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# Influence of the crystallization rate on the mixed hydrate: experimental and modelling work

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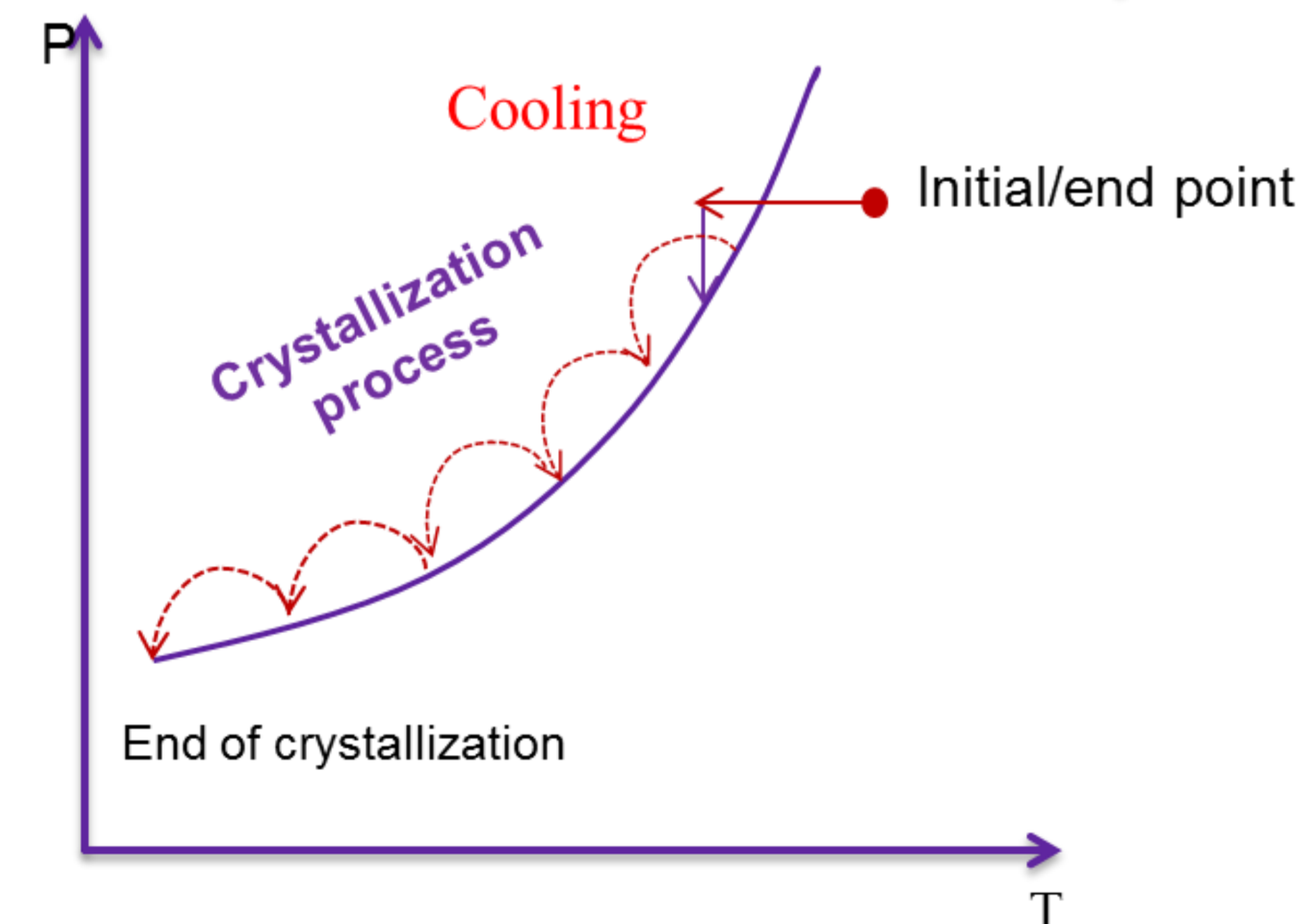
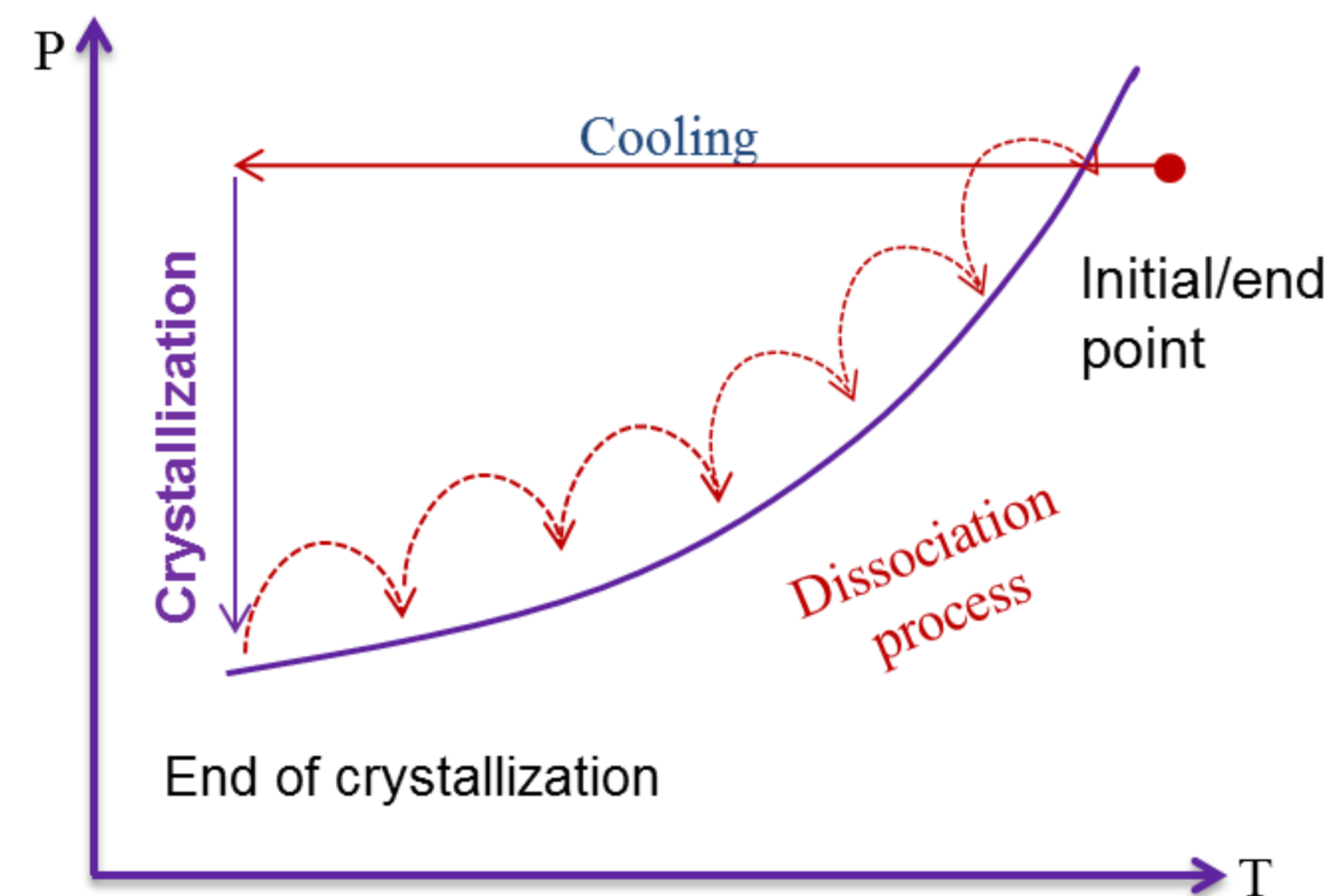
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## Introduction

During the last decade, our "GasHyDyn" team has measured equilibrium data for many gas mixtures, and this work adds new data involving propane based on different crystallization rates.

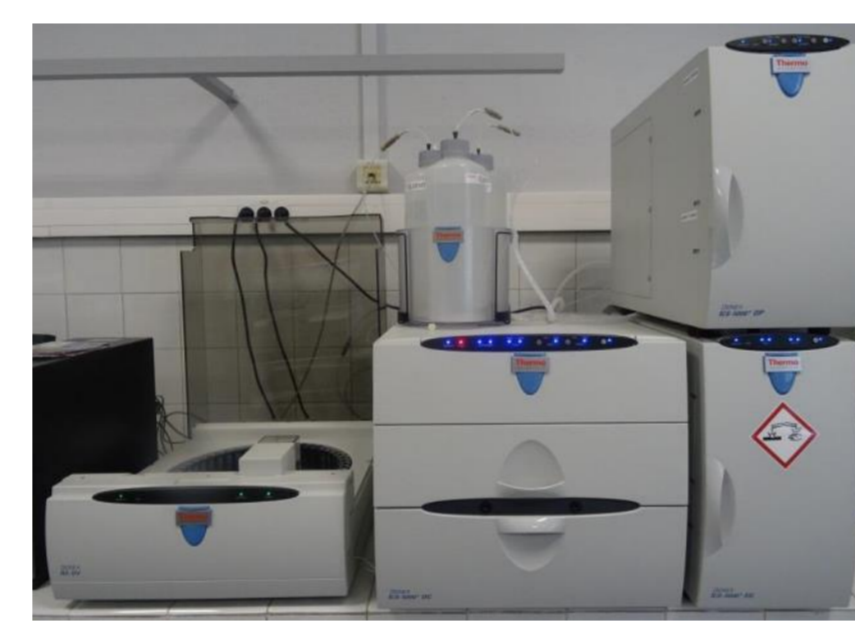
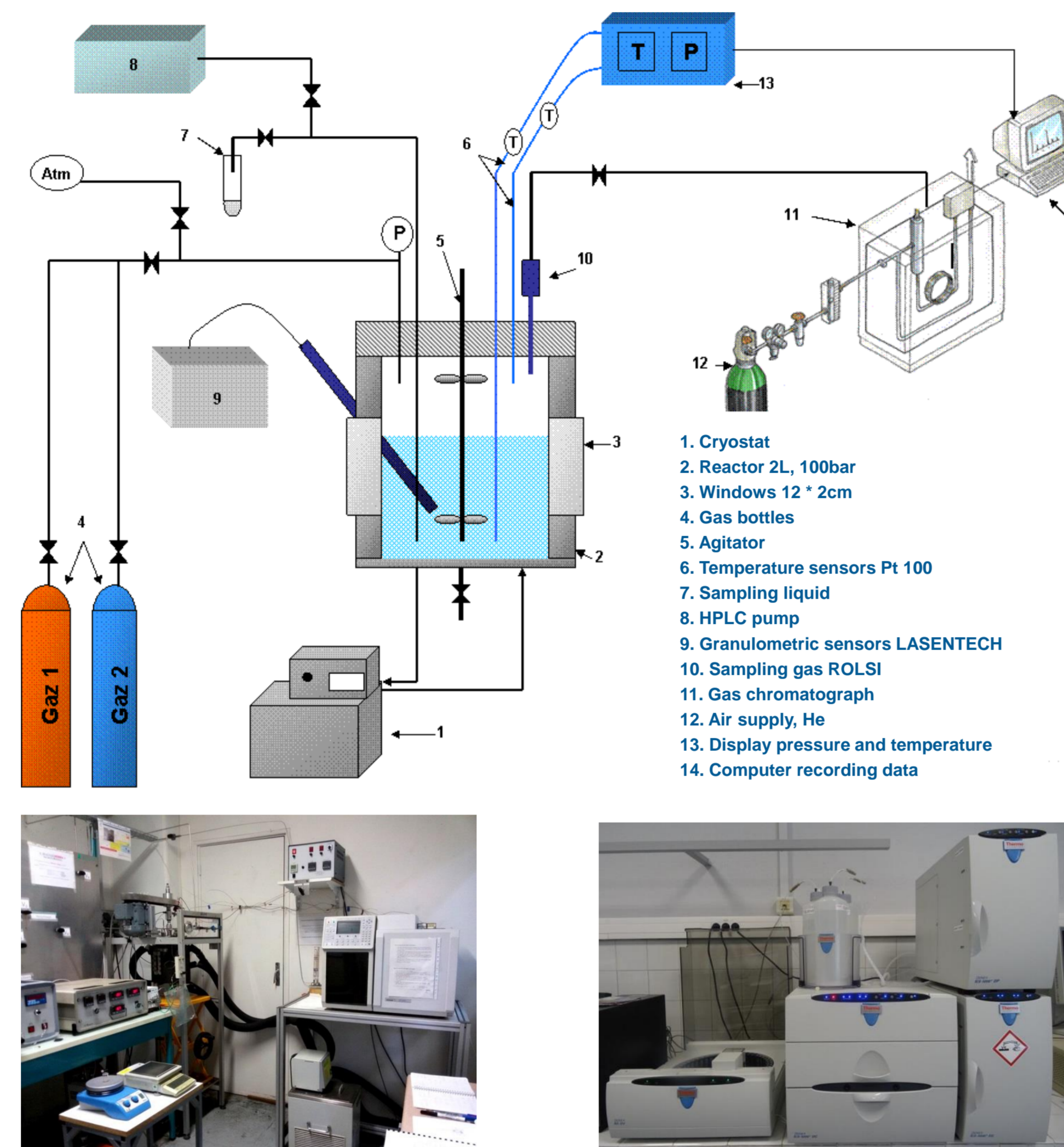
## Objectives

### ➤ Effects of crystallization rate



- Gas composition in all phases
- Hydrate volume and water conversion
- Thermodynamic model by implementing Kihara parameters

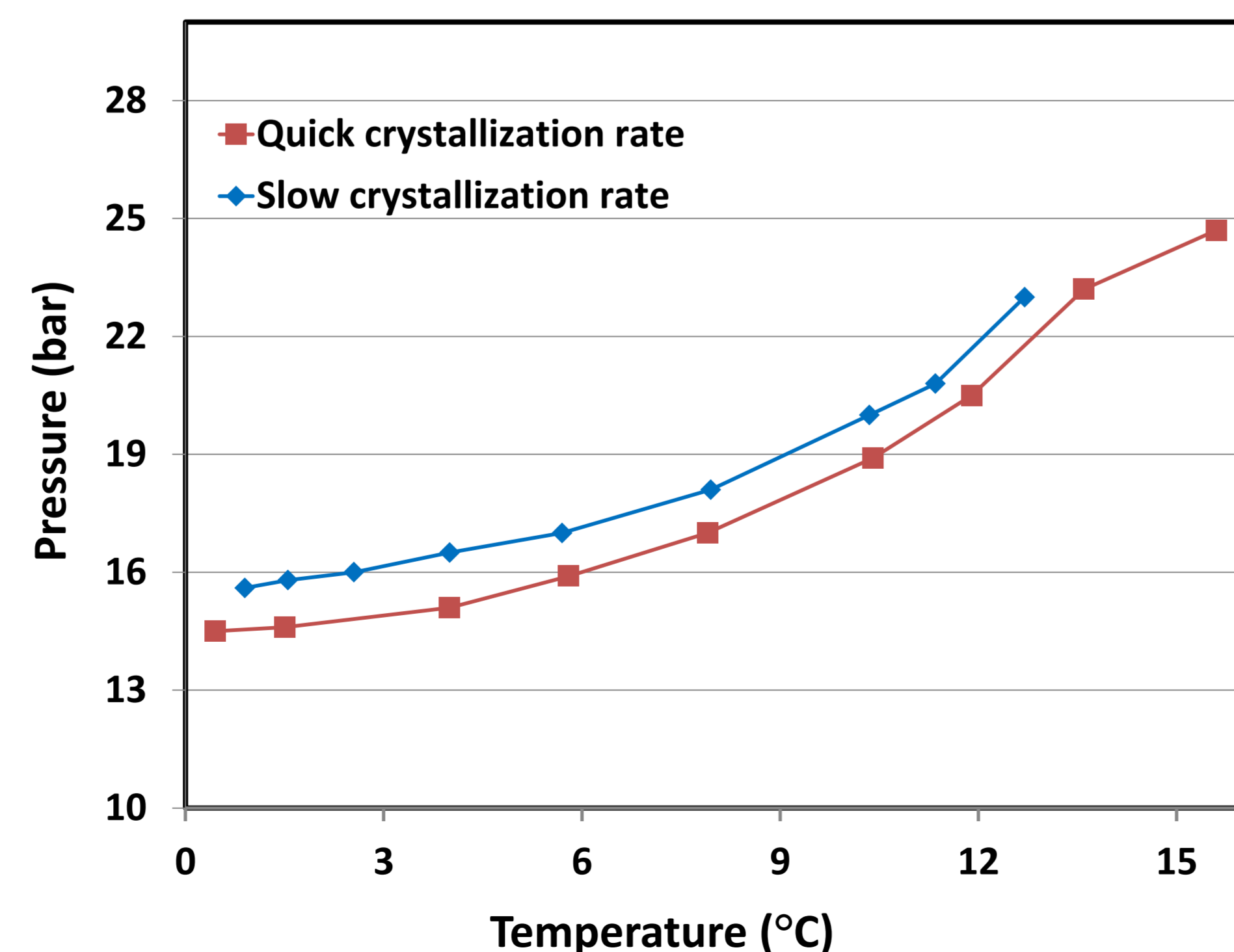
## Experimental set-up



## Results

Initial conditions of the experiments

Type of experiment	Gas composition (%)		Reactor volume (L)	Water injected (g)	Initial pressure (bar)	Initial temperature (°C)
	CH <sub>4</sub>	C <sub>3</sub> H <sub>8</sub>				
Quick crys.	86.14	13.86	2.36	801.37	16.8	10.9
Slow crys.	86.14	13.86	2.36	801.37	16.8	10.9



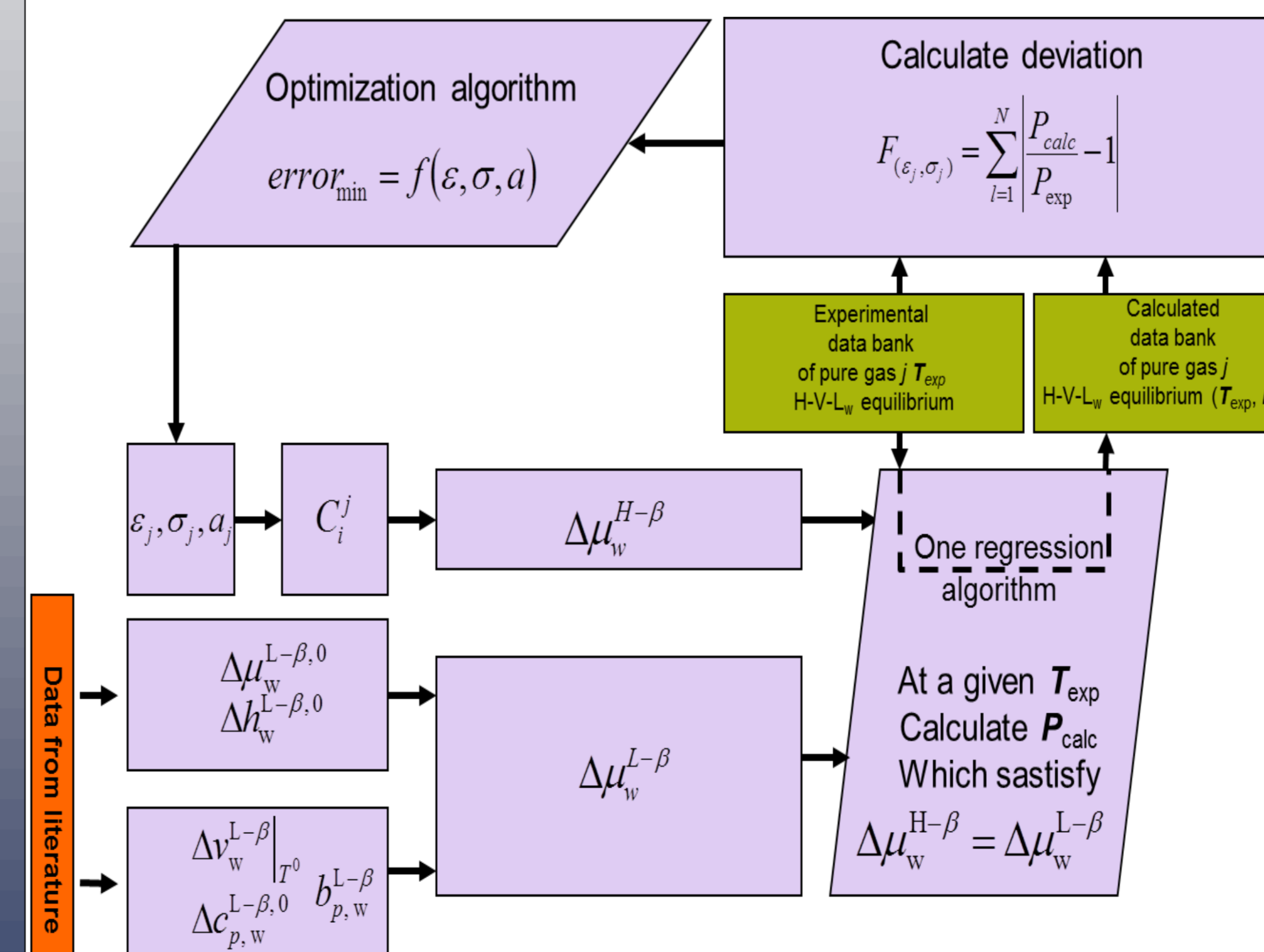
Pressure-Temperature diagram during the crystallization and final state of mixed methane-propane hydrate

The results of experiments for two different crystallization rates

Gas	Method	P (bar)	T (°C)	Molar gas fraction		Molar hydrate fraction		Water conversion (%)	Hydrate volume (cc)
				CH <sub>4</sub>	C <sub>3</sub> H <sub>8</sub>	CH <sub>4</sub>	C <sub>3</sub> H <sub>8</sub>		
Methane-Propane	Quick crystallization	14.5	0.45	0.9928	0.0072	0.6906	0.3094	20.49	207.86
		14.6	1.50	0.9911	0.0089	0.6877	0.3123	16.11	162.67
		15.9	5.80	0.9746	0.0254	0.6754	0.3246	13.99	139.78
		17	7.90	0.9624	0.0376	0.6608	0.3392	12.69	126.26
		18.9	10.40	0.9388	0.0612	0.6375	0.3625	11.17	110.54
	Slow crystallization	20	10.35	0.9364	0.0636	0.5744	0.4256	6.03	60.41
		18.1	7.95	0.9641	0.0359	0.6016	0.3984	8.23	81.90
		17	5.70	0.9795	0.0205	0.6136	0.3864	8.56	84.78
		16	2.55	0.9907	0.0093	0.6271	0.3729	11.06	108.21
		15.8	1.55	0.9927	0.0073	0.6292	0.3708	12.69	123.33

- Different rate of crystallization leads to different:
  - Final pressure
  - Hydrate volume and water conversion
  - Propane composition in hydrate phase

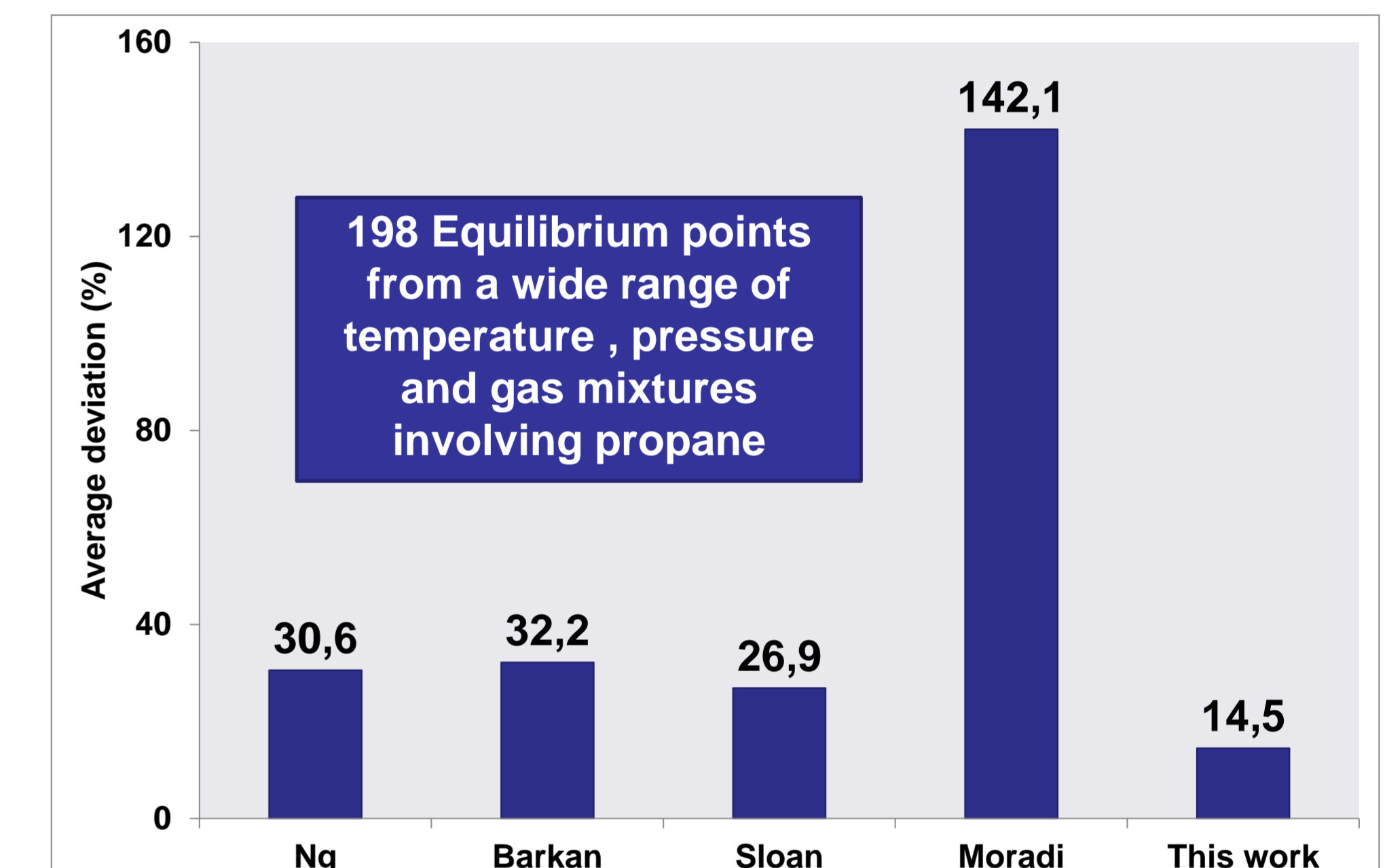
## Modelling



The algorithm of Kihara parameters optimization

Kihara parameters from literature and this work

Reference	$\epsilon/K$	$\sigma$	$a$
(Sloan, 1998)	203.31	3.3093	0.6502
(Ng and Robinson, 1977)	213.58	3.2296	0.6700
(Barkan and Sheinin, 1993)	194.55	3.3144	0.8340
(Moradi and Khosravani, 2013)	493.70	4.5190	0.6502
<b>This work</b>	<b>195.00</b>	<b>3.3400</b>	<b>0.6502</b>



The capability of hydrate equilibrium pressure prediction based on different Kihara parameters from literature and this work

## Conclusions

- ❑ Based on the results, it can be supposed that in slow crystallization process the hydrate crystal are more homogenous.
- ❑ At quick crystallization process which the driving force is high, kinetic could be dominant more than thermodynamic.
- ❑ The thermodynamic model based on the new Kihara parameters had a better accordance with a wide range of equilibrium data from literature.

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