and transportation, carbon dioxide ($CO_2$) capture from industrial/flue gases, $CO_2$ sequestration, hydrogen ($H_2$) storage, etc.[1,3,5−7,12]

Hydrogen, as a clean and novel energy resource, has gained much attention recently. Consequently, separation, storage, and transportation of this gas are among the new industrial technologies. On the other hand, it is believed that concentration of carbon dioxide ($CO_2$) has significantly increased over the past decades in the Earth's atmosphere, because of human contribution through fossil fuels consumption.[5] Because of its global warming potential, $CO_2$ capture and sequestration (CCS) has become an important area of research to mitigate $CO_2$ worldwide emissions. Since $CO_2$ separation is the most expensive step of the CCS[6,7] process, the challenge is to evaluate and develop energy efficient and environmentally friendly technologies to capture $CO_2$ produced, especially, in large-scale power plants.

Applying gas hydrate crystallization, a reversible process can be designed to replace the current pressure swing adsorption (PSA) methods in order to capture $CO_2$ and separate $H_2$ simultaneously from the generated gas stream after steam reforming operation.[8] Extremely high pressures (typically 100−360 MPa)[9] are needed to stabilize the $sII$ $H_2$ clathrate hydrate; however, $CO_2$ is enclathrated in hydrate cages under moderate pressure conditions.[1] The difference between hydrate formation pressures of these two substances determine the potential of applying gas hydrate approach for the aforementioned process.[8−10]

**Table 1. Literature Review of the Experimental Data on Compositions of the Gas and Hydrate Phases for the Carbon Dioxide + Hydrogen + Water Systems**

| authors | temperature range (K) | pressure range (MPa) | measurement of mole fraction of $CO_2$ in the gas ($y$) and hydrate ($z$) phases |
|---|---|---|---|
| Sugahara et al.[8] | 274.3−281.9 | 1.42−9.13 | $y$ |
| Kumar et al.[11] | 273.9−281.6 | 1.58−10.74 | $y$ |
| Seo and Kang[12] | 274.15 | 6.5 and 8.9 | $y$, $z$ |

To the best of our knowledge, experimental data on compositions of the gas and hydrate phases reported in the literature for the carbon dioxide + hydrogen + water ternary systems are limited. A summary of these data is given in Table 1. This literature review indicates that generating more compositional data for this system is still needed. In this work, experimental data on compositions of the gas phase under hydrate formation conditions for the carbon dioxide + hydrogen + water systems are reported in the temperature range of 273.6−281.2 K at pressures up to ∼9 MPa. An isochoric method,[13−16] combined with capillary gas phase sampling[13,17,18] and compositional analysis,[13] was used to measure the molar compositions of $CO_2$ (and $H_2$) in the gas phase at different equilibrium pressures and temperatures. The compositional data generated in this work are finally compared with literature data.

## 2. EXPERIMENTAL SECTION

**Materials.** Carbon dioxide, nitrogen, and hydrogen were purchased from Air Liquide. All gases with a purity of 99.99 mol %
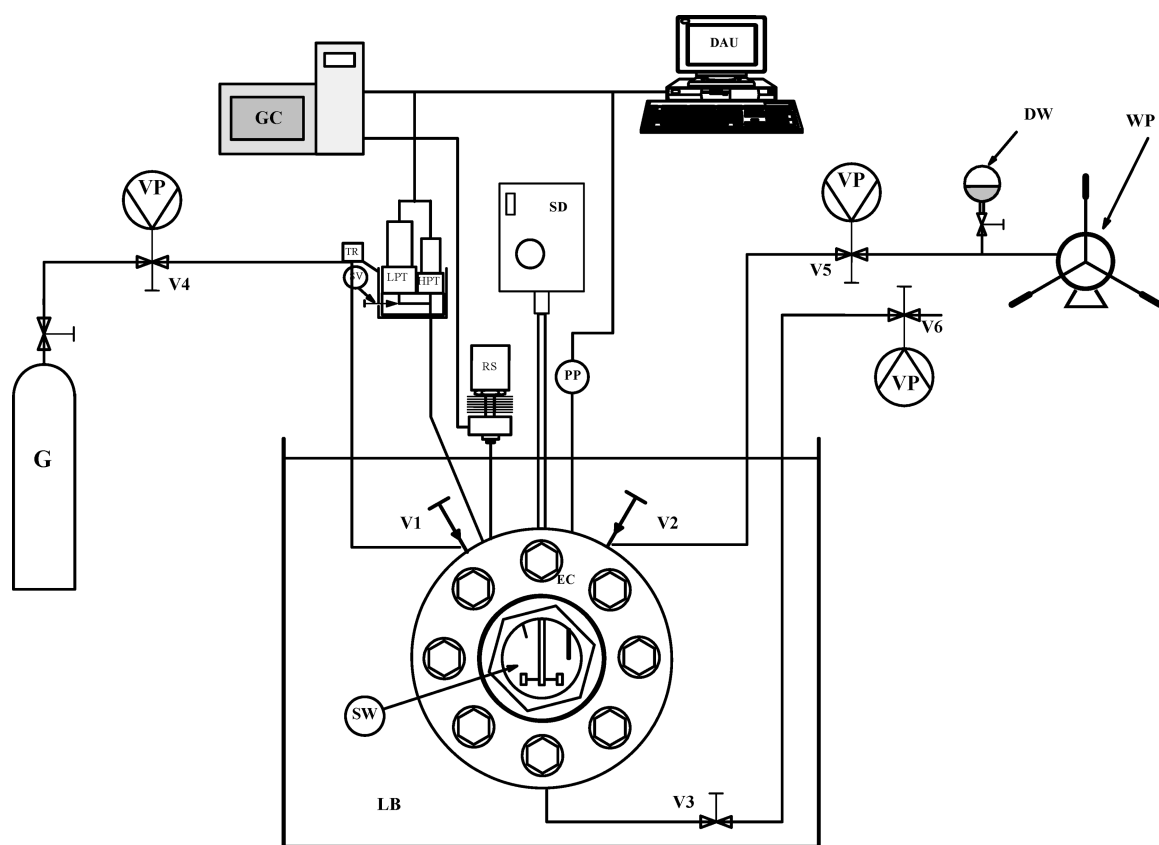
**Figure 1.** Schematic flow diagram of the apparatus. Legend: DAU, data acquisition unit; DW, degassed water; EC, equilibrium cell; G, gas cylinder; GC, gas chromatograph; HPT, "high-pressure" transducer; LB, liquid bath; LPT, "low-pressure" transducer; PP, platinum probe; RS, ROLSI sampler; SD, stirring device; SW, sapphire windows, TR, temperature regulator; $V_1$, $V_2$, $V_4$, $V_5$, feeding valves; $V_3$, $V_6$, purge valves; VP, vacuum pump; SV, isolation valve for LPT; and WP, high-pressure pump.

were used without further purification. Distilled and deionized water was used after careful degassing.

**Experimental Apparatus.** The flow diagram of the experimental setup used for measuring the compositional data is presented in Figure 1. A detailed description of the apparatus and the method used in this study is given elsewhere.[13] Briefly, the apparatus is based on the "static-analytic" technique with capillary gas phase sampling.[13,17,18] It is suitable for measurements at temperatures in the range of 233−373 K. The main part of the apparatus is a cylindrical equilibrium cell that can withstand pressures up to 60 MPa. The equilibrium cell has an inner volume of $201.5 \pm 0.5$ cm$^3$ and two sapphire windows. A motor-driven turbine agitation system (Top Industrie) ensures sufficient agitation to facilitate reaching equilibrium. Compositional analysis of the gas phase was carried out through an electromagnetic online microsampler (ROLSI)[13,17,18] connected to a gas chromatograph (Varian, Model CP3800). Temperature was controlled using a thermostatic bath (Tamson Instruments, Model TV400LT), which allows visual observation of the cell content throughout the experiments. One platinum resistance sensor (Pt100) inserted in the cell interior was used to measure the temperature in situ, within an uncertainty of $\pm 0.02$ K, after calibration against a 25-$\Omega$ reference platinum resistance thermometer. This 25-$\Omega$ reference probe was calibrated, following the ITS 90 protocol, by Laboratoire National d'essais (Paris). Pressure was measured using two pressure transducers (Druck, Type PTX611) for pressures up to 8 and 40 MPa, respectively. After calibration

against a dead weight balance (Desgranges & Huot, Model 5202S CP, Aubervilliers, France), pressure uncertainty was estimated to be within $\pm 0.002$ MPa.

**Experimental Method.** Gas mixtures composed of different ratios of $CO_2$ and $H_2$ were prepared in the previously evacuated equilibrium cell by supplying pure $CO_2$ and pure $H_2$ from the corresponding high-pressure gas cylinders through a pressure-regulating valve. Once temperature and pressure were stabilized, the valve in the line connecting the vessel and the gas cylinder was closed. After gas mixing, the feed gas was sampled and analyzed several times by gas chromatography (GC). For this purpose, the gas chromatograph was equipped with a thermal conductivity detection (TCD) device and a PORAPAK-Q packed column (length = 2 m, outer diameter (OD) = $^1/_8$ in., 80/100 mesh). The TCD device was preliminarily calibrated for $CO_2$ and $H_2$, and nitrogen was used as the carrier gas. The obtained calibration curves were fitted to second-order polynomial equations. The composition of the gas phase under a given equilibrium condition was determined from the peak area ratio of the unknown sample and the coefficients of the corresponding calibration equation for each compound. The experimental uncertainties in molar compositions are estimated to be within $\pm 1\%$.

Once the composition of the feed gas was determined, ~10% (by volume) of the cell was filled with water at a given experimental temperature using a high-pressure syringe pump (Teledyne Isco, Model 260D). All amounts of fluids supplied to

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**Table 2. Compositional Data for the Gas Phase in Equilibrium with the Hydrate and Aqueous Phases at Different Temperatures and Pressures for Various $CO_2/H_2$ Gas Mixtures + Water Systems**

| Gaseous Feed | Liquid Water−Hydrate−Gas Equilibrium | | |
| --- | --- | --- | --- |
| $CO_2$ (mol fraction) | temperature (K) | pressure (MPa) | mole fraction of $CO_2$ in the gas phase |
| 0.780 | 273.6 | 1.888 | 0.686 |
| 0.829 | 273.6 | 1.753 | 0.737 |
| 0.829 | 273.6 | 1.992 | 0.667 |
| 0.508 | 273.6 | 4.669 | 0.317 |
| 0.508 | 273.6 | 7.156 | 0.202 |
| 0.709 | 273.6 | 3.005 | 0.427 |
| 0.829 | 275.2 | 1.984 | 0.764 |
| 0.829 | 275.2 | 2.234 | 0.706 |
| 0.508 | 275.2 | 4.922 | 0.377 |
| 0.508 | 275.2 | 7.442 | 0.225 |
| 0.709 | 275.2 | 2.754 | 0.568 |
| 0.709 | 275.2 | 3.272 | 0.474 |
| 0.709 | 275.2 | 8.282 | 0.188 |
| 0.829 | 276.2 | 2.184 | 0.783 |
| 0.829 | 276.2 | 2.430 | 0.734 |
| 0.508 | 276.2 | 5.131 | 0.388 |
| 0.508 | 276.2 | 7.655 | 0.238 |
| 0.709 | 276.2 | 2.936 | 0.602 |
| 0.709 | 276.2 | 3.442 | 0.502 |
| 0.829 | 277.1 | 2.586 | 0.745 |
| 0.508 | 277.1 | 5.343 | 0.436 |
| 0.709 | 277.1 | 3.162 | 0.620 |
| 0.508 | 278.1 | 5.611 | 0.410 |
| 0.508 | 278.1 | 7.909 | 0.274 |
| 0.709 | 278.1 | 3.417 | 0.640 |
| 0.709 | 278.1 | 3.945 | 0.553 |
| 0.508 | 279.1 | 5.911 | 0.437 |
| 0.508 | 279.1 | 8.278 | 0.316 |
| 0.709 | 279.1 | 4.249 | 0.590 |
| 0.508 | 280.1 | 6.050 | 0.453 |
| 0.508 | 280.1 | 8.521 | 0.354 |
| 0.508 | 281.2 | 8.570 | 0.365 |



**Figure 2.** Pressure−gas-phase-composition ($p$−$y_{CO_2}$) phase diagram for the hydrogen (1) + carbon dioxide (2) + water (3) systems under Lw-H-G equilibrium at different temperatures. Plotted data for this work: (■) 273.6 K, (◆) 275.2 K, (●) 276.2 K, (-) 277.1 K, (+) 278.1 K, (▲) 279.1 K, (−) 280.1 K, and (*) 281.2 K.



**Figure 3.** Pressure−gas-phase-composition ($p$−$y_{CO_2}$) phase diagram for the hydrogen (1) + carbon dioxide (2) + water (3) systems under Lw-H-G equilibrium at different temperatures. Data plotted from this work: (■) 273.6 K, (◆) 275.2 K, (●) 276.2 K, (-) 277.1 K, (+) 278.1 K, (▲) 279.1 K, 280.1 K (−), and 281.2 K (* large). Literature data: (□) 274.3 K,[8] (◇) 276.5 K,[8] (○) 280.1 K,[8] (△) 281.9 K,[8] (× shadow) 273.9 K,[11] (+ large) 277 K,[11] and (* small) 274.15 K.[12]

the equilibrium cell were quantified. The isochoric method[13−16] was followed: the cell was immersed into the temperature-controlled bath and the temperature was decreased to form hydrates while fully agitating the cell contents. The temperature of the system was kept constant for at least 24 h to eliminate the metastability and allow complete hydrate formation. Hydrate formation in the cell was detected visually and confirmed by a noticeable pressure drop. The system was left under this condition for at least 4−5 h or overnight. Once hydrate formation was completed, the molar compositions of the gas phase at given temperature and pressure were determined by gas chromatography. Temperature was then increased in steps at a rate of 0.1 K/h. At each temperature step, temperature was kept constant to allow the system to reach equilibrium. Once pressure was constant, the compositions of the gas phase were analyzed successively about every hour. At least five measurements were carried out every hour until a concentration difference of
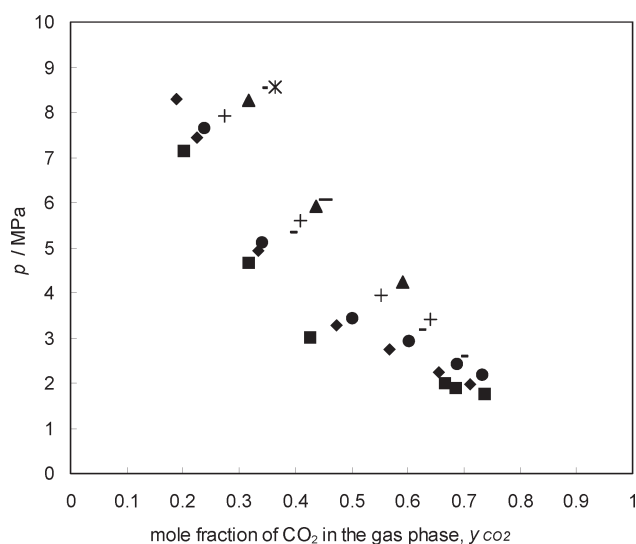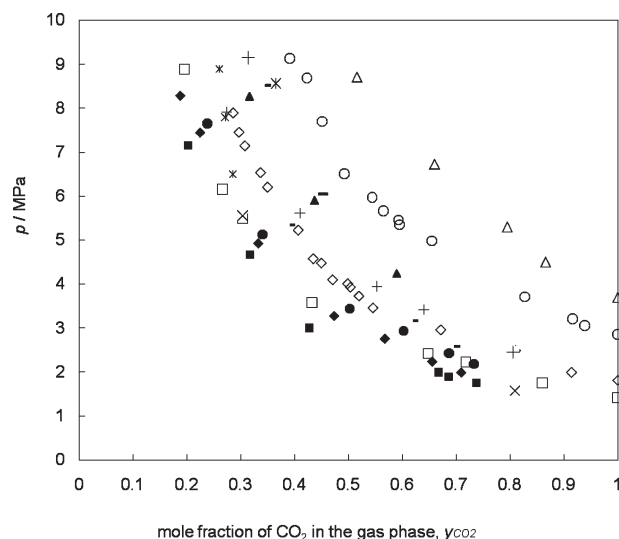
<0.001 mol fraction was obtained. At this point (typically reached within 4 h), it was assumed that equilibrium had been reached and average concentrations were registered as the composition of the gas phase at the corresponding temperature and pressure condition. To measure the equilibrium condition at a higher pressure, the pressure of the system was increased by successively supplying water to the equilibrium cell until achieving the desired pressure. In this way, several pressure ($p$), temperature ($T$), and composition equilibrium data were measured for each feed gas mixture.

**Table 3. Experimental Studies on Molar Compositions of Gas Hydrates Formed in the $CO_2$ + $H_2$ + Water Systems**

| authors | gaseous feed compositions introduced to the system/ $CO_2$ mole fraction | temperature (K) | pressure (MPa) | experimental technique | result |
|---|---|---|---|---|---|
| Sugahara et al.[8] | ND[a] | 274.3—281.9 | 1.42—9.13 | Raman micro-spectroscopy | no $H_2$ cage occupancy was observed |
| Sugahara et al.[9] | ND | 276.5 | 11.2 | Raman spectroscopy using quartz windows | no $H_2$ cage occupancy was observed |
| | ND | 274.3 | 5.06 | direct gas release method | $H_2$ molecules adsorb on the hydrate structure (0.007 water-free base mole fraction in the hydrate phase) |
| Kumar et al.[10] | 0.4 | 163—278 | 8 | powder X-ray diffraction | sI hydrate formed |
| | | | | gas chromatography of released gas from hydrate | 92 mol % $CO_2$ and 8 mol % $H_2$ were trapped in the hydrate phase |
| | | | | $^{13}$C NMR | sI hydrate formed, 100% of the large cages were occupied by $CO_2$ |
| | | | | Raman spectroscopy | sI hydrate formed |
| Seo and Kang[12] | 0.41 | 274.15 | 6.5—8.9 | $^{13}$C NMR | if silica gel is used to form hydrate, 93% of small cages and 100% of large cases are occupied by $CO_2$ the molar composition of $CO_2$ in the hydrate phase was in the range of 96.5—98.7% |
| Kim and Lee[20] | 0.2 | 123.15 | 0.1 | $^1$H MAS NMR gas chromatography of released gas from hydrate | $H_2$ was entrapped in hydrate 92.5% $CO_2$, 7.5% $H_2$ |

[a] Not determined.

## 3. RESULTS AND DISCUSSION

Compositional data for the gas phase in equilibrium with the hydrate and aqueous phases were measured at different pressures and temperatures for various $CO_2$/$H_2$ gas mixtures + water systems. Following the application of Gibbs' phase rule previously justified by Bruusgaard et al.,[19] two degrees of freedom are resulted, under liquid water—hydrate—gas (Lw-H-G) equilibrium for the ternary system studied. In this work, temperature and pressure were controlled while compositions of $H_2$ and $CO_2$ in the gas phase at hydrate equilibrium conditions were measured. The molar compositions of $CO_2$ in the feed gas along with the temperature, pressure, and compositions of the gas phase are given in Table 2 and shown in Figures 2 and 3. (The water concentration in the gas phase is assumed to be negligible). Our experimental results indicate that, as pressure increases, the composition of $CO_2$ in the gas phase decreases for any given isotherm. This may suggest that considerable enrichment of $CO_2$ in the hydrate phase takes place in the studied systems. However, it should be noted that, in $CO_2$/$H_2$ mixed hydrates, the possibility of $H_2$ enclathration into the hydrate cages is still controversial.

As mentioned earlier, Table 1 summarizes the conditions at which experimental data for the gas and hydrate phases have been reported in the literature for the carbon dioxide + hydrogen + water system. In Figure 3, we compare the experimental data measured in this work with the literature data. As can be seen, the gas-phase mole fractions of $CO_2$ measured in this work generally agree with the experimental data reported by Sugahara et al.[8] and Kumar et al.,[11] within experimental uncertainties. However, considerable deviation is observed for the composition of $CO_2$ in the gas phase reported by Seo and Kang[12] at 274.15 K.

The molar compositions of the gaseous components in the hydrate phase for the $CO_2$ + $H_2$ + water system have been the subject of a few studies in the literature.[8−10,12,20] Table 3 summarizes these studies. As can be seen, the contradictory results are mainly due to three factors: (a) temperature and pressure conditions, (b) molar compositions of the introduced gaseous feed to the system, and (c) the experimental techniques. Those who have claimed that $H_2$ can be trapped into the hydrate cages generally conducted their experiments at very low temperatures. Another factor to consider is that they used high ratios of $H_2$ to $CO_2$ in the feed gas. As this composition is increased, the possibility of $H_2$ enclathration into the hydrate cages can be intrinsically increased. Different experimental techniques used for studying the molar compositions of the hydrate phase may also affect the obtained results. Considering these facts, we assume that, under our investigated conditions, only $CO_2$ is trapped inside gas hydrate cavities. However, further experimental work, using suitable physical techniques (e.g., NMR, X-ray, or infrared spectroscopy), is still required to examine this assumption.

## 4. CONCLUSION

We have reported experimental data on molar compositions of the gas phase in equilibrium with hydrate and aqueous phases for

the carbon dioxide + hydrogen + water systems in the temperature range of 273.6—281.2 K at pressures up to ~9 MPa. The measurements were performed using an isochoric method[13−16] combined with capillary gas-phase sampling[13,17,18] and a gas chromatography technique. The experimental data generated in this work were compared with the data reported in the literature,[8,11,12] and acceptable agreement was found. Based on several investigations in the literature,[8,9,10,12,20] one can assume that $H_2$ is not trapped in the hydrate cavities in the present study.

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