

## Abstract

Gas hydrates are a crucial issue in many fields, from oil & gas industry, to carbon capture and storage, air conditioning, or even planetary science. They also have an enormous potential as an energy resource because of the tremendous quantity of methane trapped within them. To understand better the gas hydrates phenomena, understanding of the thermodynamics and the crystallization mechanisms of clathrate hydrates are required. The determination of the hydrate composition and volume is also a technical challenge and we recall in the paper the method used by our laboratory. In this work, several experiments were performed to obtain precious experimental data and the gas compositions in hydrate phase. GasHyDyn group has recently found out that the composition of gas hydrate is sensitive to the crystallization conditions. Hence in this work, it was tried to understand better the relation between the composition of hydrate during the crystallization and final state and crystallization rates. Experiments were performed in a batch reactor and there were an online gas chromatography connected to the experimental set-up and an off-line ion-chromatography to measure the gas compositions and liquid compositions, respectively. Based on these data and mass balance, the gas compositions in hydrate phase and hydrate volume can be calculated. During the last decade, our GasHyDyn team has also measured equilibrium data for many gas mixtures, and this document adds new data involving propane. In the present work, the experimental results are discussed after formation following two different experimental protocols: at quick and slow rates of crystallizations. It was observed that, from the same initial conditions, the final pressure and water conversion for two different procedures are slightly different.

## Experimental Set-up

For performing the experiments, a system (called SECOHYA) consists of a 2.36 liter autoclave reactor has been used. The reactor is equipped with two vertical stirrers with four blades, one in the liquid and one in the gas. The temperature is controlled by a cryostat. The liquid is injected in the reactor under pressure by using a HPLC pump. Temperature is monitored by two probes, one in the gas phase and the other one in the liquid phase. The pressure is measured with an accuracy of 0.01 MPa. A ROLSI sampler allows to take online sample of gas and to send it into a gas chromatograph. Liquid sample can be taken by a mechanical valve and a capillary tube. The liquid is analyzed off-line by ion chromatography (Fig. 1).

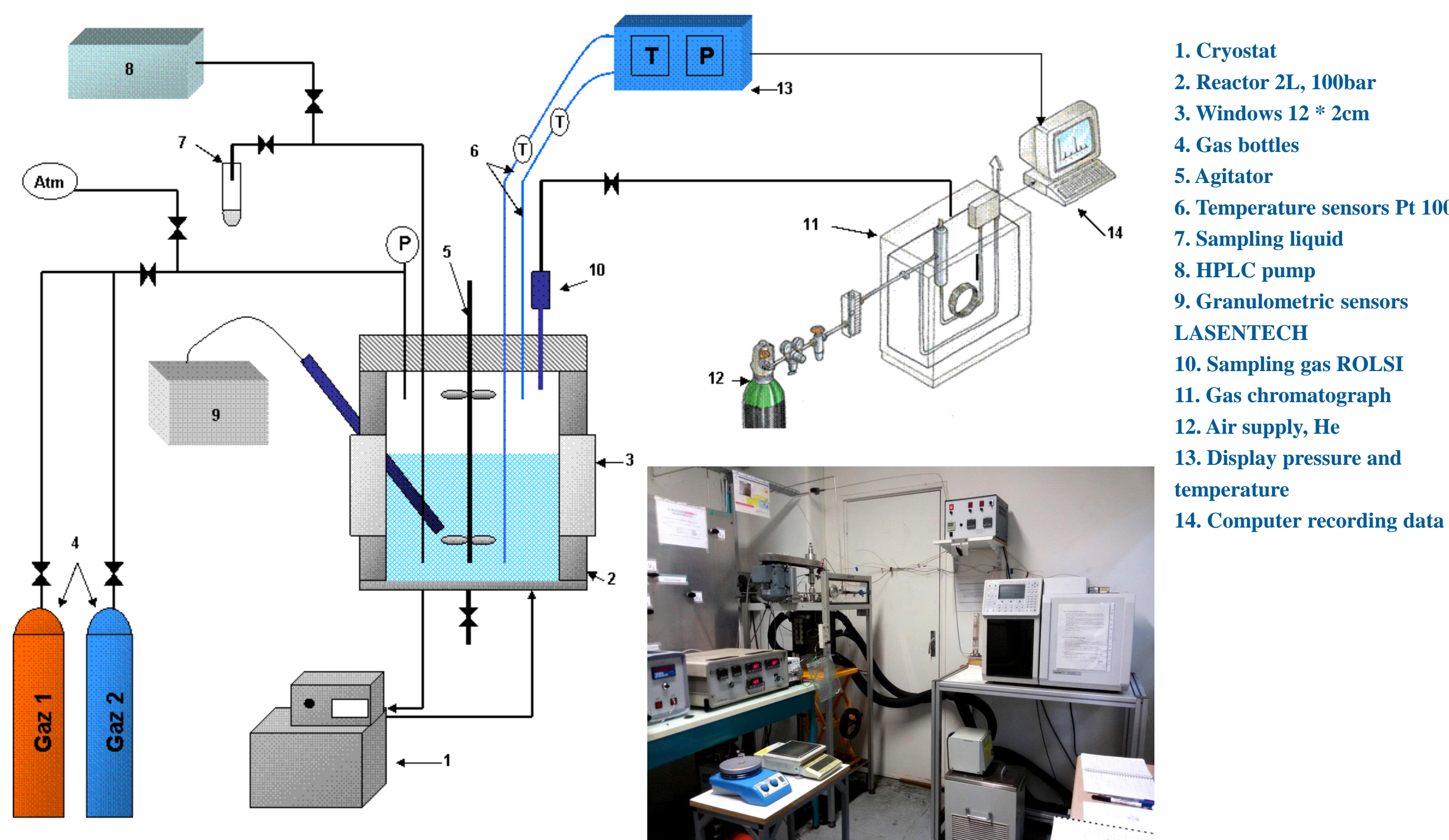


Fig. 1. The schematic diagram of the apparatus

## Experimental Procedures

In this work, we have investigated two types of crystallization; quick and slow crystallization rates, which are based on the same initial conditions. The goal is to point out the differences between the initial solution composition and the final solution composition, and to establish a link between the final state and the crystallization rate. In quick procedure, the crystallization occurs at a high supersaturation (Fig.2). But in slow procedure, Instead of decreasing very quickly the temperature to the final state, the temperature is decreased very slowly (Fig. 3). The objective of this procedure is to focus on thermodynamic equilibrium, limiting as much as possible kinetic effects.

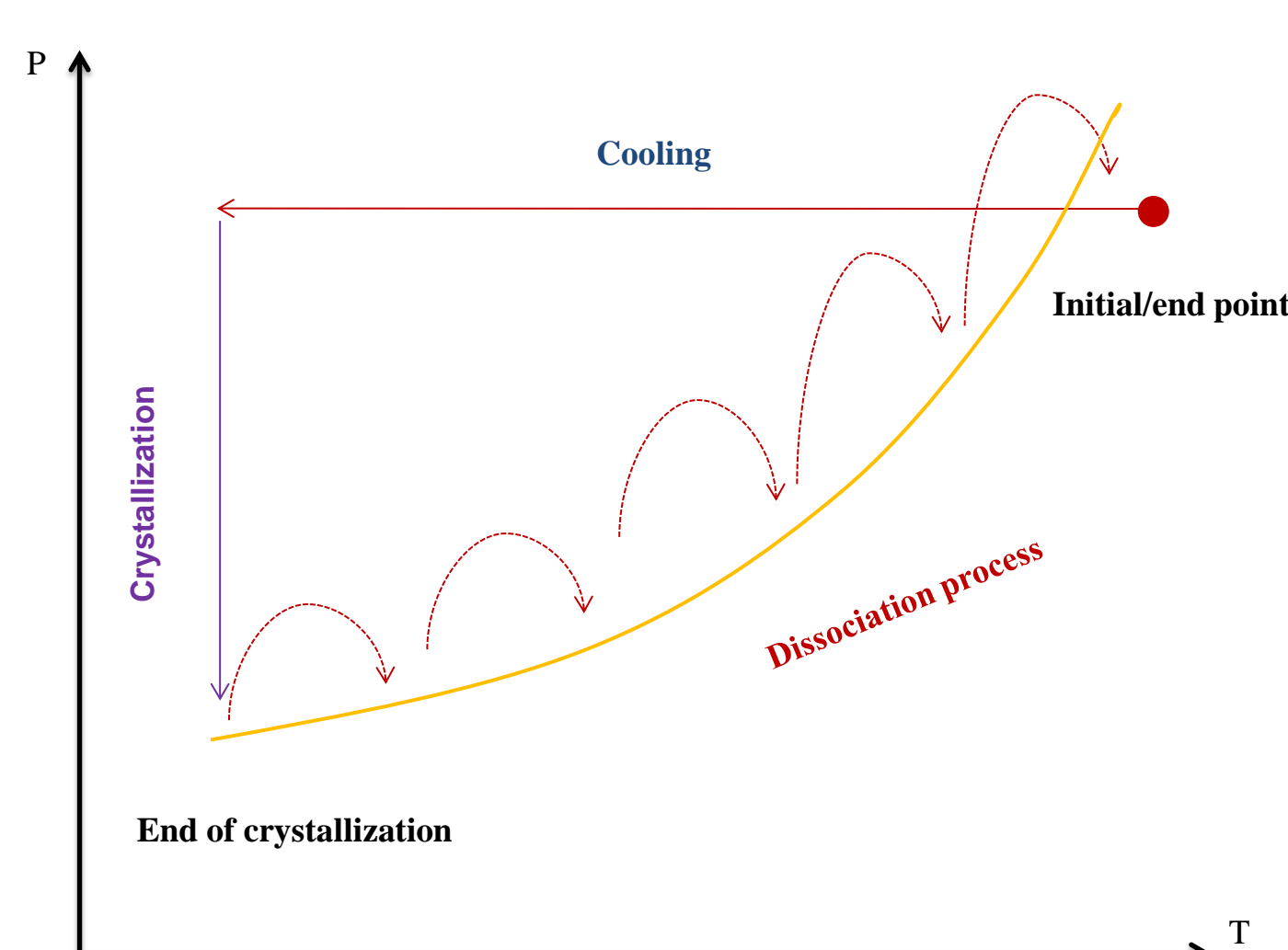


Fig. 2. P-T evolution during equilibrium experiment at high crystallization rate

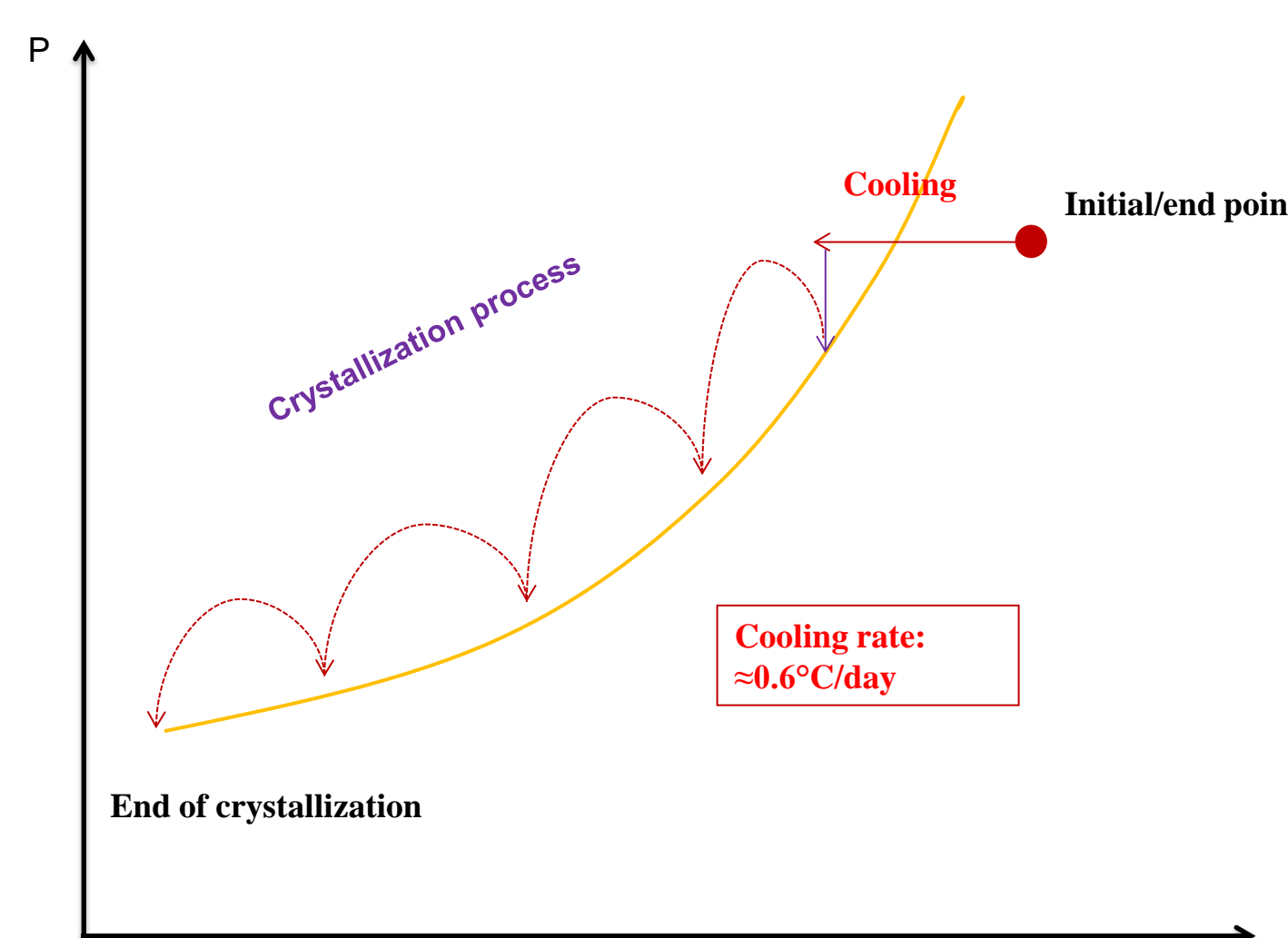


Fig. 3. P-T evolution during equilibrium experiment at slow crystallization rate

## Results and discussions

A set of experimental data on the phase equilibrium of gas hydrates in the presence of binary gas mixture of CH<sub>4</sub>-C<sub>3</sub>H<sub>8</sub> in two different approaches on the crystallization rate was obtained and shown in Fig 4 and 5.

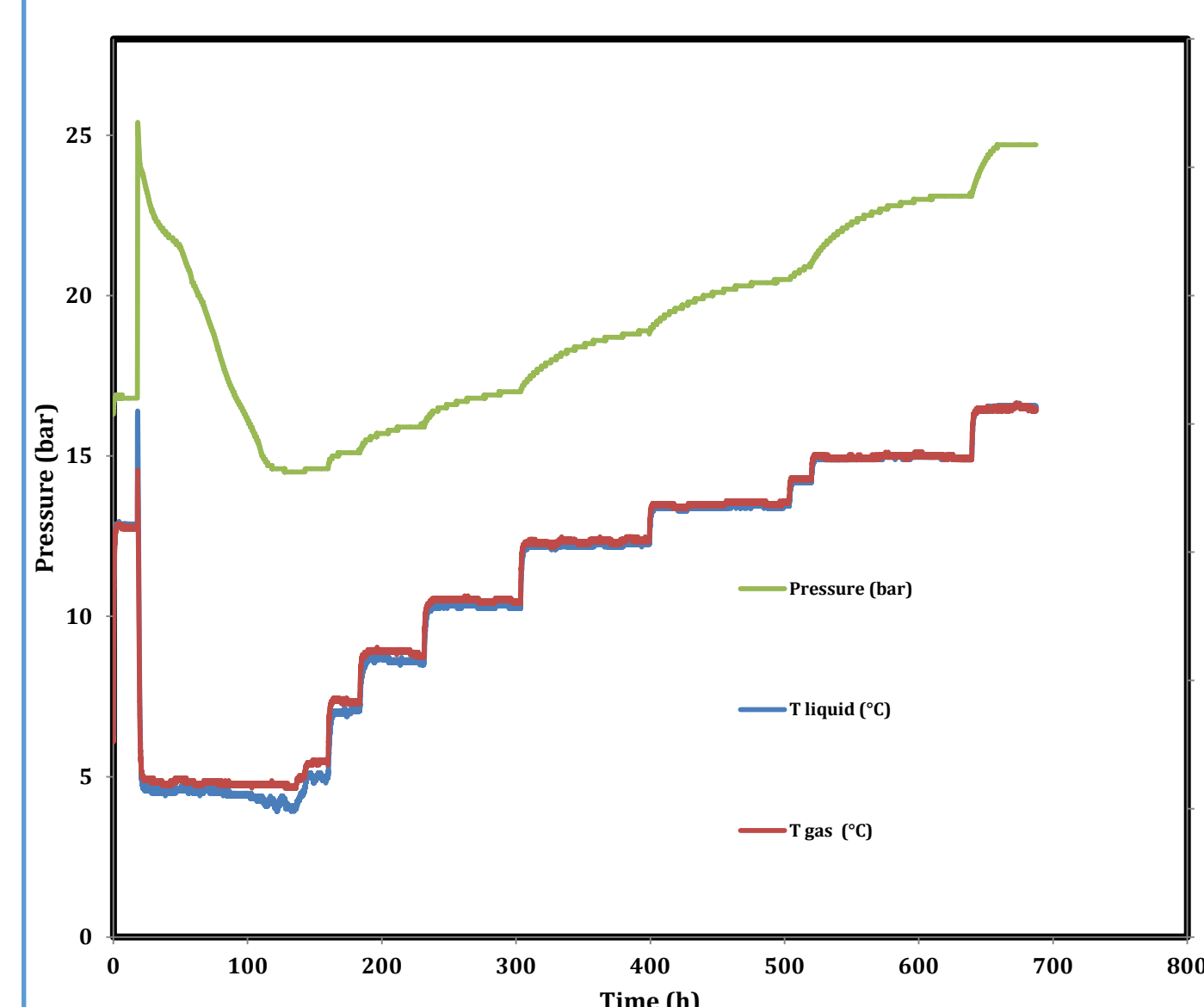


Fig. 4. The evolution of pressure and temperature during the quick crystallization process

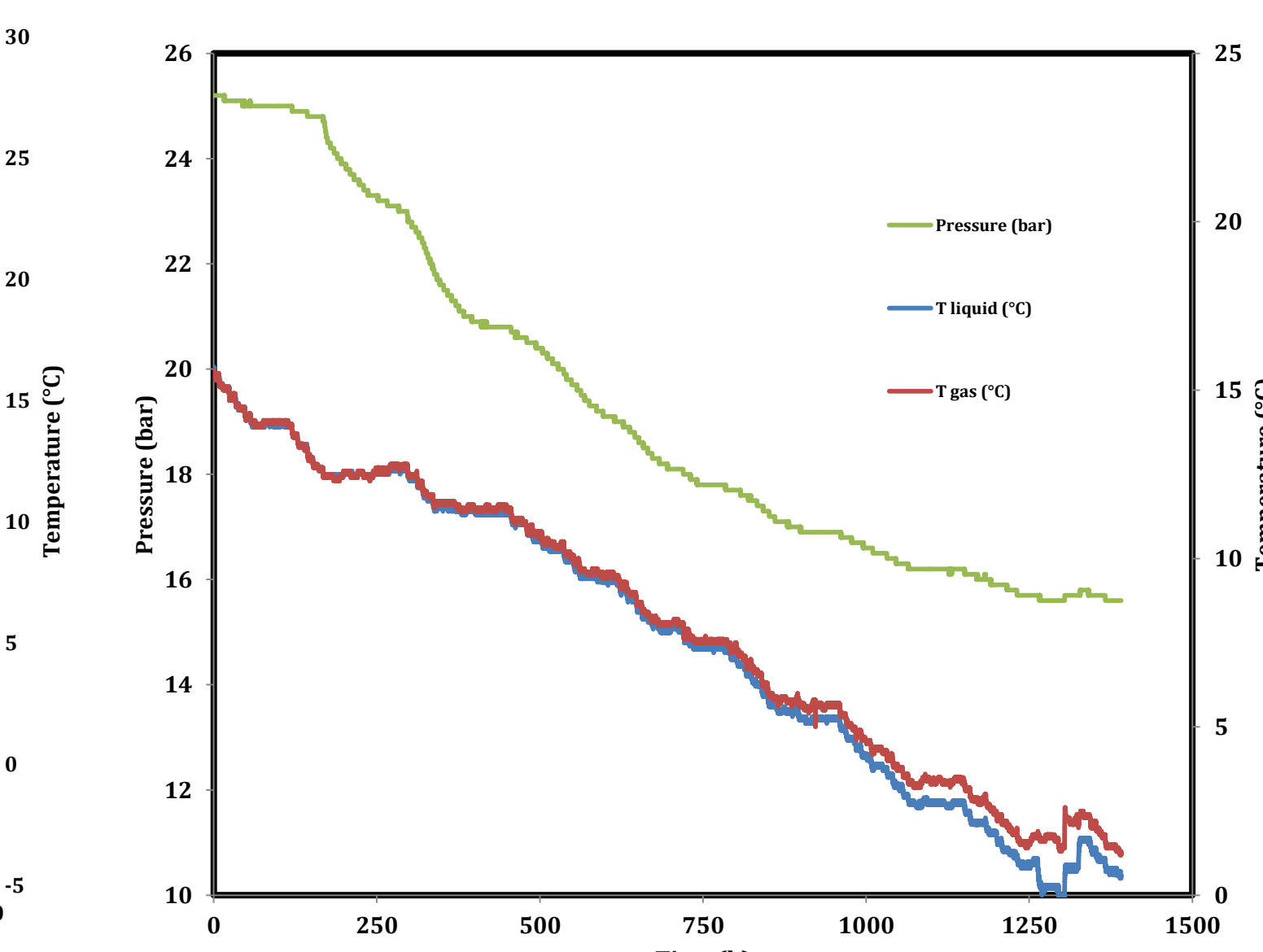


Fig. 5. The evolution of temperature and pressure during the slow crystallization

The comparison between the results of quick and slow crystallization rates has been shown in Fig. 6. It can be seen that the pressure drop in the case of slow crystallization rate is less than quick crystallization rate. So it means that there was not any leakage in our experimental set-up. Furthermore, the pressure difference at high temperature is less than low temperature. The water conversion and the change of gas composition in hydrate phase during the quick and slow crystallization are brought in Table 1.

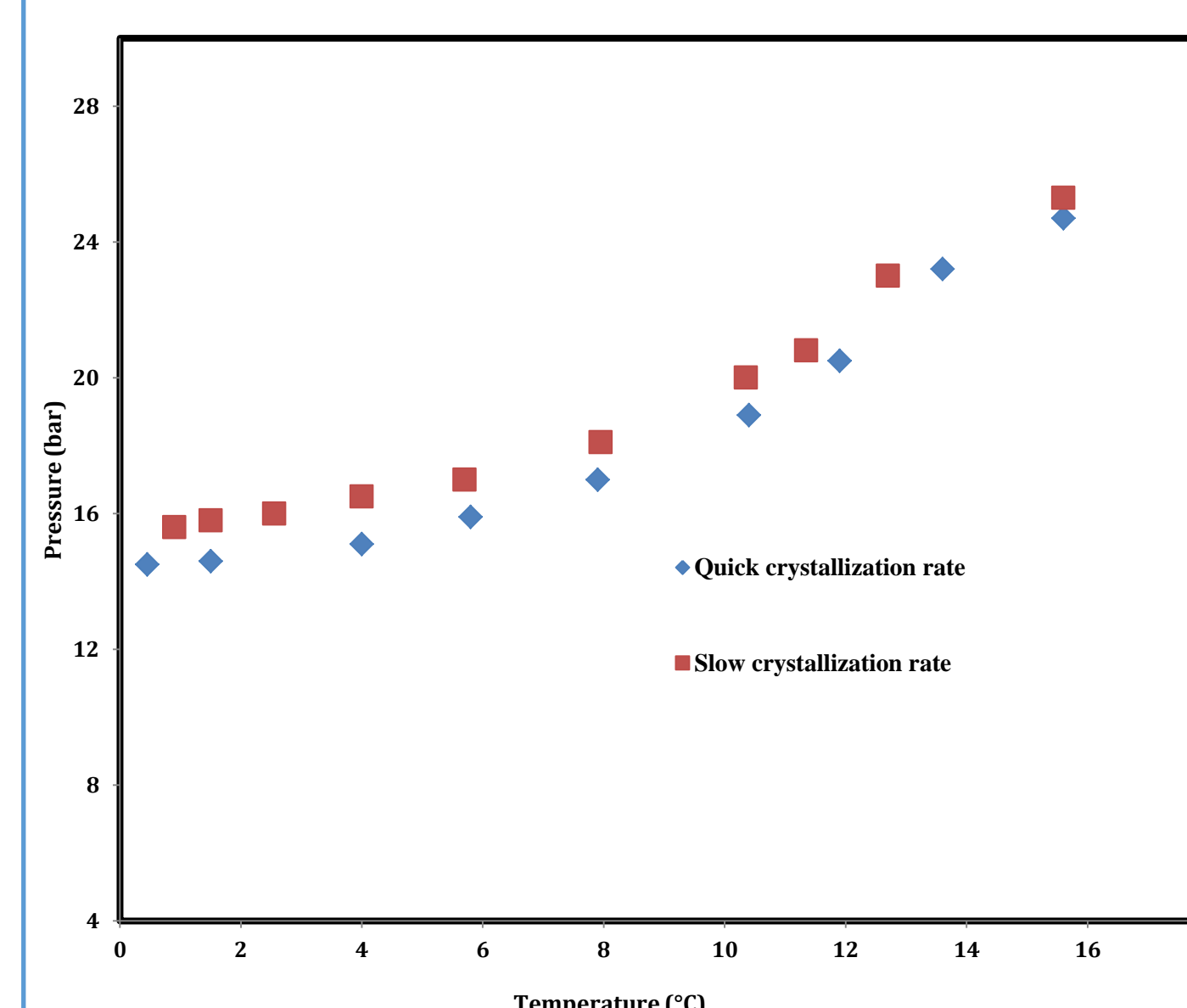


Fig. 5. The comparison between the results of equilibrium points for quick and slow crystallization rates

Quick crystallization					Slow crystallization				
T <sub>eq</sub> (°C)	P <sub>eq</sub> (bar)	C <sub>1</sub> (Mole fraction)	C <sub>2</sub> (Mole fraction)	Water conversion	T <sub>eq</sub> (°C)	P <sub>eq</sub> (bar)	C <sub>1</sub> (Mole fraction)	C <sub>2</sub> (Mole fraction)	Water conversion
0,45	14,5	0,6900	0,3100	20,395	12,7	23	0,4346	0,5654	0,7328
1,5	14,6	0,6873	0,3127	16,0229	11,3	20,8	0,5659	0,4341	6,2098
5,8	15,9	0,6756	0,3244	13,9257	10,3	20	0,5777	0,4223	6,0033
7,9	17	0,6613	0,3387	12,6243	7,95	18,1	0,6028	0,3972	8,1925
10,4	18,9	0,6390	0,3610	11,1133	5,7	17	0,6142	0,3858	8,519
11,9	20,5	0,6142	0,3858	9,7432	0,9	15,6	0,6292	0,3708	9,7061
13,6	23,2	0,4624	0,5376	7,2548	-	-	-	-	-

Table. Water conversion and the change of gas composition in hydrate phase during quick and slow crystallization

## Conclusion

In this work, the influence of crystallization rate on a binary mixture of CH<sub>4</sub>-C<sub>3</sub>H<sub>8</sub> was studied. The determination of the hydrate composition and volume were also investigated, not only at equilibrium conditions, but also during the crystallization and at non-equilibrium conditions. These parameters are really important studying about the gas mixture, because estimation of the hydrate volume can help us to determine the amount of kinetic inhibitors (KHI) to use in flow-assurance issues, and knowing the gas compositions in hydrate phase can be useful for understanding the gas hydrate phenomena. The results showed that although the initial conditions for two crystallization rates were almost the same, the pressure at final state was a little different. It can be better intercepted based on the results of water conversion. Water conversion for the quick crystallization was more than the slow crystallization. Furthermore the mole number of gases in hydrate for quick crystallization was more than slow crystallization. It means that more gases trapped in hydrate phase, hence the pressure drop must be higher. The gas compositions in hydrate phase were slightly different for both crystallization rates (slow and quick). Based on the results, it was concluded that in slow crystallization rate, the heavier molecules can be trapped in hydrate cages more than the quick crystallization rates.

## References

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