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Hydrate Formation of Hydrogen + Hydrocarbon Gas Mixtures

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Hydrate formation conditions of hydrogen + hydrocarbon gas mixtures ($H_2 + CH_4$, $H_2 + C_3H_8$, $H_2 + CH_4 + C_3H_8$, and $H_2 + CH_4 + C_2H_6 + C_3H_8$) in pure water have been measured in a sapphire cell using the "pressure search" method. The experimental temperature range was (274−280) K, and the pressure-range was (0.65−7.0) MPa. The hydrogen content in the gas mixtures varies from 22 mol % to 92 mol %.

Introduction

Hydrogen + hydrocarbon gas mixtures occur widely in petroleum refining and petrochemical processes. Pure hydrogen cannot form clathrate hydrates, because its molecule size is too small. However, gas mixtures containing hydrogen and light hydrocarbons (methane, ethane, and propane) are capable of forming hydrates. Hence, it is of interest to study the feasibility of separating hydrogen from light hydrocarbons by hydrate formation carried out at medium pressure and a temperature slightly above 0 °C. Phase equilibrium data are the basis of developing such an innovative separation process. Unfortunately, only limited hydrate formation data relating to hydrogen-containing gas mixtures that occur in coal gasification and coal liquefaction processes are available in the open literature.[1−3]

In this work, as a first step in investigating the feasibility of developing a hydrogen recovery process based on hydrate technology, we have systematically measured hydrate formation data for 12 synthetic hydrogen + hydrocarbon gas mixtures (including binary, ternary, and quaternary mixtures) using the "pressure search" method. The experimental temperature range was (274−280) K, and the pressure range was (0.65−7.0) MPa. The hydrogen content in the gas mixtures varies from 22 mol % to 92 mol %.

Experimental Section

Experimental Apparatus. The apparatus used in this work has been described in detail in our previous papers.[4−6] The schematic diagram of the apparatus is given in Figure 1. The apparatus consists of a cylindrical transparent sapphire cell (2.54 cm in diameter, effective volume 60 cm^3) installed in an air bath and equipped with a magnetic stirrer for accelerating the equilibrium process. The formation/dissociation of the hydrate crystals in the solution can be observed directly through the transparent cell wall. The accuracies of temperature and pressure measurements are ±0.2 K and ±0.025 MPa, respectively.

Materials and Preparation of Samples. Analytical grade (99.99%) hydrogen, methane, and propane supplied by Beifen Gas Industry Corporation were used in preparing the synthetic gas mixtures. A Hewlett-Packard gas chromatograph (HP5880A) was used to analyze the composition of gas samples.

Table 1. Hydrogen + Hydrocarbon Gas Mixtures Studied

	composition (mole %)			
mixture	H_2	CH_4	C_2H_6	C_3H_8
M1	36.18	63.82		
M2	22.13	77.87		
M3	87.22			12.78
M4	81.64			18.36
M5	74.18			25.82
M6	44.89	30.30		24.81
M7	52.78	24.58		22.64
M8	73.19	12.20		14.61
M9	92.11	2.79		5.10
M10	70.82	16.55	6.09	6.54
M11	79.14	12.37	3.58	4.91
M12	88.93	5.31	1.93	3.83

Table 2. Hydrate Formation Conditions of Hydrogen + Hydrocarbon Gas Mixtures

T/K	P/MPa	T/K	P/MPa	T/K	P/MPa
M1		M2		M3	
274.3	4.46	274.3	3.72	275.2	2.20
275.3	4.85	275.4	4.03	276.2	2.58
276.3	5.32	276.2	4.36	277.3	3.20
277.3	5.88	277.2	4.75	278.3	4.00
278.2	6.63	278.2	5.34		
M4		M5		M6	
274.2	1.26	274.2	0.85	274.8	0.65
275.2	1.44	275.2	1.01	275.2	0.68
276.3	1.74	276.2	1.30	276.2	0.77
277.3	2.22	277.2	1.70	277.1	0.88
278.1	2.72	278.2	2.40	278.4	1.08
M7		M8		M9	
274.5	0.70	274.2	1.44	274.2	2.74
275.3	0.76	275.3	1.72	275.3	3.08
276.2	0.87	276.2	2.06	276.2	3.43
277.4	1.04	277.3	2.48	277.3	4.04
278.2	1.15	278.3	3.02	278.4	4.98
		279.3	3.64		
		280.2	4.44		
M10		M11		M12	
274.1	1.14	275.3	1.46	274.5	3.56
275.3	1.35	276.3	1.78	275.4	4.06
276.1	1.57	277.3	2.16	276.5	4.76
277.0	1.86	278.5	2.57	277.3	5.56
278.4	2.32	279.2	3.28	278.4	7.02
279.2	2.96				

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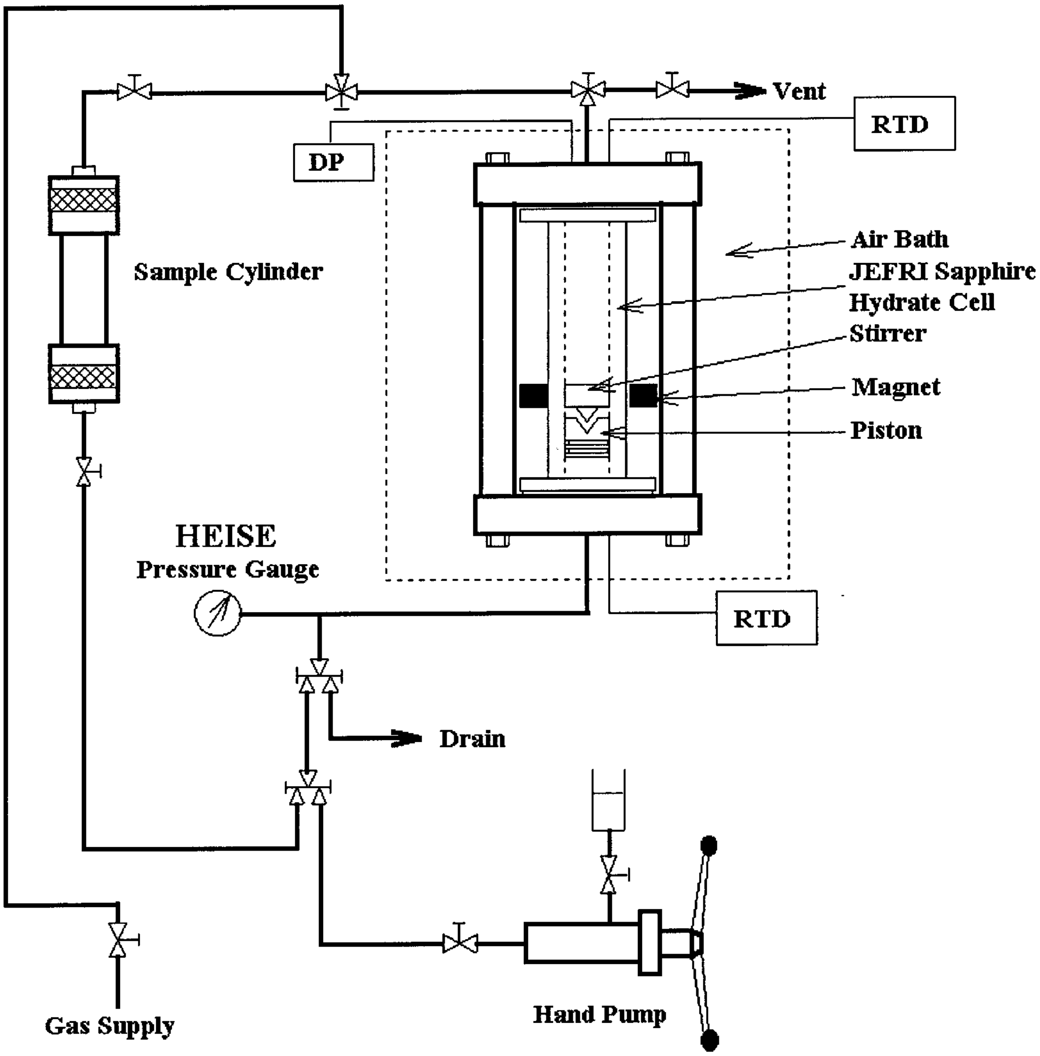

Figure 1. Schematic of the experimental apparatus: DP, differential pressure transducer; RTD, resistance thermocouple detector.

Experimental Procedure. First, the transparent cell was washed using distilled water; then it was rinsed three times with deionized water. After the cell was thoroughly cleaned, about 10 cm^3 of deionized water was added to the cell and the cell was placed in the air bath. The vapor space of the cell was purged with the gas mixture under study. A gas sample was collected and analyzed to ensure the absence of air. The air bath temperature was then adjusted to the chosen temperature. Once the temperature was stabilized, the pressure in the cell was increased to ~1 MPa higher than the estimated equilibrium pressure (using in-house software) via the floating piston. When a trace of hydrate was observed, the pressure was reduced slightly to let the hydrate crystals decompose slowly. When all the hydrate crystals disappeared, the pressure of the system was then raised by a small pressure step of 0.05 MPa until the hydrate appeared again. When the temperature and pressure of the system could be maintained constant for 4−6 h with a trace amount of hydrate crystal present (clinging to the cell wall or floating on the water), the system was taken at the equilibrium condition.

If all the hydrate crystals were decomposed during the period, the pressure of the system was increased slightly until a trace of hydrate crystals appeared again and the above-mentioned observation was repeated. Once the equilibrium pressure at a chosen temperature was established, the experimental run was terminated. For each gas mixture the above operation was repeated for a series of temperatures. The uncertainties of the temperature and pressure measurements are ±0.2 K and ±0.04 MPa, respectively.

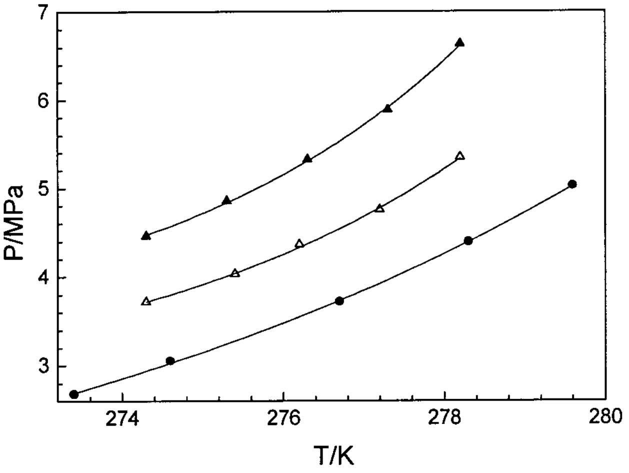

Figure 2. Hydrate formation conditions of hydrogen + methane gas mixtures: (●) pure methane;[7] (▲) M1; (△) M2.

Experimental Results and Discussion

The compositions of the 12 synthetic hydrogen + hydrocarbon gas mixtures studied in this work and the hydrate

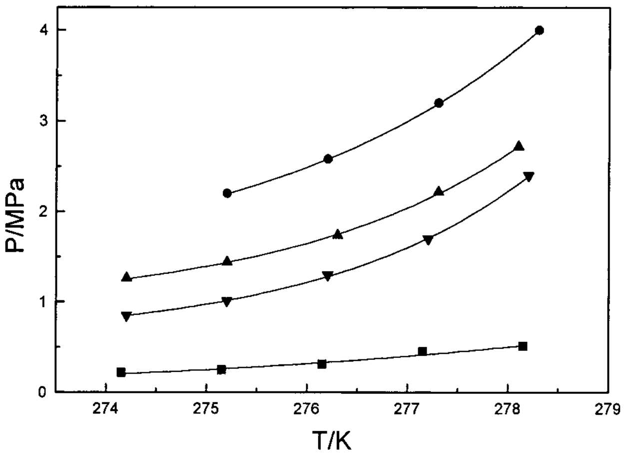

Figure 3. Hydrate formation conditions of hydrogen + propane gas mixtures: (■) pure propane;[8] (●) M3; (▲) M4; (▼) M5.

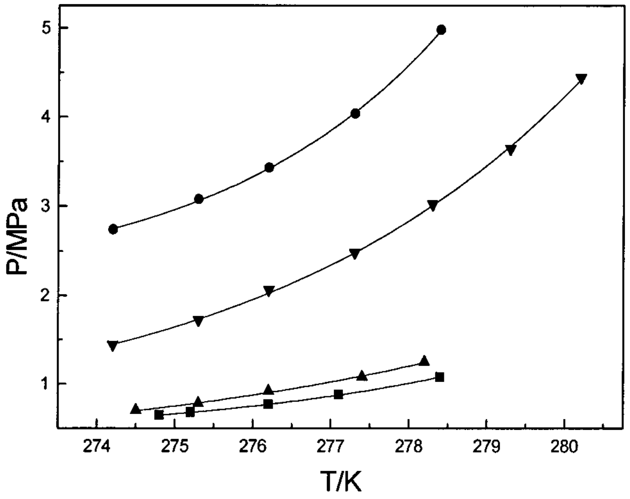

Figure 4. Hydrate formation conditions of hydrogen + methane + propane gas mixtures: (■) M6; (▲) M7; (▼) M8; (●) M9.

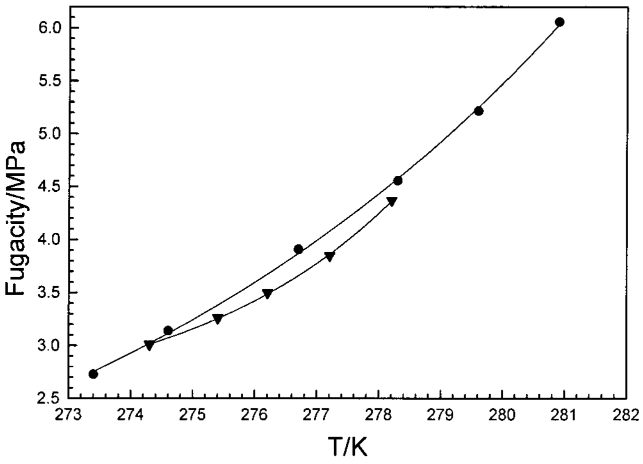

Figure 5. Comparison of the partial fugacity and pure component fugacity of methane at hydrate formation conditions: (▼) M2; (●) pure methane.[7]

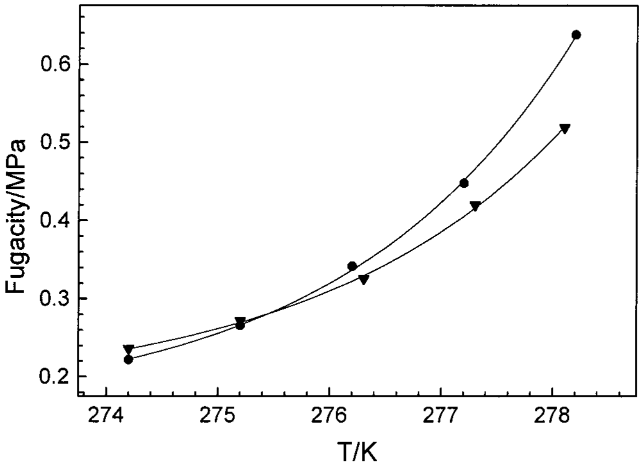

Figure 6. Comparison of the partial fugacity and the pure component fugacity of propane at hydrate formation conditions: (▼) M4; (●) pure propane.[8]

formation conditions (*T* and *P*) for each gas mixture are tabulated respectively in Tables 1 and 2. Typical results are plotted in Figures 2−4.

The experimental results indicate that the hydrate formation pressures of hydrogen + methane and hydrogen + propane gas mixtures are higher than those for pure methane[7] and pure propane.[8] It is reasonable that the partial pressure of methane/propane in a gas mixture is lower than the system pressure.

Figures 5 and 6 show the comparisons of the partial fugacity of methane/propane in a mixture containing hydrogen with the fugacity of pure methane/propane at various hydrate equilibrium conditions. The fugacities were calculated using the modified Peng−Robinson equation of state for hydrogen-containing systems proposed by Liu and Wang.[9] It can be seen from these figures that the presence of hydrogen shows little effect on the difference between the partial fugacity and the pure component fugacity of methane/propane at $T < 275$ K; however, the effect on propane could be significant at higher temperatures.

Conclusions

The hydrate formation data of 12 hydrogen + hydrocarbon gas mixtures were measured in the temperature range (274−280) K and the pressure range (0.65−7.0) MPa using the "pressure search" method. The reported data are valuable for studying the feasibility of separating hydrogen from light hydrocarbons through hydrate technology and for testing the existing hydrate models/software. The preliminary results obtained by the undergoing separation experiments on the (H_2 + CH_4) system are encouraging; the hydrogen content in a (H_2 + CH_4) mixture could be enriched to ~90 mol % under medium pressure (<5 MPa) at (274−276) K.

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