2nd International Forum on Recent Developments of CCS Implementation

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Development of a Novel Experimental Apparatus for Hydrate Equilibrium Measurements

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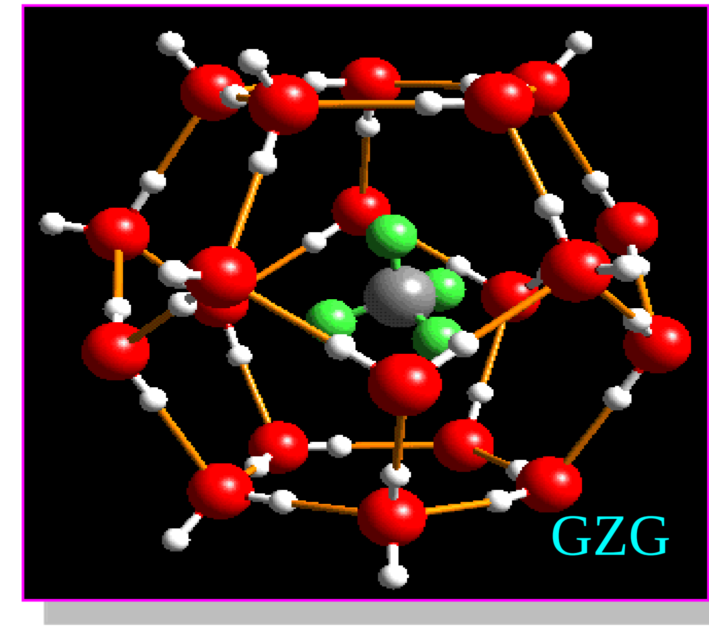
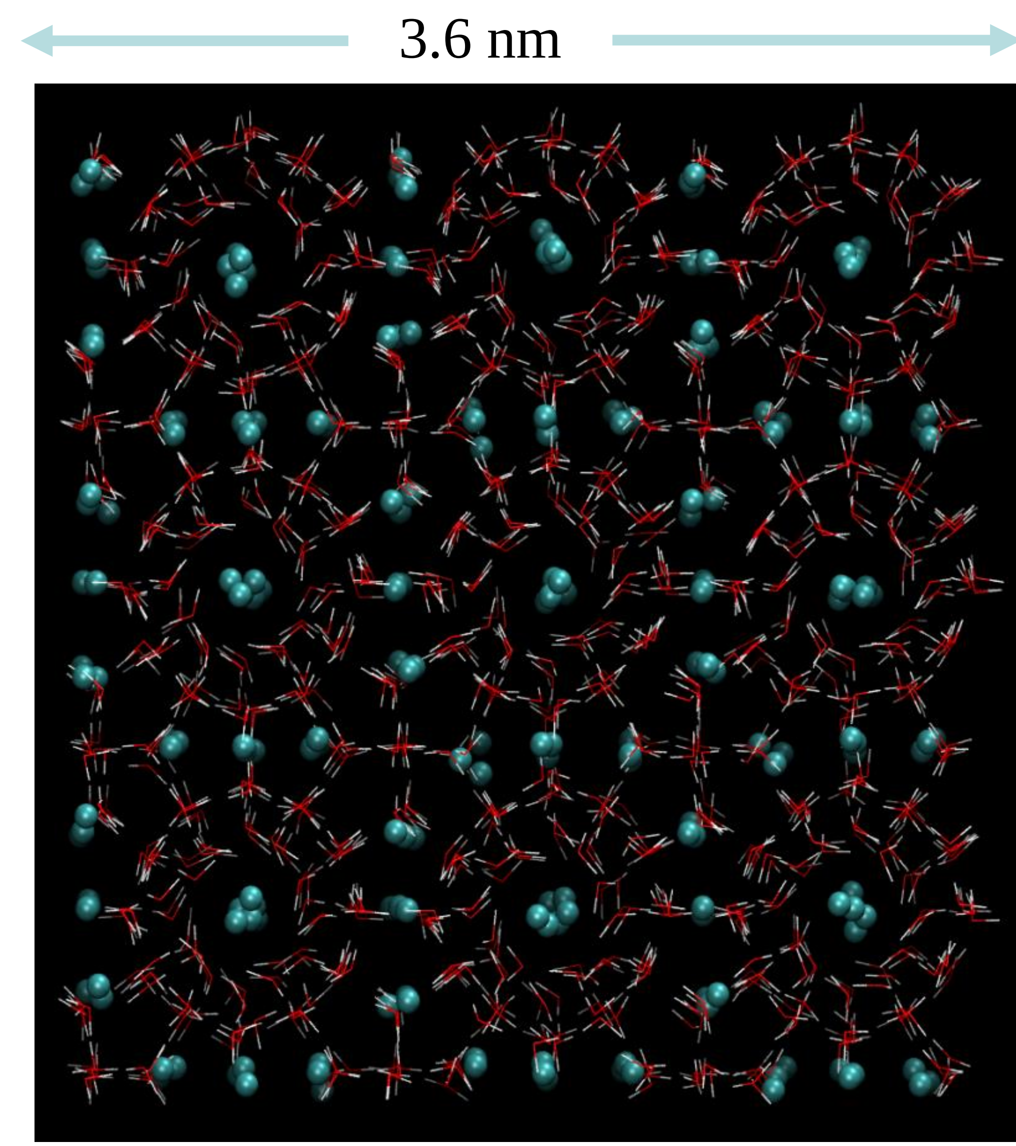
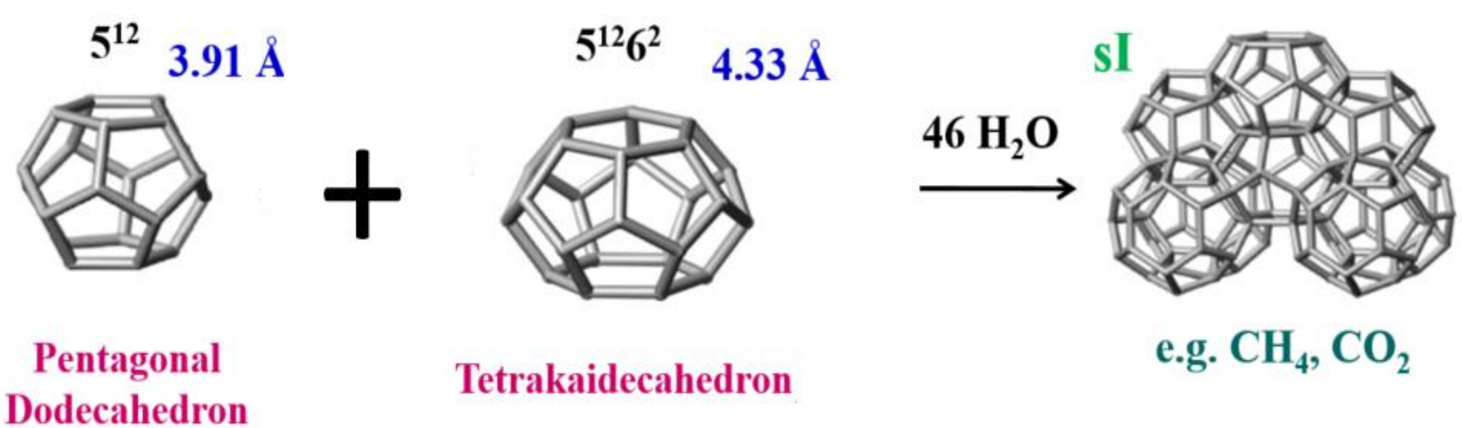
Hydrate Background

- Self-assembled, crystalline structures.
- Formed by water molecules creating a solid lattice that encages "guest" molecules.
- Structures are only stable at high pressures, low temperatures, and in the presence of guest molecules.
- More than 130 different molecules form hydrates ***(e.g., CH_4, CO_2, H_2, hydrocarbons, Ar, Kr, N_2, O_2 etc.)***.







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The impact of the quality of CO_2 on transport and storage behaviour

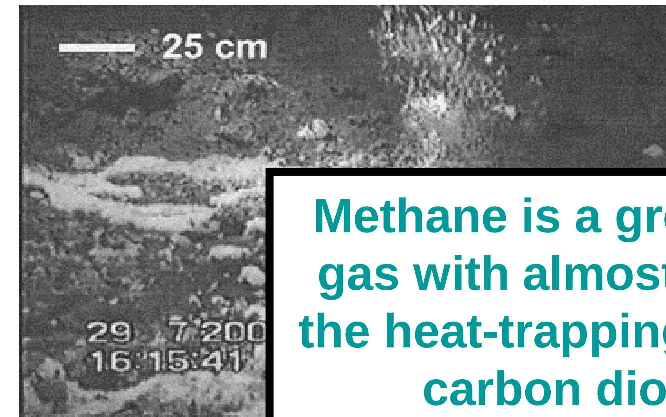
CO_2QUEST

Hydrate Applications

Blocking pipe-lines

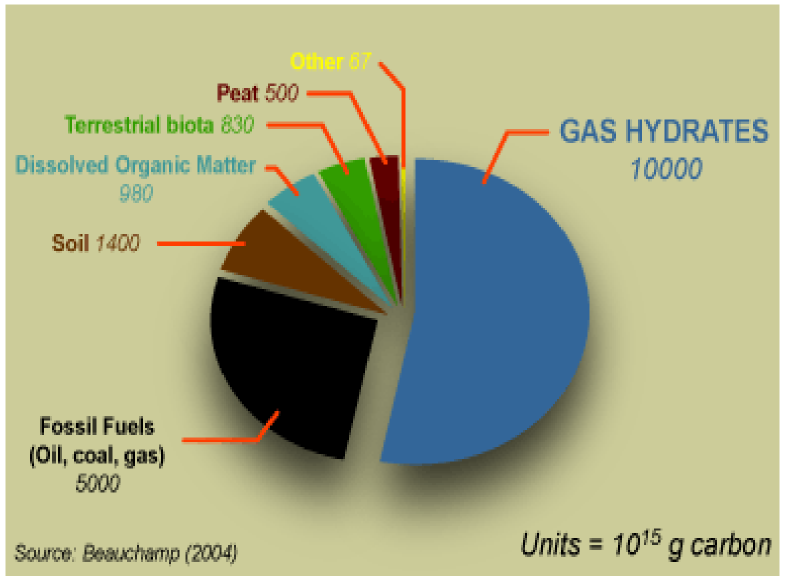
Flow Assurance/Safety

- Sudden methane release
- CO_2 sequestration



Methane is a greenhouse gas with almost 30 times the heat-trapping ability of carbon dioxide.

Global Climate Change



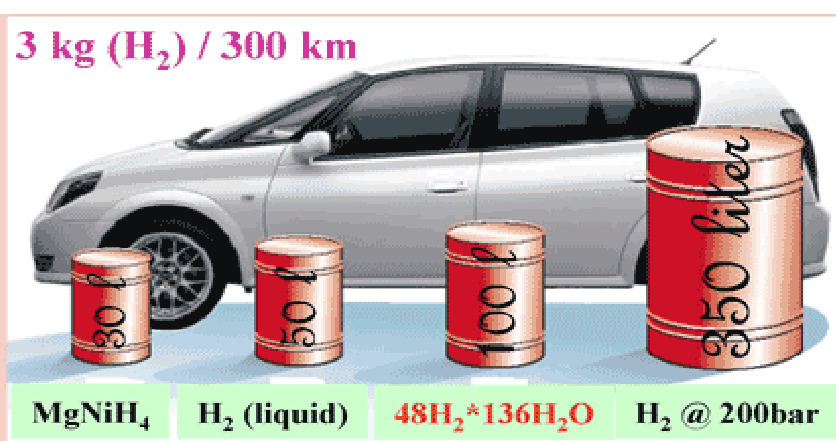
Potential Energy Resource

Separation Technology

- Gas Mixtures
- Water Desalination

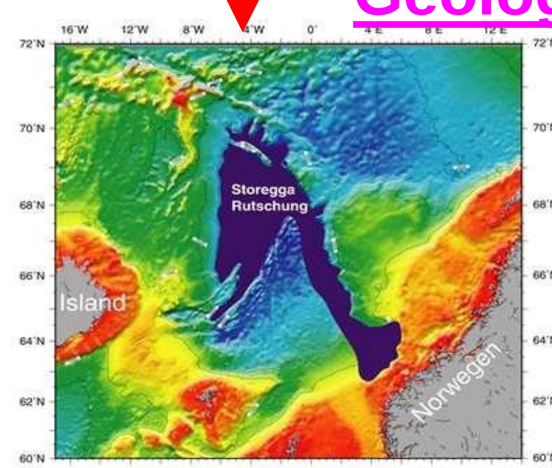
Gas Storage and Transport

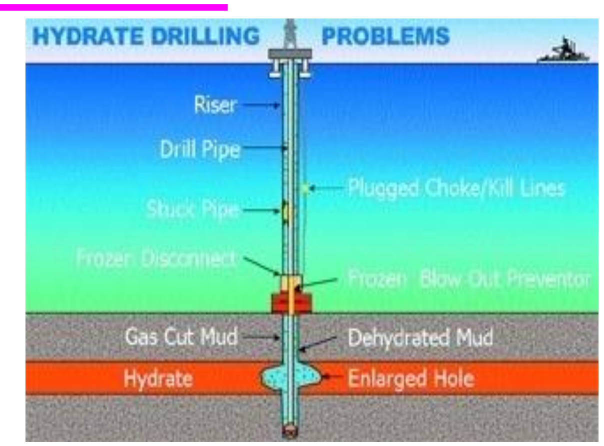
- H_2, CH_4, CO_2



LANL modification of figure in:
Nature, **414**, 353 (2001).

Geologic Hazard





Oceanic slope collapsing

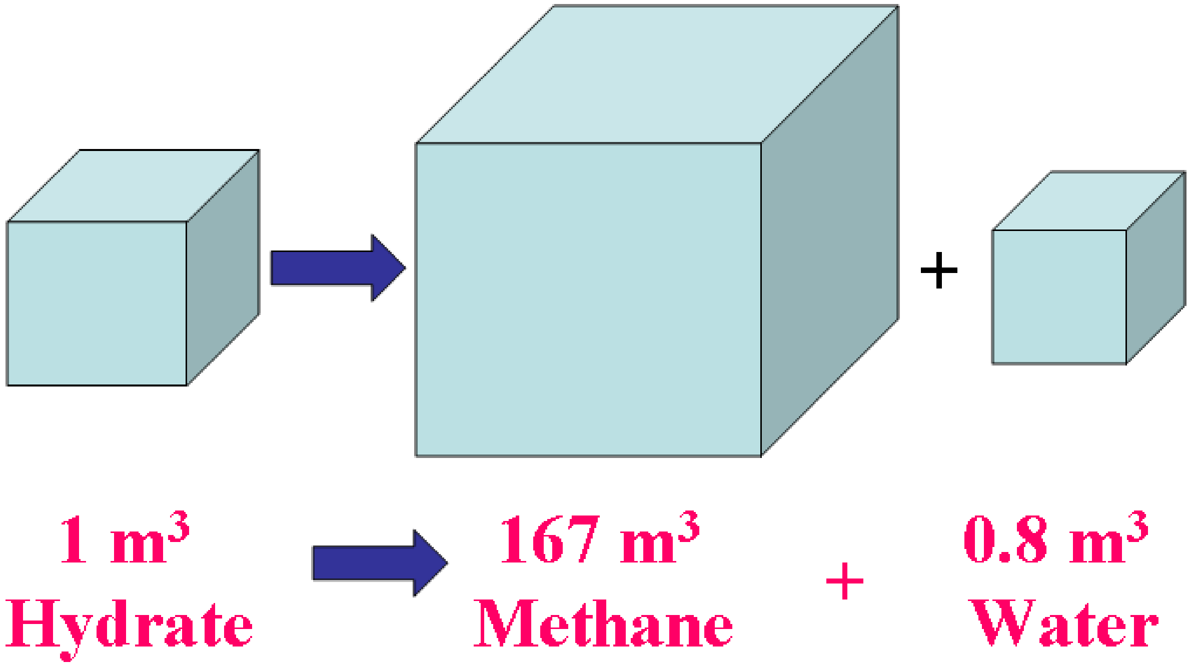
Danger to oil platforms

Gas Storage and Transport

Utilize the hydrate capability to incorporate large amount of gases in the solid structure.

- **Transport stranded CH_4 gas.**
- **Transport gas into slurries.**
- **Store Hydrogen.**
- **Store CO_2 in CO_2-hydrate pellets.**
- **…**

Complete reversibility, easy recovery process, fast kinetics, moderate temperatures, non-toxicity, low flammability, H_2O as by-product.



Significant Potential in Future Applications !!!

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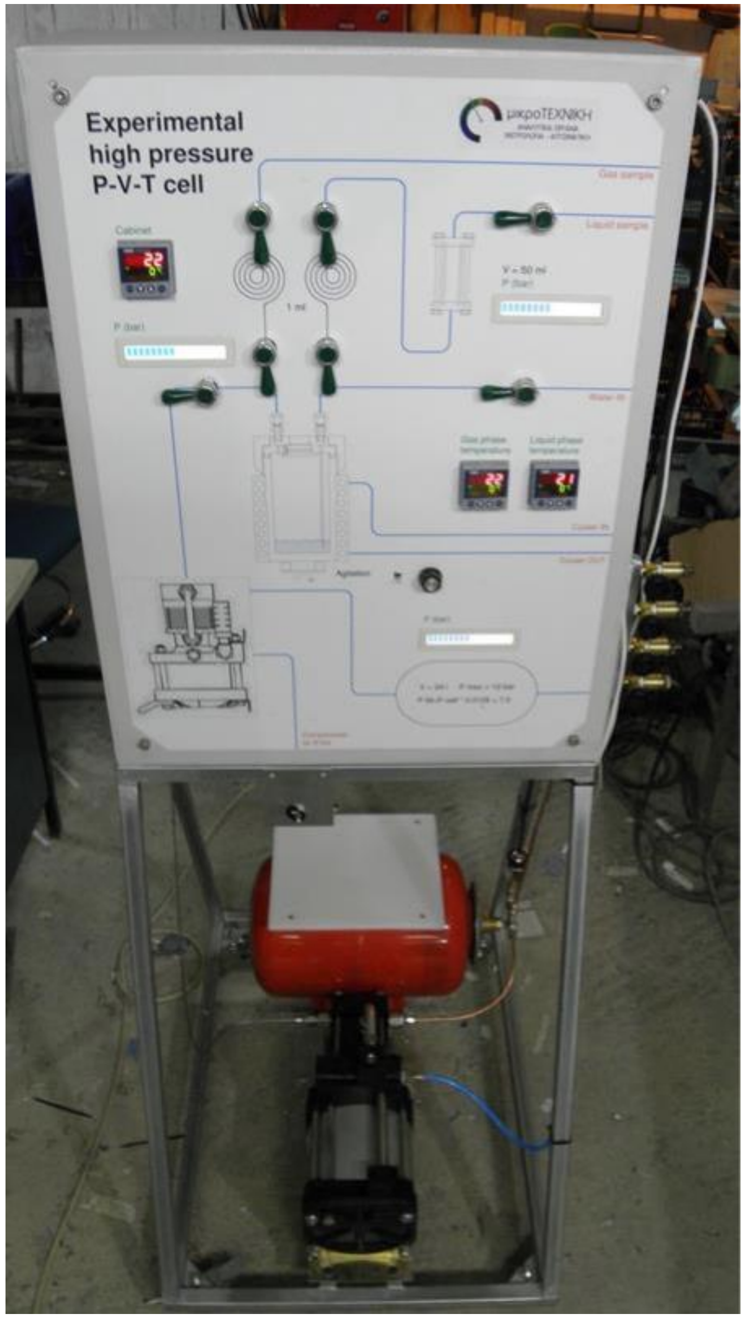
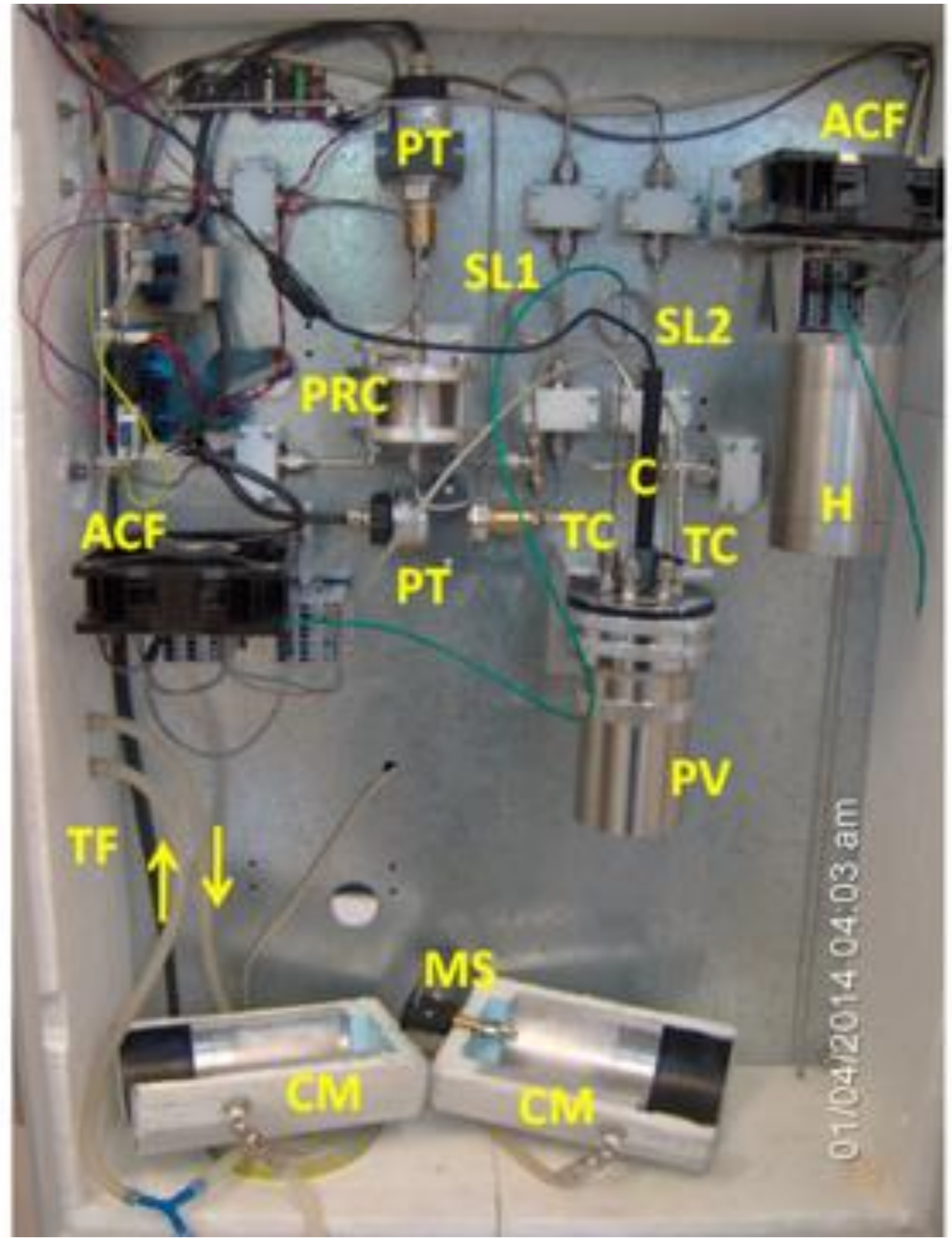
Experimental Apparatus

- **Measure the pressure (*P*) and temperature (*T*) conditions during three-phase (H–L_w–V or H–L_w–L_g) equilibria of pure gases**
- **Perform quantitative analysis of the liquid phase (i.e., solubility measurements) that is under three-phase (H–L_w–V or H–L_w–L_g) equilibrium conditions**



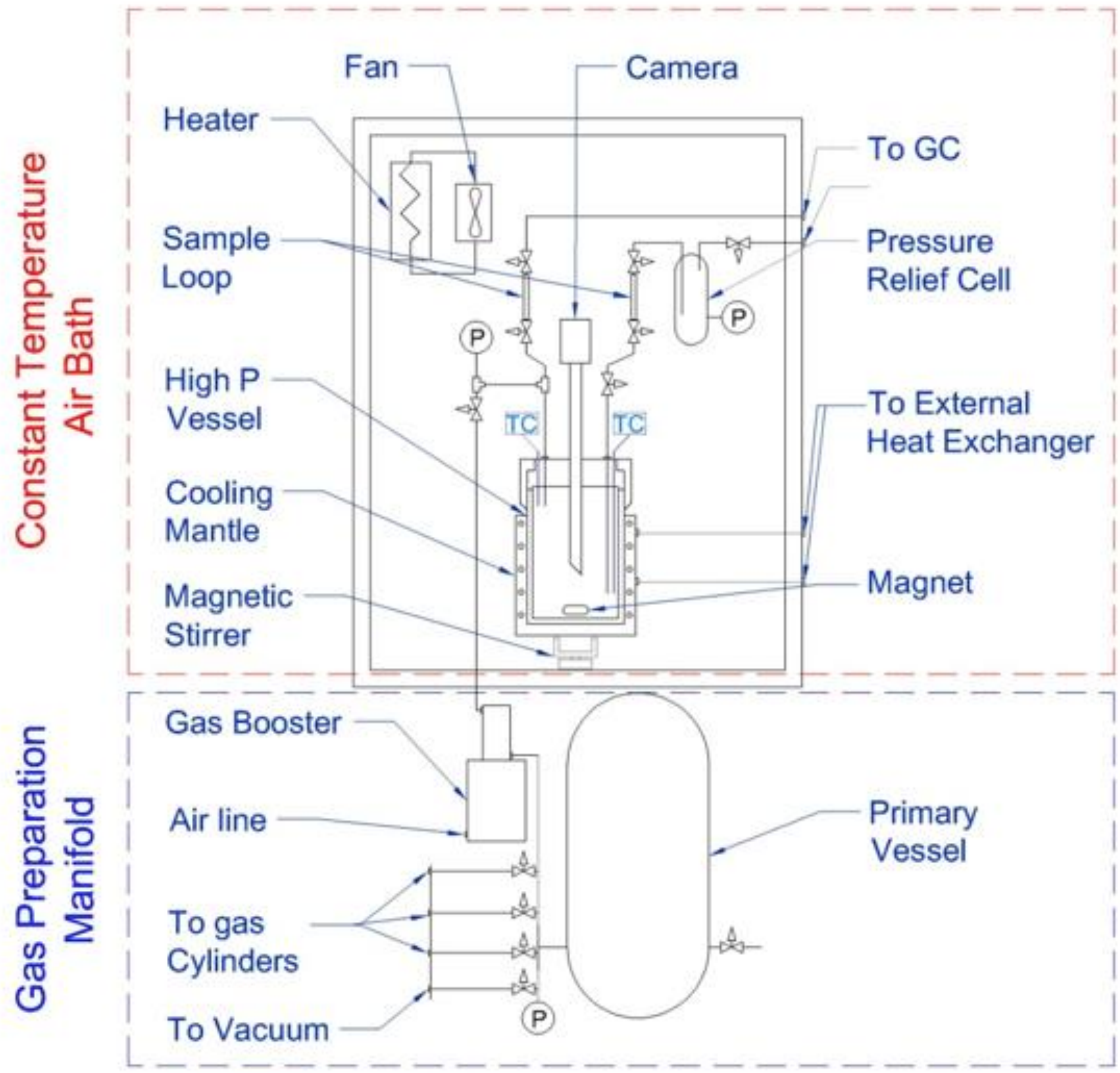


Thermostated Air Bath

Notation Used

PV : Pressure Vessel
PT : Pressure Transducer
TC : Thermo Couple
PRC: Pressure Relief Cell
ACF: Air Circulating Fan
SL1 : Gas Sampling Loop
SL2 : Liquid Sampling Loop
CM : Cooling Mantle
MS : Magnetic Stirrer
TF : Thermal Fluid
C : Camera
H : Heater

1. Preparation manifold
2. Thermostated air cabinet
3. PVT cell
4. Pressure relief cell for liquid sampling
5. Electronics and monitoring
6. Julabo temperature control system
7. Gas chromatograph



Three-phase (H–L_w–V or H–L_w–L_g) equilibrium measurements

- **Isochoric Pressure Search (IPS) Method**
  - **Cell filled with liquid H_2O and gas at a temperature and pressure that correspond to VLE region and kept closed - volume is kept constant.**
  - **Isochoric Cooling through consecutive temperature and subsequent pressure drops**
  - **Metastability limit achieved – Hydrate formation takes place, indicated by a sharp pressure drop**
  - **Hydrate formation is completed – the intense pressure drop stops**
  - **Isochoric heating through consecutive temperature and subsequent pressure increases until hydrate dissociation is completed**
  - **The hydrate equilibrium point is taken as the point in a pressure-temperature plot, where the dissociation (heating) trace intersects the cooling trace.**

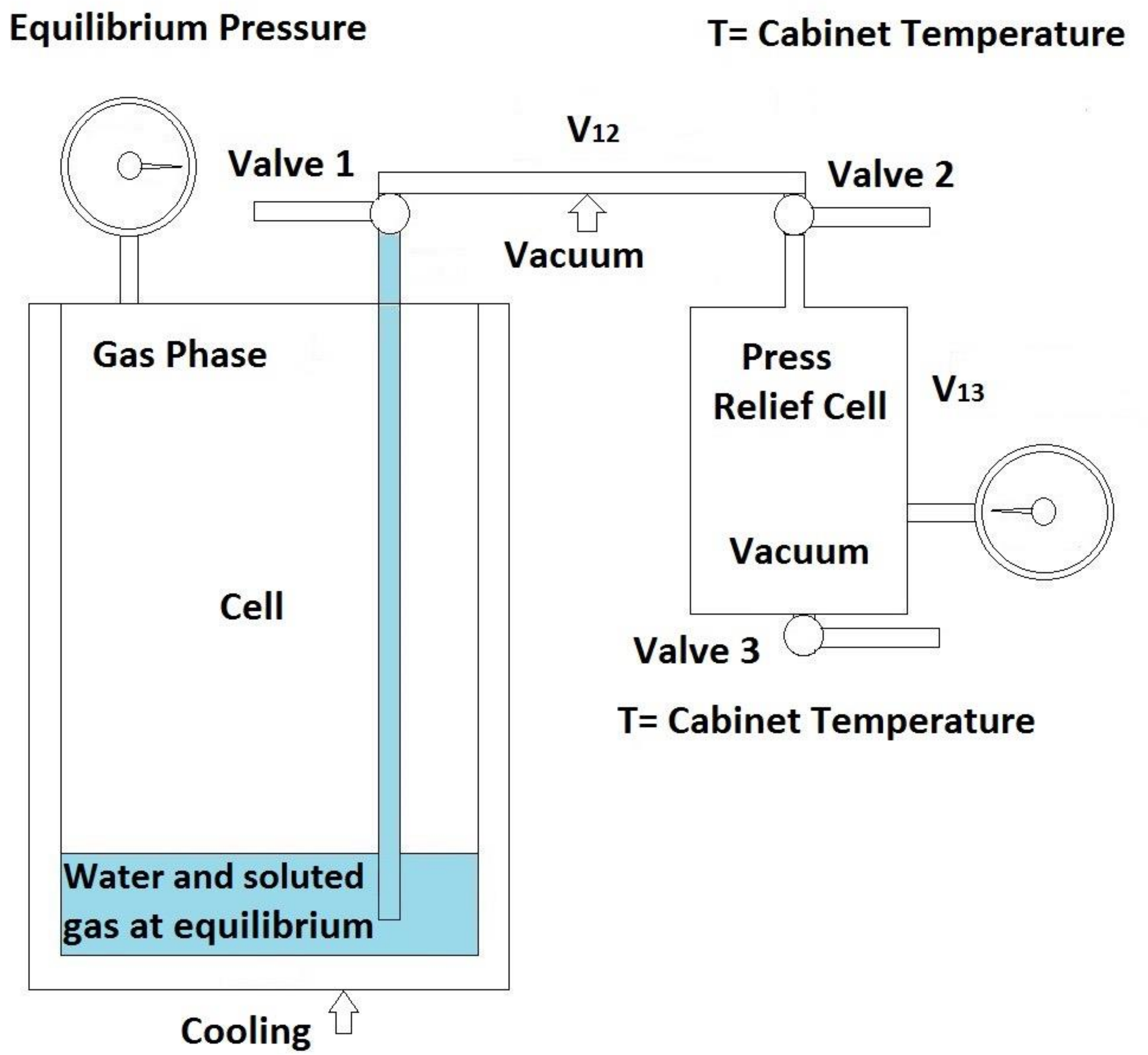
Three-phase (H–L_w–V or H–L_w–L_g) equilibrium measurements

- **The Phase Boundary Dissociation (PDB) Method.**
  - **A modification to the IPS method**
  - **When a hydrate system contains excess amount of free H_2O the system contains all three phases (H−L_W–V) throughout the duration of the experiment.**
  - **At pure hydrate formers (i.e., systems with 3 phases), two components exist in the system (i.e., guest and H_2O)**
  - **according to the Gibbs Phase rule, there is one degree of freedom (i.e., a single value of pressure at any given temperature)**
  - **Such a system would dissociate along the H−L_W–V phase boundary for as long as all three phases coexist**

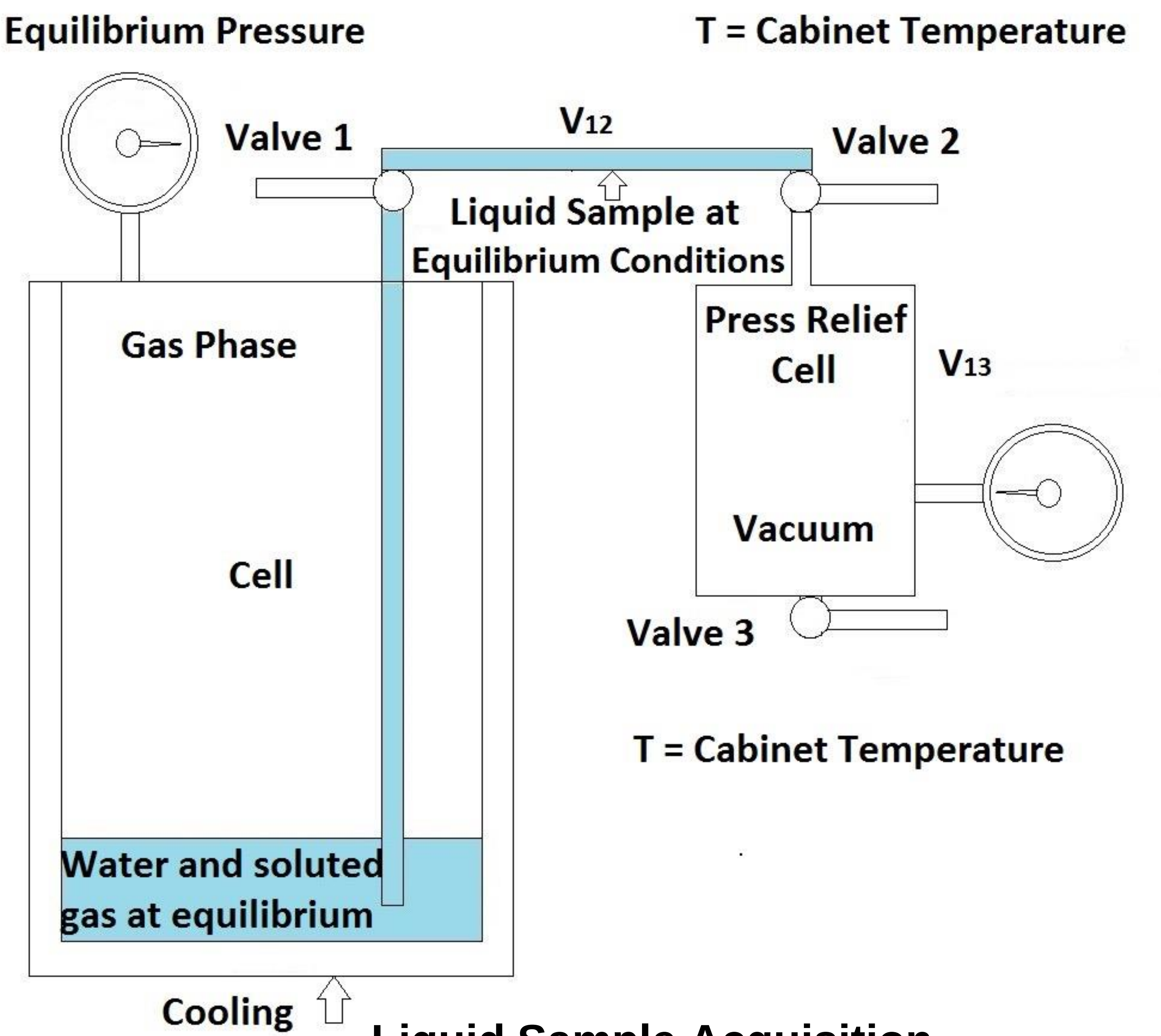
Three-phase ($H–L_w–V$ or $H–L_w–L_g$) equilibrium measurements

- **The Phase Boundary Dissociation (PDB) Method.**
  - **The cell is filled with 40:1 molar ratio of H_2O to the guest gas, so excess H_2O is always present and left to equilibrate**
  - **The temperature is set to 273.25 K for 6 h, to form hydrates and allow the system to reach equilibrium.**
  - **The system is heated in steps of 0.5 K for 4 h before the next temperature step is taken and a data point recorded, to prevent metastability .**
  - **This process is continued until the hydrate is fully dissociated and the equilibrium point could be taken, as confirmed by a sharp change in d*P*/d*T*.**
  - **Each data point is treated the same as the data recorded from a single IPS method experiment.**

Solubility Calculation

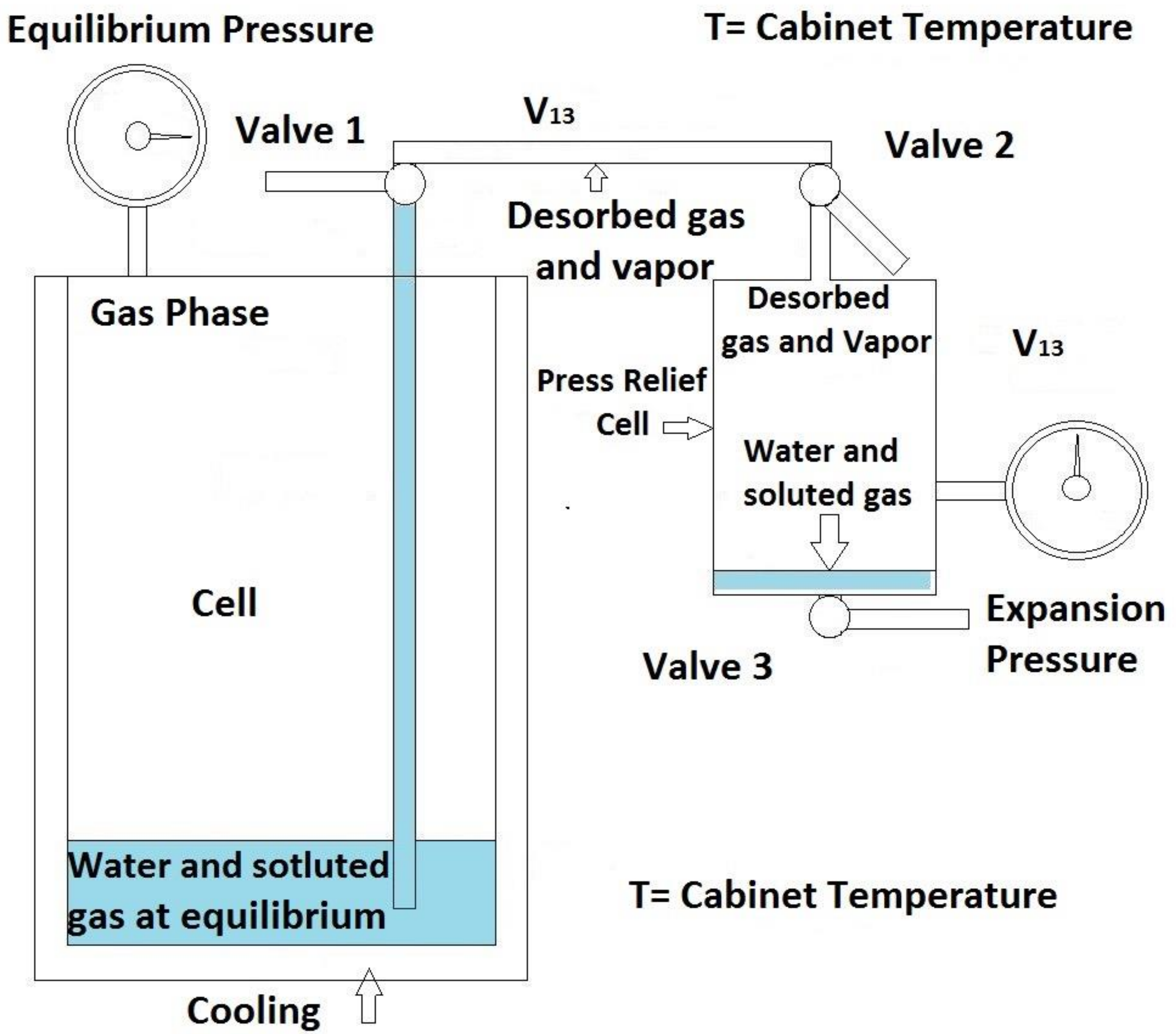


System at Equilibrium point



Liquid Sample Acquisition

$$V_{H_2O} + V_{gas} = V_{12}$$



Expansion to pressure relief cell

Solubility Equations

$$V_{gas} = \left[\frac{(P - P_g) \cdot (V - V_{H_2O})}{z \cdot R \cdot T} + \frac{\rho \cdot V_{H_2O}}{\frac{18.015}{1000}} \cdot \left(\frac{moles_{\,gas}}{moles_{\,H_2O}} \right) \right] \cdot \tilde{v}_{gas}$$

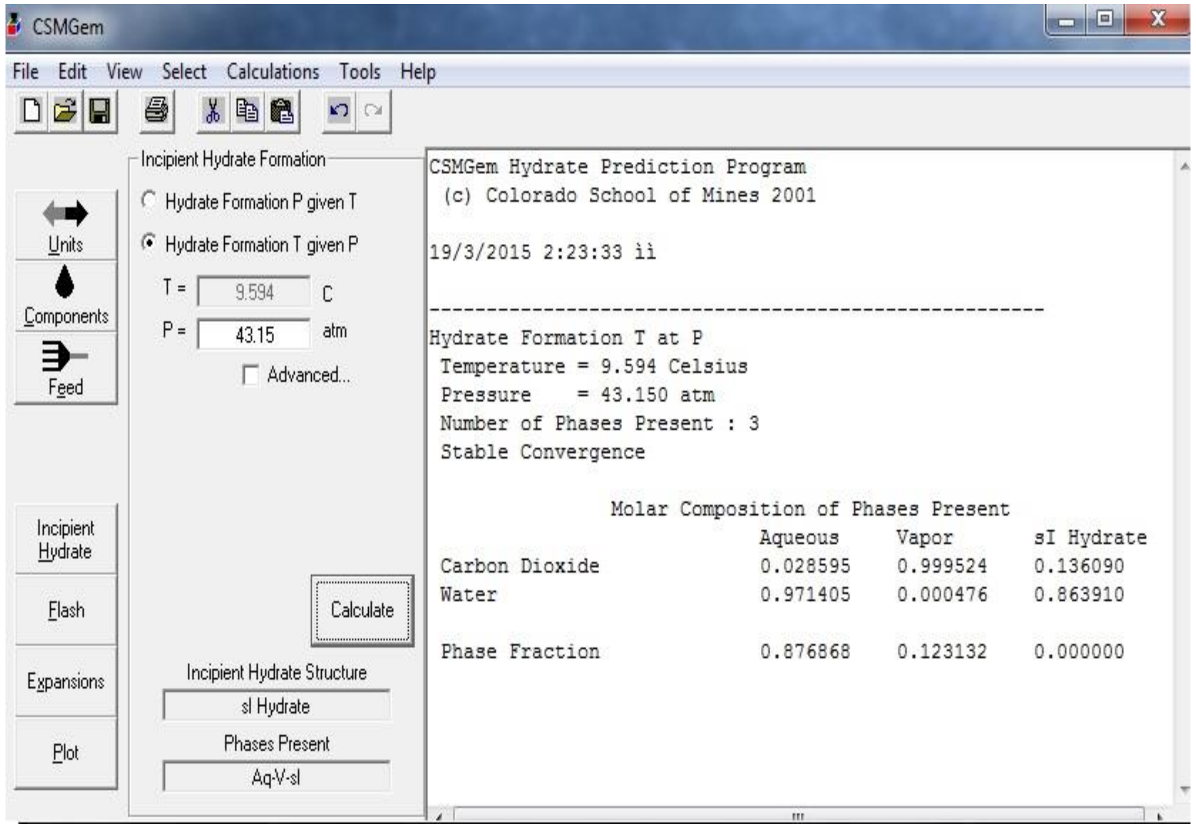
$$n_{gas} = \frac{(P - P_g) \cdot (V - V_{H_2O})}{z \cdot R \cdot T} + \frac{\rho \cdot V_{H_2O}}{\frac{18.015}{1000}} \cdot \left(\frac{moles_{\,gas}}{moles_{\,H_2O}} \right)$$

$$x_{gas} = \frac{n_{\,gas}}{n_{\,H_2O} + n_{\,gas}}$$

CSMGem

The Colorado School of Mines Clathrate Prediction Program

- CSMGem can calculate multiphase equilibria at any given temperature and pressure using an algorithm based on Gibbs energy minimization.
- CSMGem is tailored specifically to the hydrocarbon industry
- Phase equilibria can be calculated for the following conditions:
  - Incipient hydrate formation temperature at a fixed pressure
  - Incipient hydrate formation pressure at a fixed temperature
  - Fixed temperature and pressure
  - Fixed temperature and specified phase fraction (i.e., dew and bubble points)
  - Fixed pressure and specified phase fraction (i.e., dew and bubble points)
  - Expansion through a valve (i.e., fixed pressure and enthalpy)
  - Expansion through a turboexpander (i.e., fixed pressure and entropy)
- CSMGem can also plot phase boundaries when used in conjunction with MS Excel

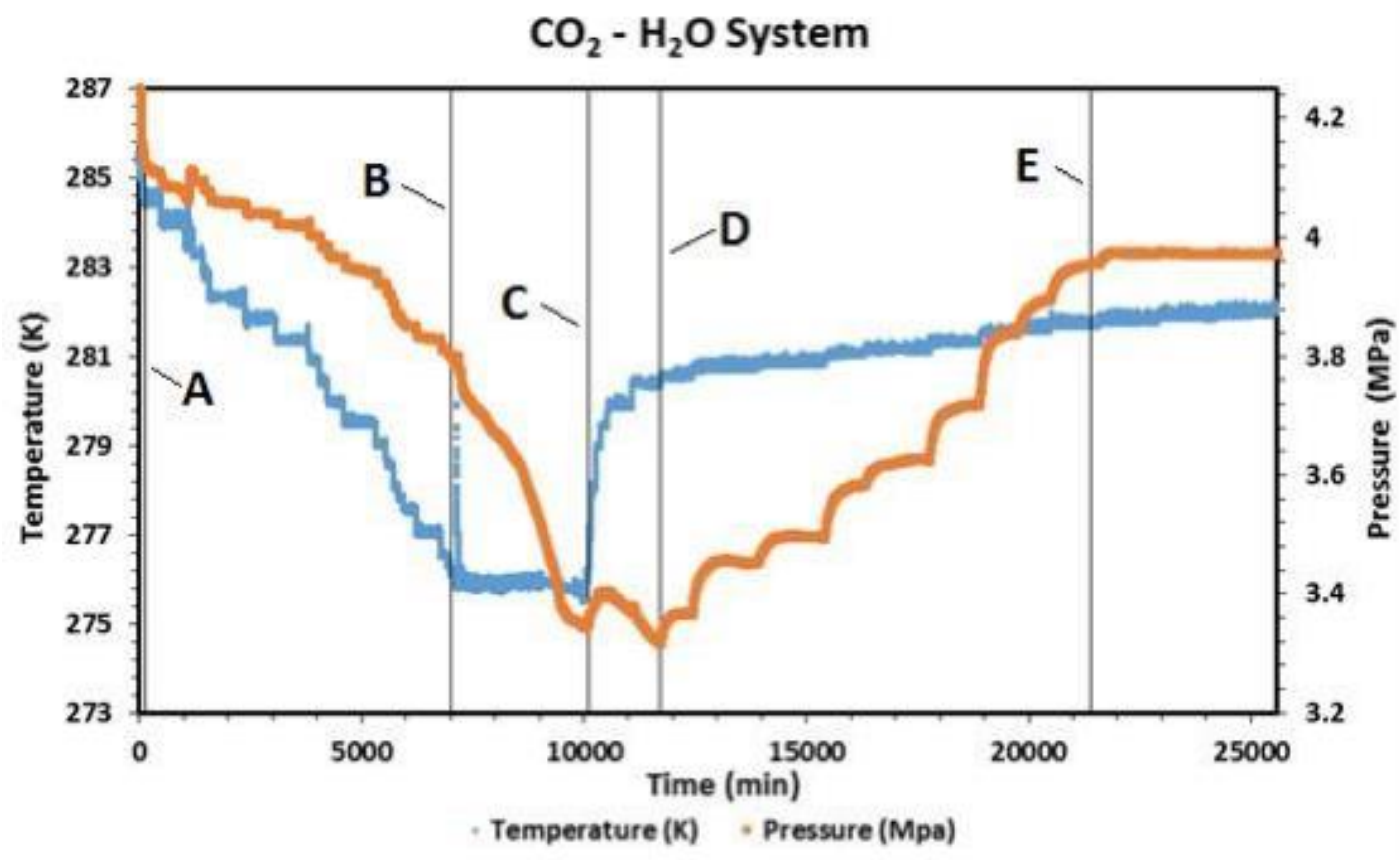


Results

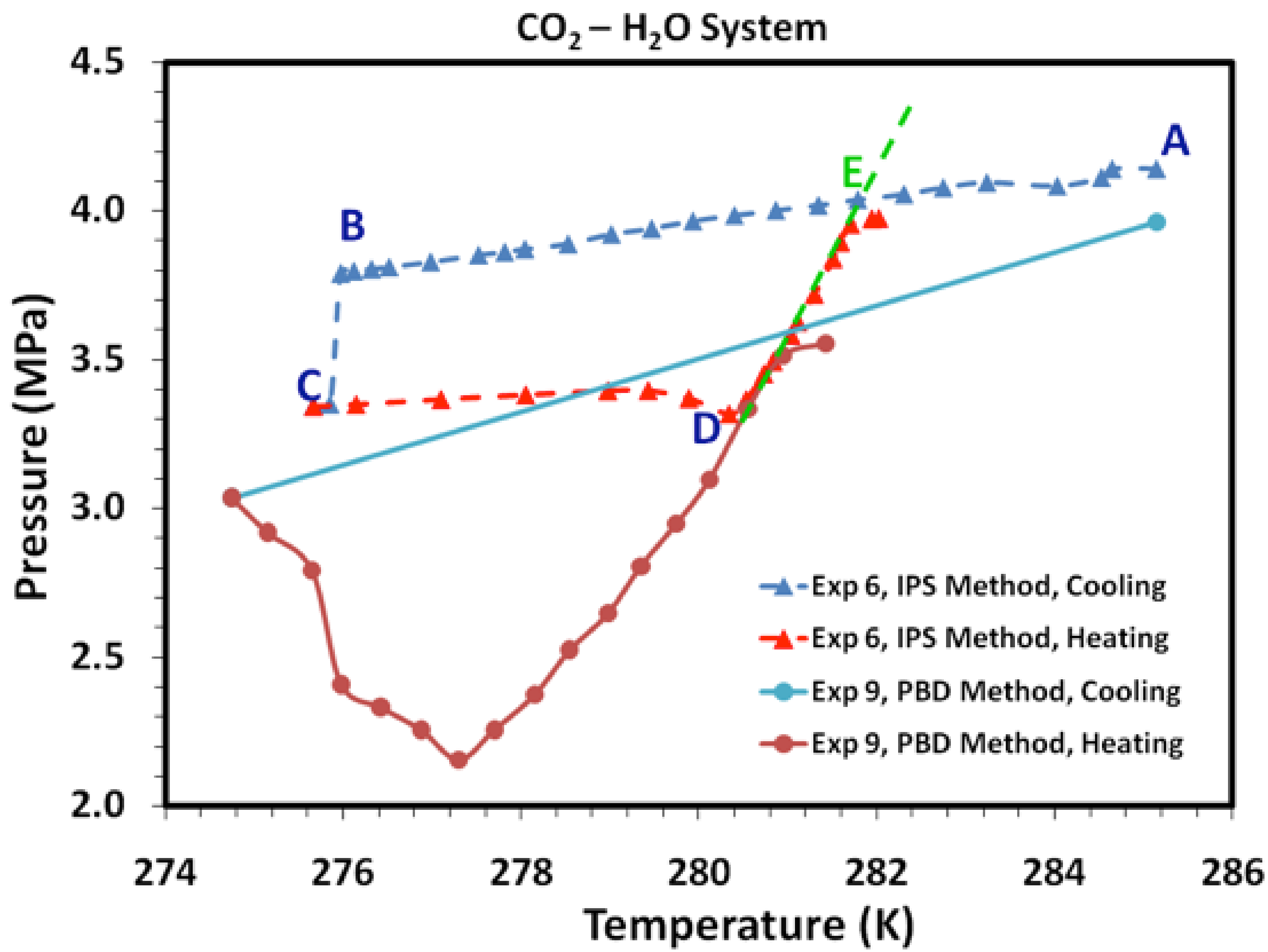
- Gas hydrate systems examined
  - Carbon dioxide – water
  - Methane – water

- Initial Experimental Conditions
  - Pressure range 2.5 – 8.5 MPa
  - Temperature range ~ 283 K

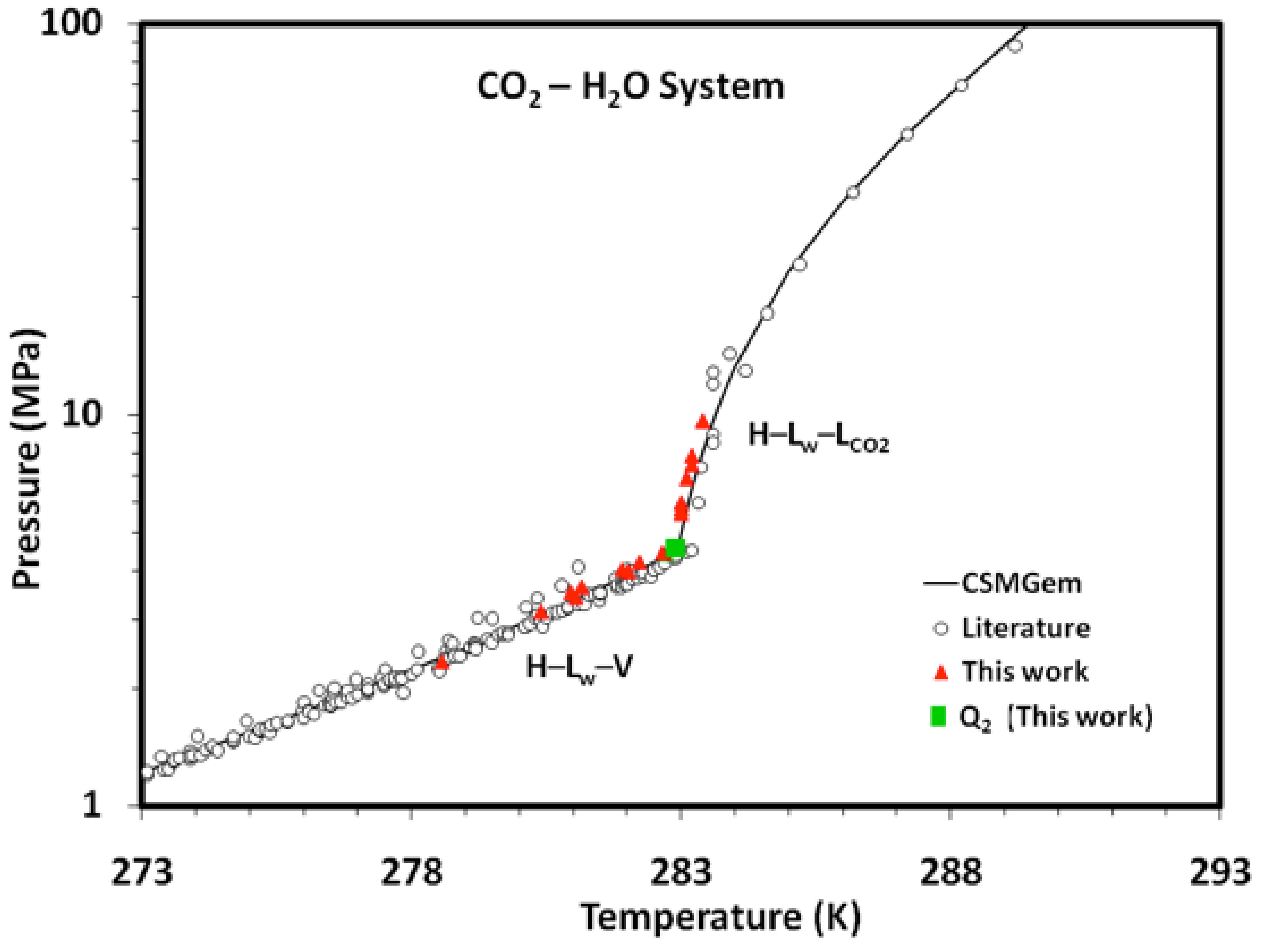
Time evolution of the pressure and temperature of an experiment



Pressure *vs*. Temperature diagram showing the cooling and heating cycles for two characteristic experiments for the CO_2 – H_2O system



Pressure *vs.* Temperature at three-phase equilibrium conditions for the system $CO_2 – H_2O$



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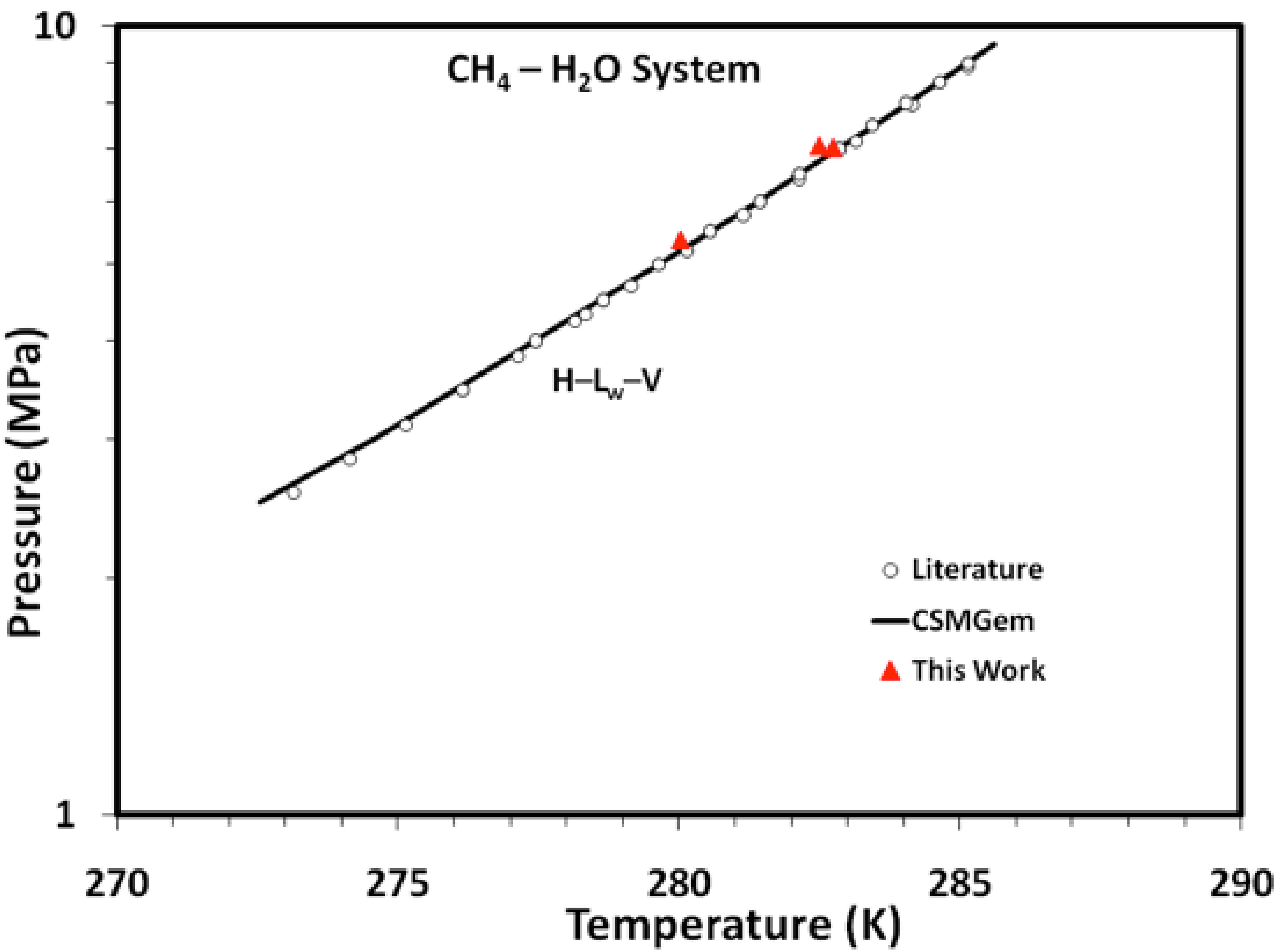
Reported values for the upper quadruple point of CO_2 + H_2O

Case	P (MPa)	T (K)	Reference
A	4.502	283.1	Unruh and Katz
B	4.468	283.3	Robinson and Metha
C	4.650	283.1	Fan and Guo
D	4.480	283.27	Mooijer-van den Heuvel et al.
E	4.510	282.924	CSMGem
F	**4.57 ± 0.03**	**282.9 ± 0.2**	**This work**

Pressure *vs.* Temperature at three-phase equilibrium conditions for the system CH_4 – H_2O



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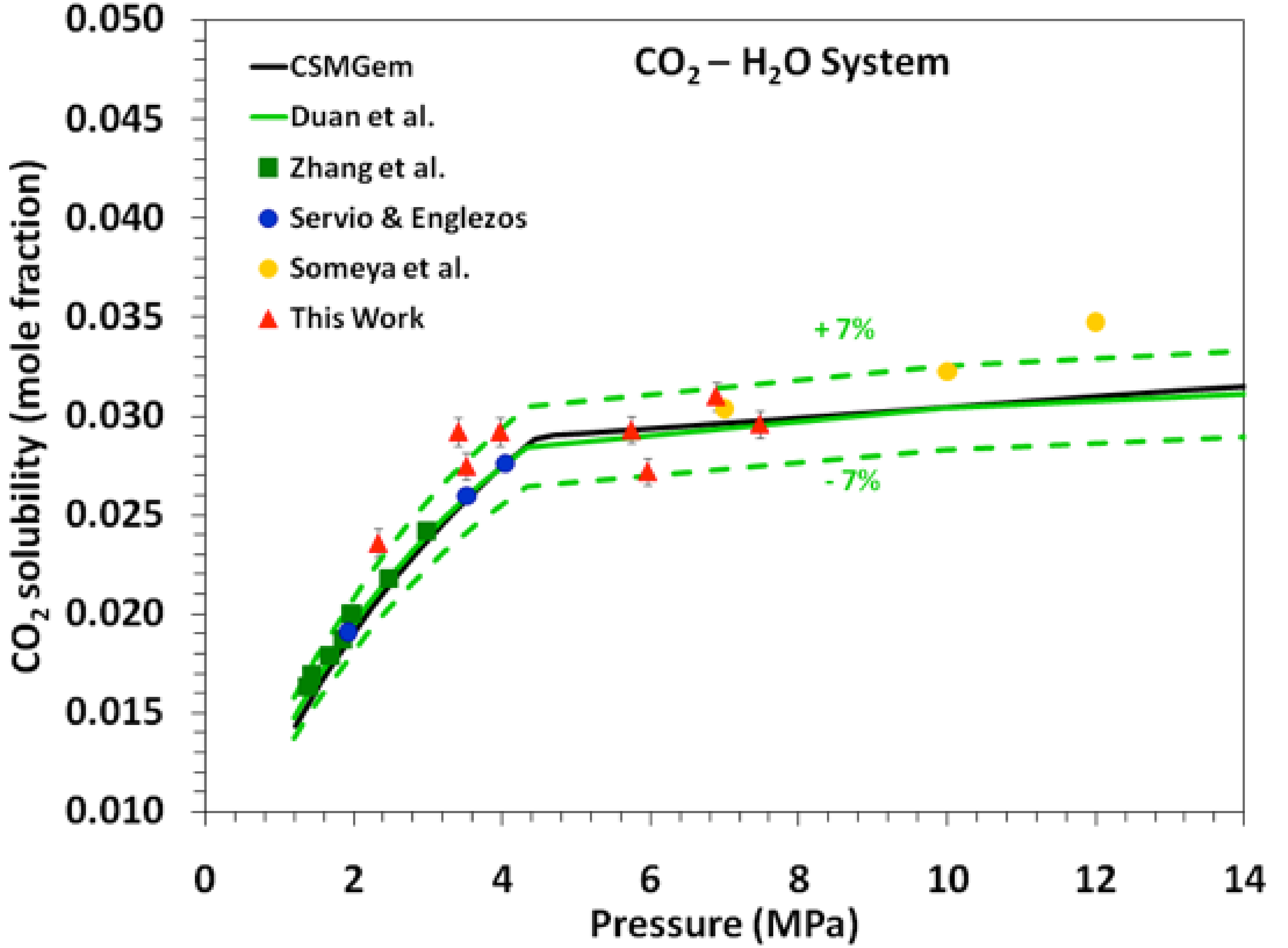
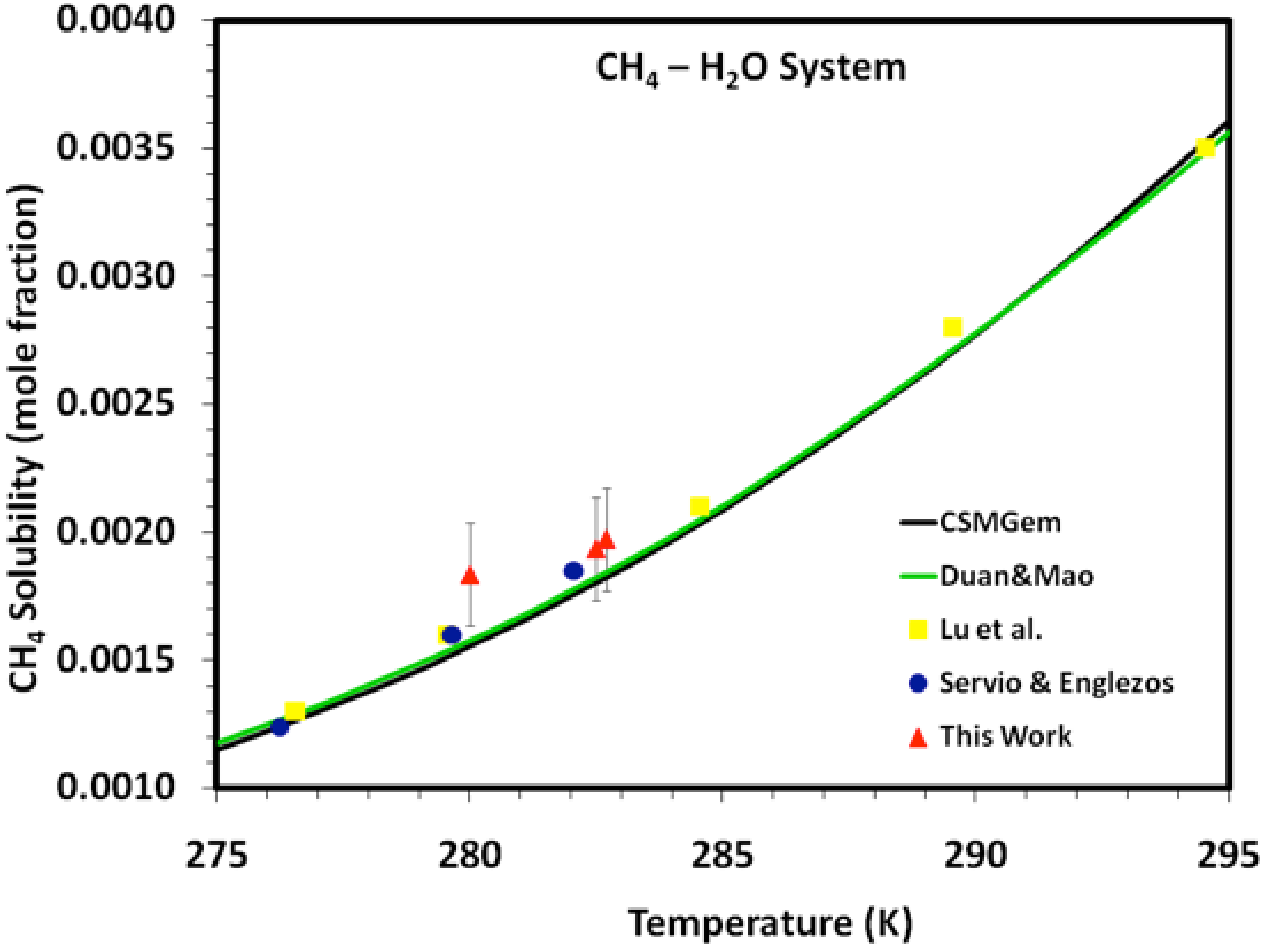
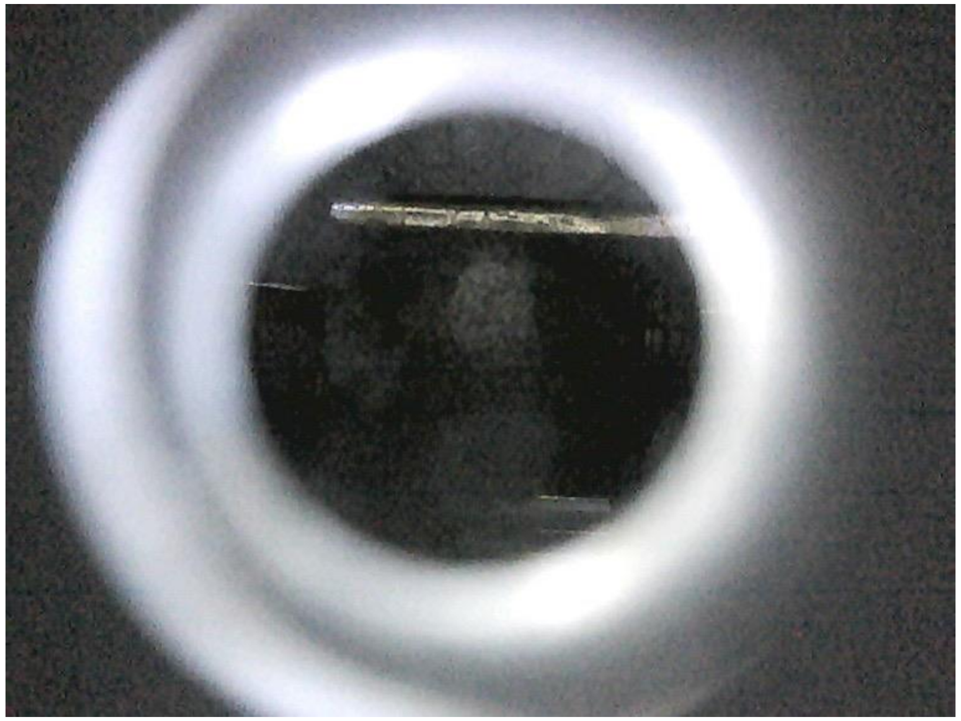
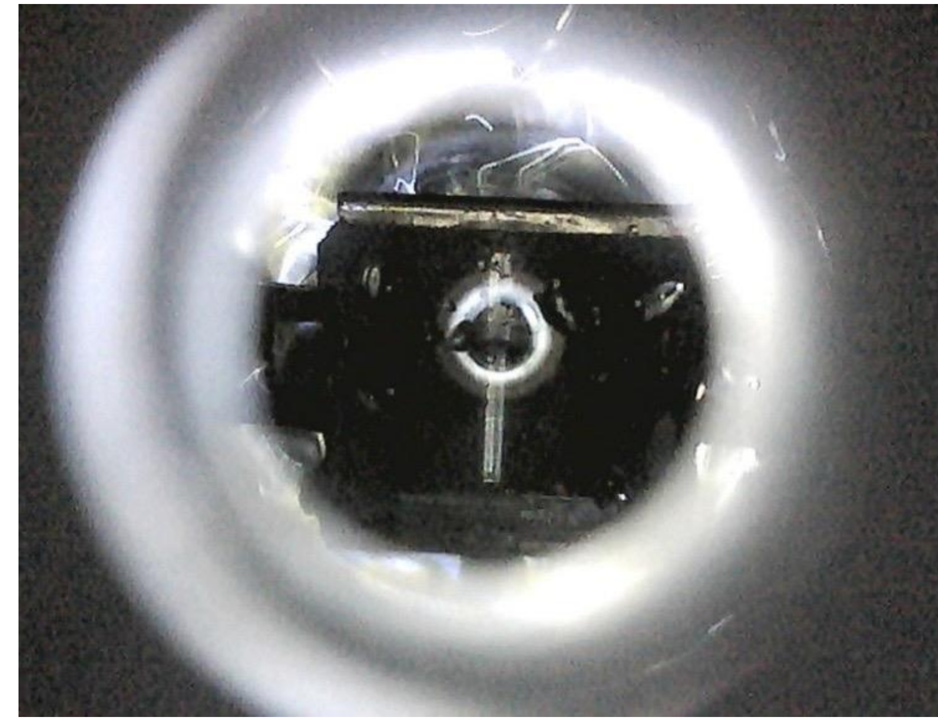
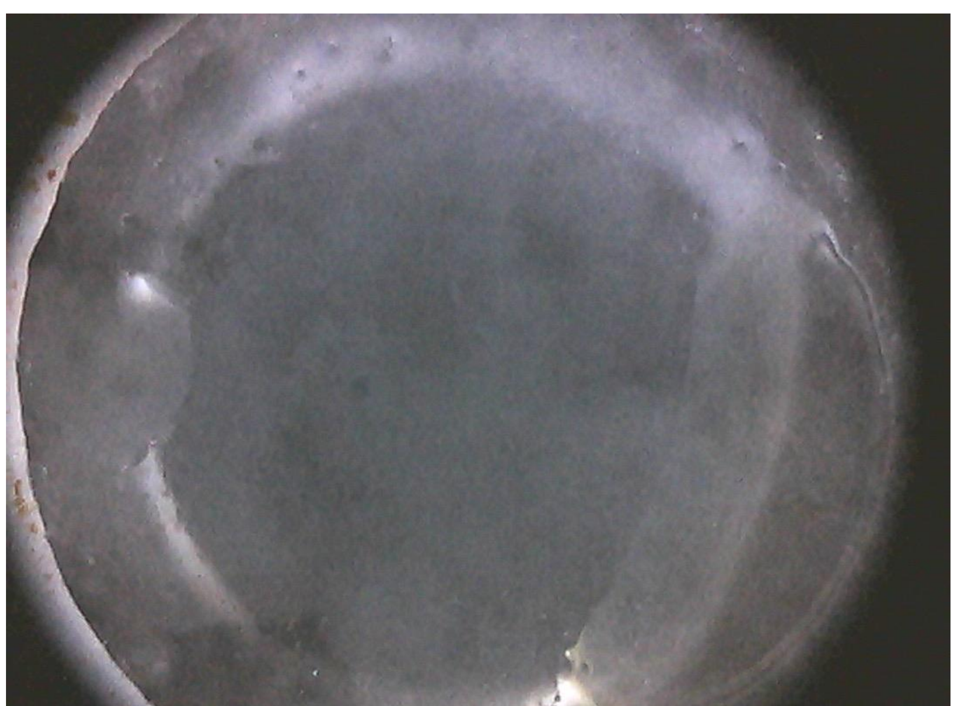
Solubility of CO_2 in H_2O under three-phase (H–L_w–V or H–L_w–L_{CO2}) equilibrium conditions, as a function of pressure



Solubility of CH_4 in H_2O under three-phase (H–L_W–V) equilibrium conditions, as a function of temperature



	Carbon Dioxide Clathrate formed	Equilibrium point
Gas Carbon Dioxide		
Liquid Carbon Dioxide		

Conclusions

- A novel experimental apparatus was designed and constructed for measuring the three-phase equilibrium conditions of pure gas and gas mixture hydrates
- Equilibrium points for carbon dioxide - water and methane - water systems were obtained, using existing experimental conditions alongside new, not reported yet
- The upper quadruple point was calculated with sufficient accuracy
- The solubility of the gas in the aqueous phase was measured under three-phase equilibrium conditions

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Acknowledgements

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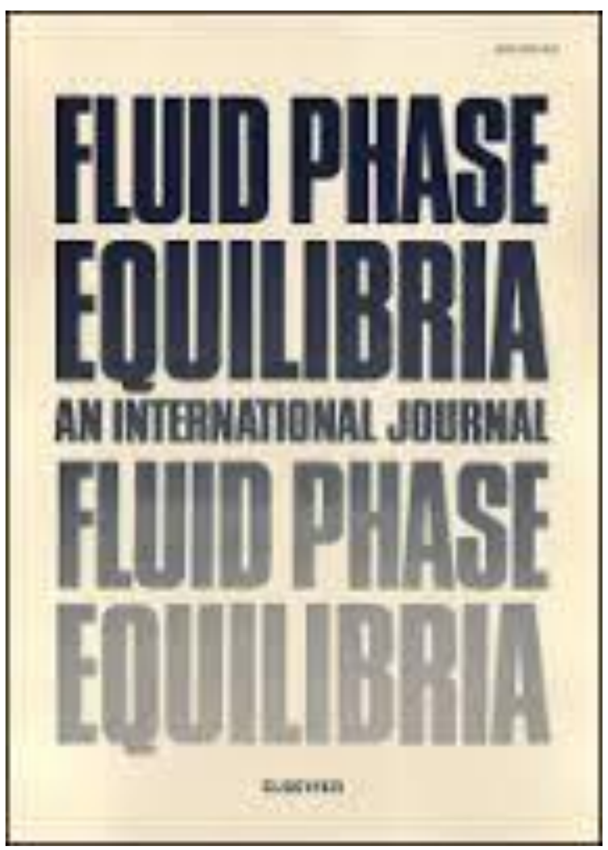

This work is submitted to

Fluid Phase Equilibria

“***Development of a Novel Experimental Apparatus for Hydrate Equilibrium Measurements***“

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