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Vapor−Liquid Water−Hydrate Equilibrium Data for the System $N_2 + CO_2 + H_2O$

Hallvard Bruusgaard, Juan G. Beltrán, and Phillip Servio*

Department of Chemical Engineering, McGill University, Montreal, Quebec, H3A 2B2, Canada

Three phase equilibrium conditions for the $N_2 + CO_2 + H_2O$ system in vapor−liquid water−hydrate ($V-L_W-H$) equilibrium were determined. The temperature and pressure conditions studied were in the range of (275 to 283) K and (2.0 to 22.4) MPa, respectively. As the system has 2 degrees of freedom, pressure and temperature were fixed, and gas composition was measured when equilibrium was achieved. The collected data represent points on an equilibrium plane. It was found that along any given isotherm on the plane the hydrate equilibrium pressure increases with increasing mole fraction of nitrogen in the gas phase.

Introduction

Gas hydrates are nonstoichiometric crystalline solids that form when molecules from a gas or volatile liquid, suitable for hydrate formation, are enclosed in a cage consisting of water molecules.[1] Hydrates were first discovered in 1810 by Sir Humphry Davy.[2] During the following 100 years, the interest in these icelike structures was purely academic. Research was put into discovering the different compounds capable of hydrate formation and the respective temperature−pressure conditions at which these hydrates formed. The interest in hydrates accelerated after the discovery of hydrates in gas pipelines in the 1930s when hydrates were found to clog the pipelines, becoming a major concern to the rapidly growing gas and oil industry.[3] Since then, a large amount of industrial resources have been used in the development of inhibitors as well as in finding the thermodynamic properties of hydrate formation.[4] Natural gas hydrates are found in a large amount at the bottom of the ocean as well as in permafrost regions.[5] It is currently estimated that the hydrocarbon reserves found in hydrates exceed more than twice that of all other hydrocarbon sources combined.[6] The use of hydrates in storage of carbon dioxide on the bottom of the ocean has been suggested as a way of reducing greenhouse gas emissions into the atmosphere.[7]

CO_2 and N_2 are known to form S_I and S_{II}, respectively.[8] Davison et al. suggested that nitrogen occupied and stabilized the small cage of structure II.[9] In the case of a gas mixture, the resulting hydrate structure is reported to differ according to the gas ratios. For the N_2-CO_2 system, 85 mol % of N_2 has been reported as the boundary of coexisting S_I and S_{II} hydrate.[10] Seo et al. later performed studies using X-ray diffraction and NMR, and he confirmed that the $N_2 + CO_2$ system forms structure I hydrate at loading compositions from (3 to 20) mol % of CO_2 and structure II at loading composition of 1 % of CO_2.[11] The equilibrium values for the nitrogen + carbon dioxide + water ($N_2 + CO_2 + H_2O$) system in hydrate−liquid water−vapor ($H-L_W-V$) equilibrium have also been previously studied. Fan et al. were among the first to study the mixture at low concentrations of nitrogen.[12] Kang et al. followed this study by reporting equilibrium points for the entire range of gas mixture ratios.[13] In both cases, equilibrium temperature and pressure values are reported along with the loading compositions of gas. In the data presented, the equilibrium vapor phase is assumed constant with changing pressure and temperature. Kang et al. also modeled $H-V$ equilibrium for the $N_2 + CO_2 + H_2O$ system and reported the hydrate−vapor composition. In a more recent study, Linga et al. studied the kinetics of the $N_2 + CO_2 + H_2O$ system, and a few equilibrium points were reported in the study at 273.7 K.[14] This paper presents equilibrium values for the system $N_2 + CO_2 + H_2O$ under $H-L_W-V$ equilibrium: temperature, pressure, and vapor phase composition equilibrium values are reported. The work illustrates the vast difference between loading and equilibrium composition of the gas phase of a mixture. In addition to temperature and pressure, at least one more variable is required to justify the equilibrium point. The work is inspired by previous work by Beltrán et al. performed on a different system.[15] This work acquires the equilibrium points through the use of a new technique, justified by the phase rule applied to binary gas-phase mixtures under $H-L_W-V$ equilibrium. The procedure is described in detail in the Experimental Section, and the application of the phase rule is explained in the Discussion section.

Experimental Apparatus

Experiments were carried out in a Jefri-DBR phase behavior system (Oilphase-DBR- Schlumberger) (Figure 1). The heart of the system was a high-pressure PVT cell consisting of a glass cylinder (20 cm in height and total void volume 150 cm^3), secured between two full-length sight glass windows, inside a stainless steel frame. This design allowed for unimpaired visibility of the entire contents of the cell. Pressure was regulated through an automated, high-pressure, positive displacement pump (Oilphase-DBR-Schlumberger). The hydraulic fluid inside the pump was connected to a floating isolation piston located inside the PVT cell. The piston isolated the hydraulic fluid from the process side of the PVT cell. Controlled displacement of the isolation piston allowed for volume changes in the process chamber, thus providing an effective way to control pressure. The PVT cell was mounted inside a temperature-controlled air bath by means of a bracket, attached to a horizontal shaft. An

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* Corresponding author. Tel.: +1-514-398-1026. Fax: +1-514-398-6678. E-mail: phillip.servio@mcgill.ca.

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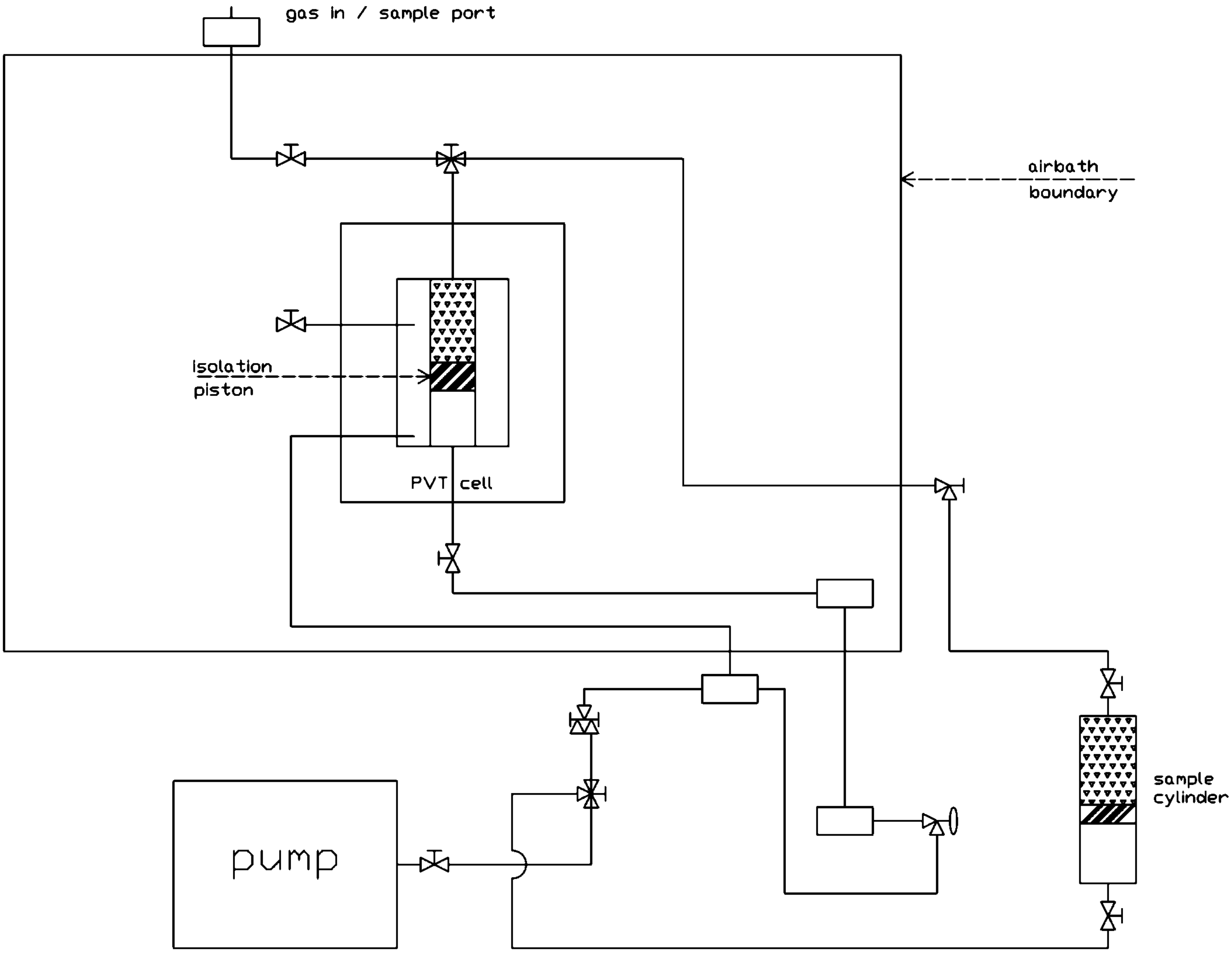

Figure 1. Jefri-DBR phase behavior system.

electric motor powered the shaft, which oscillated through sixty degrees about its center of gravity at forty cycles per minute. Temperature and pressure inside the PVT cell were monitored with a platinum RTD probe and a pressure transducer (both supplied with the phase behavior system). Using a coverage factor of $k = 2$ and assuming the corresponding standard uncertainty had a normal distribution, each expanded uncertainty was estimated to be $U_T = 0.2$ K and $U_P = 14$ kPa, for temperature and pressure, respectively.

Vapor-phase samples were taken using a previously evacuated sample bomb and analyzed with a gas chromatograph (Varian CP3800) equipped with a gas sampling, injection valve. After injection, separation of the gas mixture was achieved by passing the sample through an arrangement consisting of a 0.5 m × 1/8″ precolumn, packed with 80−100 mesh Hayesep T (Varian Inc.), and a 2.6 m × 1/8″ column, packed with 80−100 mesh Hayesep R (Varian Inc.). The effluent was monitored with a thermal conductivity detector.

Experimental Procedure

The process side of the prevacuumed pressure cell was filled with 10 cm^3 of deionized distilled water followed by the addition of a gas mixture. The pressure cell was sealed; the refrigeration unit was started; and the desired temperature was defined. The electrical motor was then switched on to cause the liquid to move to reduce the concentration gradients within the system. The system was pressurized to a value within the hydrate formation region and left overnight to equilibrate and saturate. To form hydrates, it was often found necessary to increase the pressure of the system followed by a rapid drop in pressure. After achieving hydrate formation, it was necessary to force the hydrate from the interface into the bulk. The pressure was lowered temporarily to ensure that all the hydrates on the interface would start decomposing and start dropping into the liquid phase. When all the interfacial hydrates had dropped into the liquid, the system pressure was increased to a value where hydrates would not form on the interface. This step was repeated until a pressure was found where the hydrate appeared as a stable crystal in the bulk. The system was then left to equilibrate, and pressure, temperature, and system volume as well as the presence of hydrates in the bulk were monitored. When all parameters reached steady state values, a gas sample was taken of the gas phase and analyzed in the GC.

The estimated standard uncertainties were as follows: for temperature $u_T = 0.3$ K, for pressure $u_p = 0.03$ MPa, and for vapor phase mole fraction $u_{y1} = 0.02$. With a coverage factor of $k = 2$ and assuming the corresponding standard uncertainty had a normal distribution, each expanded uncertainty was estimated to be $U_T = 0.6$ K, $U_P = 0.06$ MPa, and $U_{y1} = 0.04$.

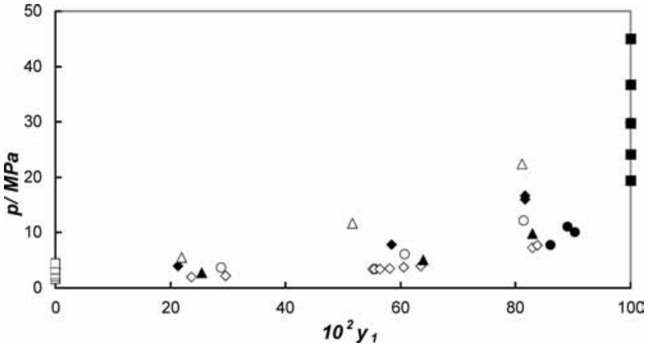

Figure 2. Hydrate−liquid$_{aq}$−vapor equilibrium isotherms for the system containing nitrogen + carbon dioxide + water. Equilibrium, vapor-phase mole fraction of N_2, y_1. Δ, this work at 283 K; ◆, this work at 281 K; ○, this work at 279 K; ▲, this work at 277 K; ◇, this work at 275 K; ●, ref 14 at 273.7 K; □, CO_2 data adapted from ref 17; ■, N_2 data adapted from ref 18.

Results and Discussion

To confirm the accuracy of the system used, pure nitrogen and pure carbon dioxide equilibrium points were determined using the classical isothermal pressure method.[15] The obtained data were found to agree with literature data.[17,18] The obtained data points had a pressure difference of less than 4 % at a given temperature for the two systems when compared to known values.

For binary gas systems under $H-L_W-V$ equilibrium, the phase rule states that the degree of freedom (DF) for the system is 2. By setting the system temperature and pressure, the composition of the various phases will have to adjust accordingly to achieve equilibrium. This means that regardless of the composition of the initial mixture used, the same equilibrium (temperature, pressure, and vapor phase compositions) will have to be achieved. This is valid at any given temperature and pressure which resides between the equilibrium values for the pure components. The result of a system with two degrees of freedom is an equilibrium plane rather than equilibrium lines. Unlike the search methods used on systems containing pure gases to determine equilibrium (isotherm and isobar search method), gas mixture equilibrium can be achieved by fixing temperature and pressure as well as monitoring the internal volume of the system.[16] When the system volume no longer requires adjustments to maintain constant pressure at a constant temperature, the system has reached equilibrium. Gas sampling was conducted several times up to 10 h after the system was at equilibrium to confirm that the gas phase composition was no longer changing.

Figure 2 presents the obtained data for the $N_2 + CO_2 + H_2O$ system in $H-L_W-V$ equilibrium, where mole fraction of nitrogen is plotted vs pressure at various isotherms ranging from (2 to 10) °C. The isotherms represent lines on the $H-L_W-V$ equilibrium plane. The data obtained are also listed in Table 1. It can be seen from the graph that along any given isotherm the hydrate equilibrium pressure increases with increasing mole fraction of nitrogen in the gas phase. The data presented in Table 1 also illustrate the importance of differentiating between loading and equilibrium composition. Loading composition is irrelevant from a thermodynamic point of view. With all components present, any equilibrium point on the equilibrium plane should be possible to achieve from one specific loading composition. However, it is expected that loading composition will affect the kinetics. As most previous data only reported loading composition, the only data points possible to compare to literature values are those for the pure mixtures, as well as the data points provided by Linga.[14] Linga's data do not cover a wide enough range of concentrations to confirm any trends observed in the current data; however, it is worth noticing that the few points reported are located on or very close to the equilibrium plane modeled from the obtained data.

Table 1. Hydrate−Liquid−Vapor Equilibrium Temperature *T*, Pressure *p*, Vapor-Phase Mole Fraction of Nitrogen y_1, and Loading Composition of Nitrogen y_{1L}, for $N_2 + CO_2 + H_2O$ in the $H-L_W-V$ System

T/K	*p*/MPa	$10^2 y_1$	$10^2 y_{1L}$
275.3	1.6	0.0	0.0
275.3	2.0	23.7	20.0
275.3	2.2	29.6	20.0
275.3	3.4	55.7	50.0
275.3	3.4	55.2	50.0
275.3	3.4	55.5	50.0
275.3	3.5	56.4	50.0
275.4	3.6	58.2	50.0
275.3	3.8	60.5	50.0
275.2	4.0	63.5	50.0
275.3	7.3	83.0	79.0
275.4	7.7	83.8	79.0
275.6	20.1	100.0	100.0
277.4	2.7	25.5	20.0
277.2	5.1	63.9	50.0
277.4	9.9	83.0	79.0
279.4	3.6	28.9	20.0
279.0	6.1	60.7	50.0
279.3	12.1	81.5	79.0
281.0	4.0	21.3	20.0
281.1	7.8	58.4	50.0
281.1	16.0	81.7	79.0
281.1	16.7	81.7	79.0
282.9	5.5	22.0	20.0
283.1	11.7	51.7	50.0
283.0	22.4	81.1	79.0

Conclusion

Equilibrium conditions for the $N_2 + CO_2 + H_2O$ system in $H-L_W-V$ equilibrium were determined, and temperatures, pressures, and vapor phase compositions were reported. Experimental isotherms of the system were presented. It was found that along any given isotherm the hydrate equilibrium pressure increases with increasing mole fraction of nitrogen in the gas phase. Due to the lack of current literature values, no data or trend comparison was possible.

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