

New Developments in Hydrogen Storage

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Abstract

In this work, phase behaviour measurements on the binary clathrate hydrate system cyclopentane + H₂ are reported. Cyclopentane was found to be a better promoter than tetrahydrofuran for the synthesis of hydrogen clathrate hydrates. Besides phase equilibrium data also experimental information on the kinetics of formation and decomposition of the cyclopentane promoted hydrogen clathrate hydrate is reported in a pressure range from 2.5 up to 10.0 MPa. Although cyclopentane is a water insoluble promoter (contrary to tetrahydrofuran), it also forms structure sII clathrate hydrate with hydrogen.

1. Introduction

Clathrate hydrates are crystalline structures consisting of cages that are formed by hydrogen-bonded water molecules. In these cages guest molecules can be hosted and, depending on their geometry and strength of interaction they may have with the surrounding water molecules, they can be stabilized such that their melting point can be significantly above the melting point of pure ice at the same pressure [1]. The potential of these compounds to store hydrogen was first described by Mao et al. [2]. They showed that hydrogen clathrate hydrate could be stabilized at extreme conditions only, i.e. at pressures up to 230 MPa. The storage of hydrogen in its molecular form in the clathrate cages offers some advantages that make them attractive for further study, as it is of great interest to stabilize the hydrogen hydrates at relatively low pressures and elevated temperatures to explore the possibility of using these solids as a safe hydrogen storage material in the transportation sector. Florusse et al. [3] proved that application of a second guest molecule, tetrahydrofuran, made it possible to stabilize the hydrogen clathrate hydrate at pressures as low as 5.0 MPa and at near ambient temperatures. The search for better promoters and clathrate hydrate structures as well is an active field of research as there is the need to discover molecules able to stabilize the system at more attractive conditions for mobile applications. At the same time, another extremely important question regards the kinetics of formation and decomposition of gas hydrates [4,5]. The most challenging area in hydrates is to move beyond the time-independent thermodynamics, to time-dependent kinetic measurements. Two questions are essential for a better knowledge of gas hydrates, and these are, when will the hydrates be formed and how fast will they dissociate [1]. Published information on the kinetics of formation of hydrogen hydrates is sparse. Lee et al. [6] make a brief reference to this subject to demonstrate that the presence of a dispersed phase should improve the kinetics. The interest in these new experiments relies on the fact that cyclopentane is an insoluble molecule in water, contrary to our previous experiments with THF, that is water soluble. The rates of formation and decomposition of the clathrate hydrates have to be considered for large-scale applications of storage and transportation. In this study, cyclopentane (CP), known to be sII hydrate former was tested and the hydrate forming conditions are presented. This work also presents kinetics of hydrate formation and dissociation at different conditions for the binary system H₂ + CP.

2. Experimental

2.1 Materials

Cyclopentane (CAS [287-92-3]), was purchased from Merck. Doubled distilled water was used. Hydrogen, (99.998 mol %) was supplied by Hoek Loss. All chemicals were used without any further purification.

2.2 Experimental Procedure: Phase Behavior

The measurement of the melting curves of the systems cyclopentane + water and H₂ + cyclopentane + water were performed in a caillietet equipment in a similar manner to that described by Raessi et al. [7]. Briefly, samples consisting of both components are confined in the top-end of a capillary glass tube and sealed by a mercury column. The composition of the sample is determined from the injected amount of

cyclopentane and water and the reading of the pressure of the gas, when hydrogen is present, in a calibrated volume at a known temperature. The capillary tube is placed into an autoclave, where the mercury reservoir is connected to a hydraulic oil system that can be pressurised with a screw-type hand-pump. In this way, the mercury column is both a seal for the sample and pressure-transmitting medium. The sample can be kept at a constant temperature, within 0.01 K, by circulating a heat-transferring medium around the tube with a thermostatic bath (Lauda). The temperature of the fluid near the top of the tube is read by a platinum resistance thermometer (A Laboratories) with an accuracy of 0.01 K. The pressure conditions of the phase transitions are measured with a dead-weight pressure gauge (de Wit), with a smallest weight of 0.005 MPa.

2.3 Experimental Procedure: Kinetics

A high-pressure stainless steel vessel with an internal volume of approximately 150 cm³, is immersed in a thermostatic bath cooled by means of a controller that maintained the temperature within ± 0.1°C. The refrigeration was provided by a cryostat and a mixture of ethylene glycol + water was used as the cooling medium. The temperature inside the vessel was monitored both in the gas phase and in the liquid phase by two thermocouples (New Port Omega type T), which have an accuracy of 1.0 °C. The vessel is initially loaded with a mixture of 5.6 wt % of the promoter (cyclopentane) in double distilled water (3.8 mol) and a magnetic internal stirrer. Hydrogen is added into the cell until the desired pressure is attained. The pressure inside the cell is measured with a pressure transducer (a piezo-resistive AE SML series pressure sensor, 0 to 25 MPa). The pressure and temperature of the system were monitored by a computer based data acquisition system.

A typical experiment began by loading the high pressure vessel with the sample (water + promoter). The air in the system was flushed by loading the vessel with hydrogen and subsequently releasing the pressure. This procedure was repeated three times and hence the concentration of nitrogen and oxygen was in the ppm range. The initial temperature was set to 282 K for all experiments, and after the temperature stabilized the system was pressurized with hydrogen to the desired operating pressure. The temperature of the system was then slowly reduced while the system was being stirred. The temperature was never lowered below 273 K to prevent the formation of ice instead of the gas hydrate. Pressure and temperature changes were monitored by the data acquisition system that collected data every 40 seconds.

When the hydrate was formed the reverse process was carried out. When pressure and temperature are stable, i.e., when the hydrate growth stopped, the system was slowly heated up to the initial temperature without any stirring. The system was allowed to reach equilibrium while the computer was acquiring the changes in pressure and temperature.

3. Results and Discussion

3.1 Phase Equilibrium Measurements

This work presents experimental data on the equilibrium conditions for structure II hydrogen hydrates, using cyclopentane as a promoter. Figure 1 depicts the phase equilibrium results for the systems studied.

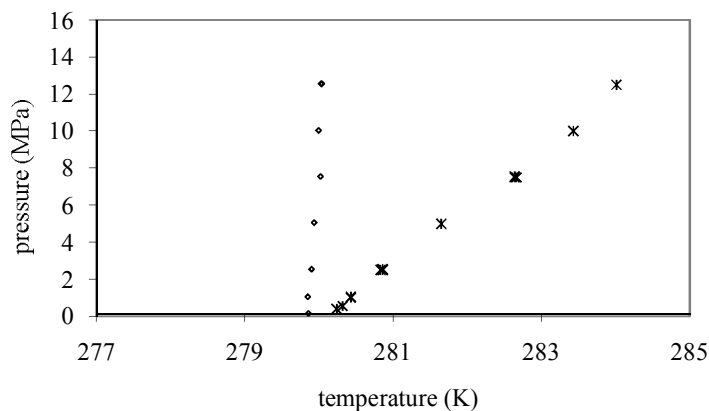


Figure 1. Melting curves for the systems cyclopentane + water (◇) hydrogen + cyclopentane + water (*).

The p, T diagram presented corresponds to the melting curves of the hydrates, i.e., the maximum temperature at which the hydrate is stable for a given pressure. The experimental data points limit the region where a solid phase, that is to say hydrogen hydrate, exists. As it can be observed the formation of the pure cyclopentane hydrate is temperature independent, i.e., for any given pressure, the temperature of hydrate formation is nearly the same.

3.2 Kinetic measurements

The better understanding of clathrate hydrates involves the performance of time dependent kinetic experiments. The interest in these new experiments relies on the fact that cyclopentane is an insoluble molecule in water, contrary to our previous experiments with THF, that is water soluble. Figure 2 shows the pressure and temperature trace for the experiment run at 2.5 MPa.

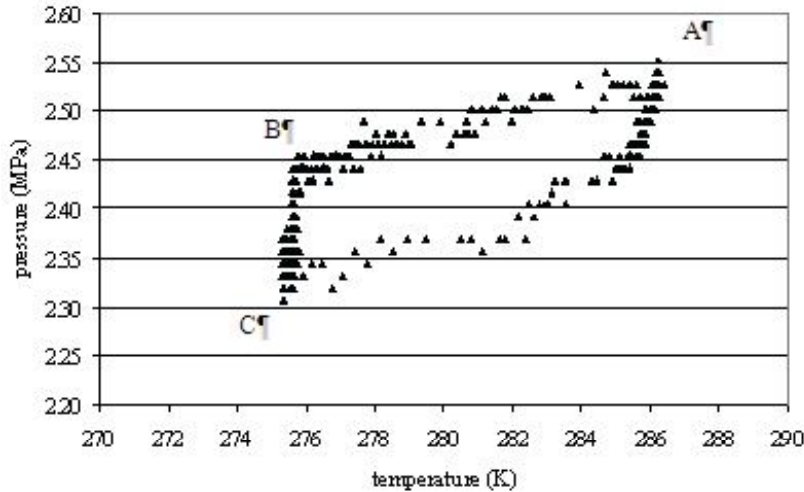


Figure 2. Pressure-temperature pathways during formation and decomposition of hydrogen hydrates.

In the beginning of the experiment (point A) temperature is stable and the system was pressurized with hydrogen. Cooling and stirring started at this moment. From A to B, as the temperature is lowered, the pressure also decreases, due to two effects: firstly the solubility of the gas in the liquid phase and secondly due to gas contraction upon cooling. At point B the hydrate starts to be formed at approximately constant temperature and there is a sharp decrease in pressure due to the entrapment of the gas in the solid phase. The dissociation of the hydrate begins when the system is heated to the initial temperature. Pressure starts increasing again due to the increase in temperature until a certain temperature where the hydrate dissociates and the gas entrapped in the solid phase is completely released.

Each data point (p,T) can be converted into the number of moles using the the following equation for real gases:

$$P \cdot V = n \cdot Z \cdot R \cdot T$$

P is the pressure, V is the volume of the gas phase, n is the number of moles of hydrogen present in the gas phase, Z is the compressibility factor, R is the gas constant and T is the temperature of the gas phase. The factor Z is calculated from the cubic equation of Peng and Robinson:

$$Z = \frac{1}{(1-b/V)} - \frac{a(T)}{RT} \frac{1}{(V+2b-b^2/V)}$$

wherea $a(T)$ and b are expressed in the form:

$$b = \frac{0.07780RT_c}{P_c}$$

$$a(T) = 0.45724 \frac{(RT_c)^2}{P_c} \left[1 + \beta(1 - \sqrt{T/T_c}) \right]^2$$

$$\beta = 0.37464 + 1.5422\omega - 0.26992\omega^2$$

As it can be seen, the p, T trace during formation and decomposition of the hydrate is quite similar to the one that was obtained for the system THF + H_2 . However, when we consider the time scale there is an enormous difference on the behaviour and rate of formation of the two different types of hydrates. At the same initial pressure the system with THF forms much faster (Figure 3). This is due to the fact that THF is a water-soluble compound whereas CP is not.

An interesting observation is the fact that for the same initial pressure the hydrogen uptake is very similar in both systems. In Figure 4 the effect of the initial pressure on the number of gas moles consumed is evidenced.

Table 1 summarizes the experiments performed with the system cyclopentane + H_2 .

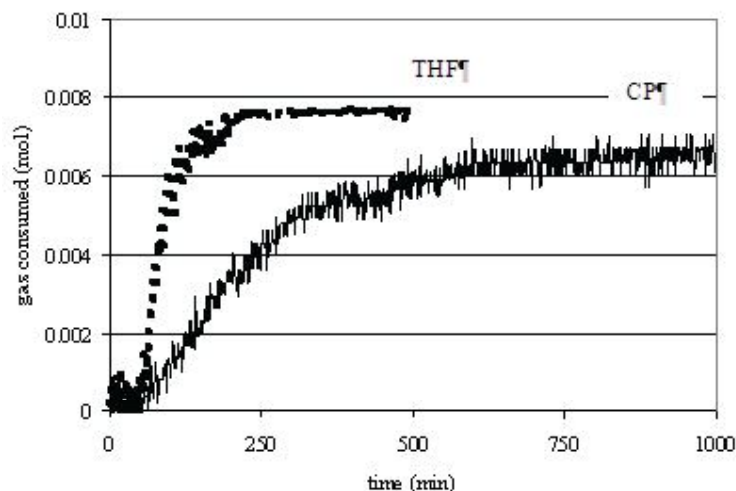


Figure 3. Hydrogen uptake (5.5 MPa) for the systems THF + H_2 and cyclopentane + H_2 .

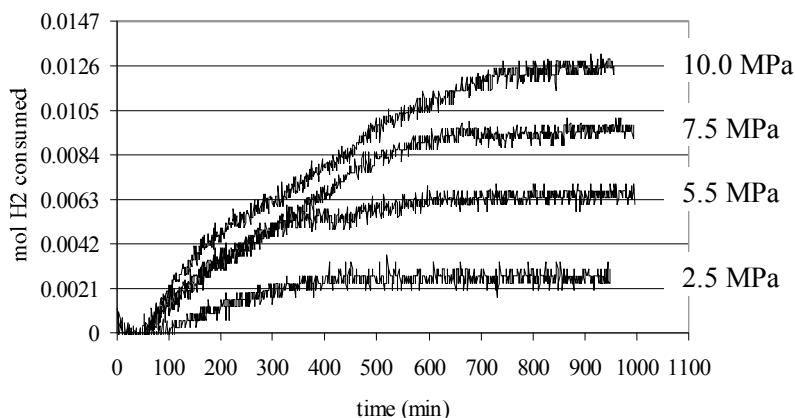


Figure 4. Hydrogen uptake for the system cyclopentane + H_2 at different initial pressures.

Table 1. Experiments performed with the system cyclopentane + H_2 .

# Experiment	Pressure (MPa)	Hydrogen in solid phase (mmol)
1	2.5	2.7
2	5.5	6.7
3	7.5	9.5
4	10.0	12.6

Regarding the hydrogen release from the binary system cyclopentane + H₂ the dissociation of the hydrate as a function of time is presented in Figure 5. A comparison with hydrogen release from the clathrate hydrate stabilized with THF is shown in Figure 6.

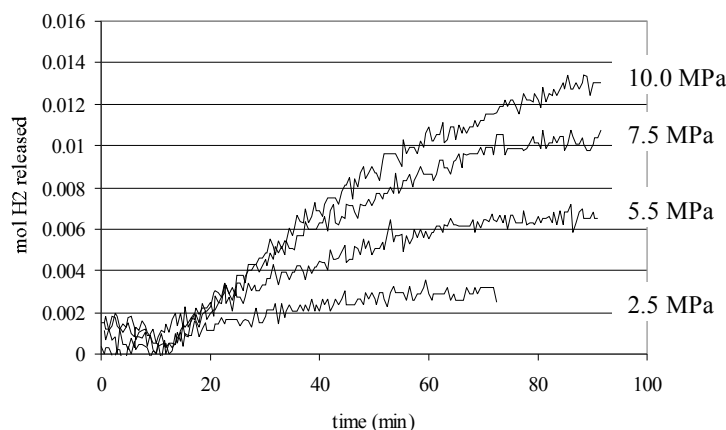


Figure 5. Hydrogen release for the system cyclopentane + H₂ at different pressures.

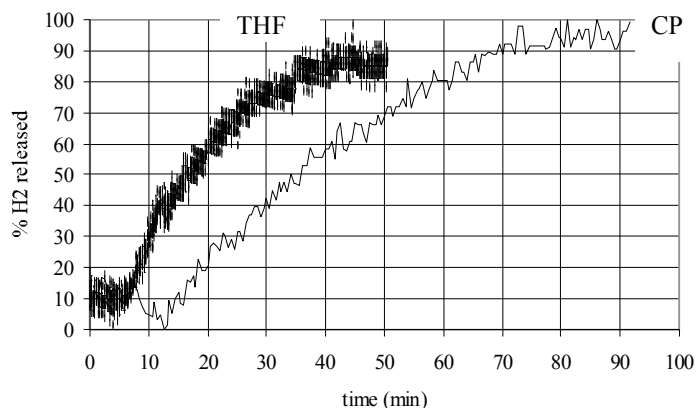


Figure 6. Hydrogen release (7.5 MPa) for the systems THF + H₂ and cyclopentane + H₂.

From these experiments we can observe that the release of hydrogen is much faster from the hydrate stabilized with THF and nearly 80% is released after 30 min. For the system stabilized with cyclopentane the release is slower and the same 80% of hydrogen are released in 1 hour. These results are very important to evaluate the feasibility of gas clathrate hydrates for mobile applications.

4. Conclusions

Phase behaviour on a new clathrate system is presented. Hydrogen hydrates can be synthesized at pressures as low as 1 bar when cyclopentane is used as promoter. Additionally, experimental data on the kinetics of hydrogen hydrates formation is presented in this work. Data evidences the pressure influence on amount of hydrogen stored in the hydrate phase, when increasing the initial pressure, the number of moles of gas consumed also increases. Comparing with the kinetics of the system THF + H₂, the amount of hydrogen stored is similar, however when the time scale is considered there is a large difference between the two systems. While hydrogen hydrates are formed in less than 50 minutes for the system using THF as an additive molecule, it takes nearly ten times more for the hydrogen clathrate to be formed with cyclopentane. This is due to the fact that THF is a water-soluble molecule whereas cyclopentane is water-insoluble. The same effect is observed during the hydrate decomposition step. However, to have a slower hydrogen release from the hydrate, can be beneficial for some applications.

Acknowledgements

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Author Biography

Dr. Peters is an internationally recognized scholar in Chemical Engineering. He has been a motivating driving force at the Laboratory for Applied Thermodynamics and Phase Equilibria of the Delft University of Technology in The Netherlands. This laboratory is without question the most outstanding laboratory for phase equilibrium studies in the world. At this laboratory Cor Peters has made outstanding original contributions to the understanding of complicated phase equilibria, not only in binary but also in multi-component fluid mixtures. Dr. Peters is an experimenter and thermodynamic modeler characterized by high standards of quality and by audacious undertaking of projects of considerable complexity. He has received and continues to receive many invitations to lecture at International Conferences. His list of plenary and keynote lectures at major international meetings can compete with that of any distinguished professor.