On the Use of Ionic Liquids in Order to Inhibit/Promote CO_2 Hydrates

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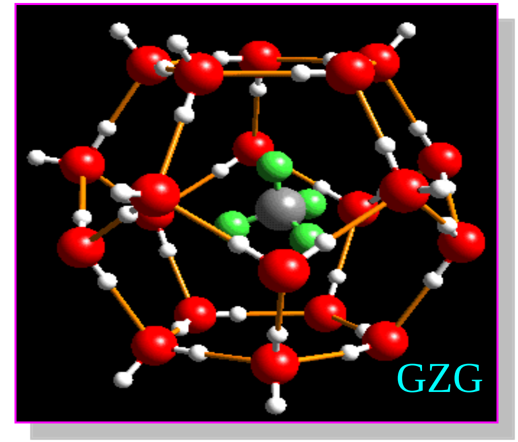
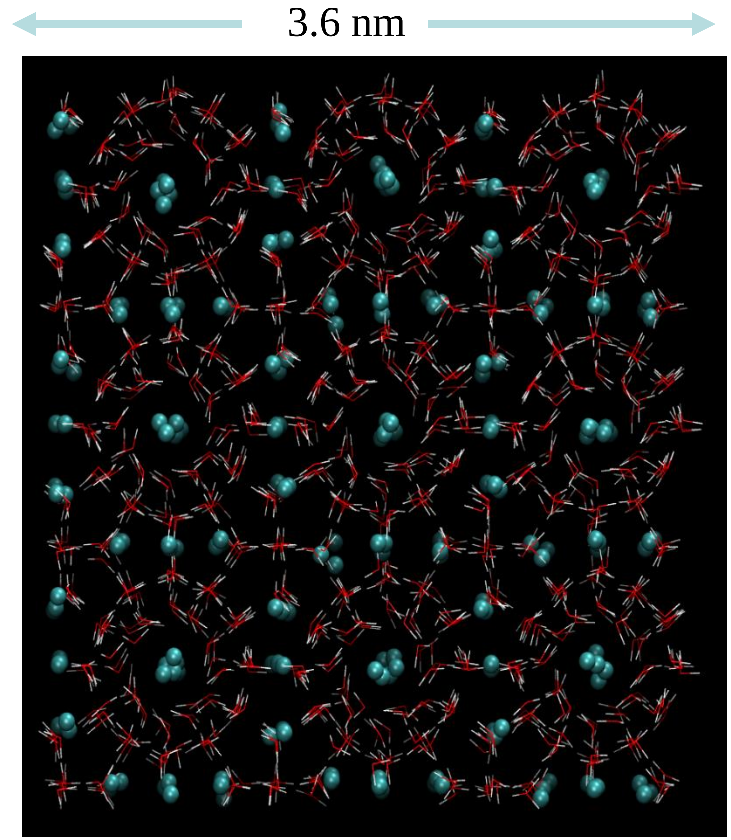
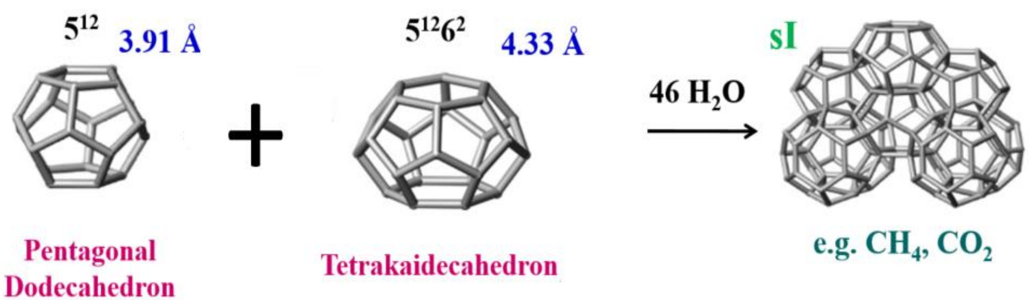
Hydrate Background

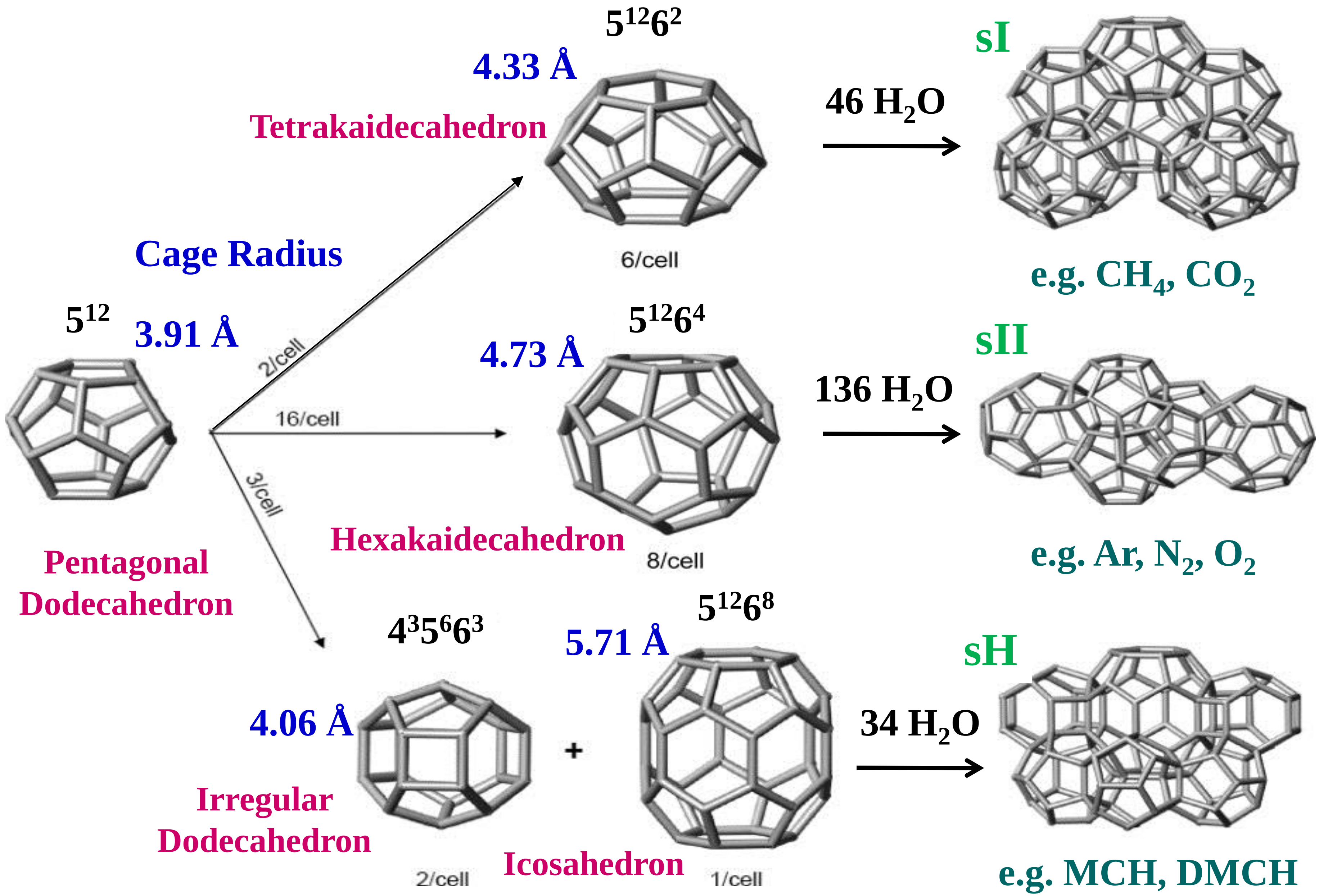
- Self-assembled, crystalline structures.
- Formed by water molecules creating a solid lattice that encages “guest” molecules.
- Structures are only stable at high pressures, low temperatures, and in the presence of guest molecules.
- More than 130 different molecules form hydrates ***(e.g., CH_4, CO_2,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





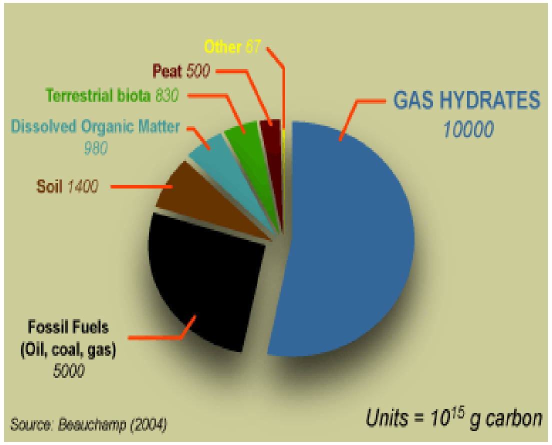


Cages in Gas Clathrate Hydrates



Hydrate Applications

Potential Energy Resource

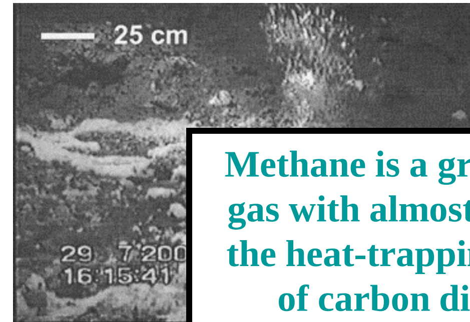


Flow Assurance/Safety

Blocking pipe-lines

Global Climate Change

- Sudden methane release
- CO_2 sequestration



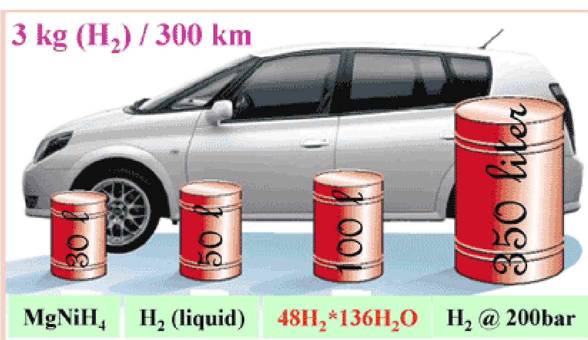
Methane is a greenhouse gas with almost 30 times the heat-trapping ability of carbon dioxide.

Separation Technology

- Gas Mixtures
- Water Desalination

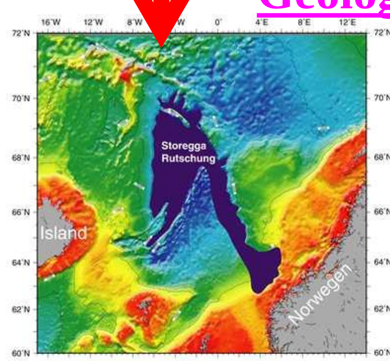
Gas Storage and Transport

- H_2, CH_4, CO_2

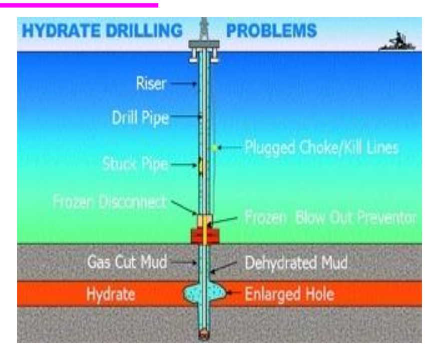


LANL modification of figure in:
Nature, **414**, 353 (2001).

Geologic Hazard



Oceanic slope collapsing



Danger to oil platforms

Hydrate Applications

Gas Storage and Transport
Potential Energy Source
Global Climate Change

Flow Assurance/Safety
Separation Technology
Geologic Hazard
Global Climate Change

Major Question Asked

Cage Occupancies

P-T hydrate equilibrium conditions

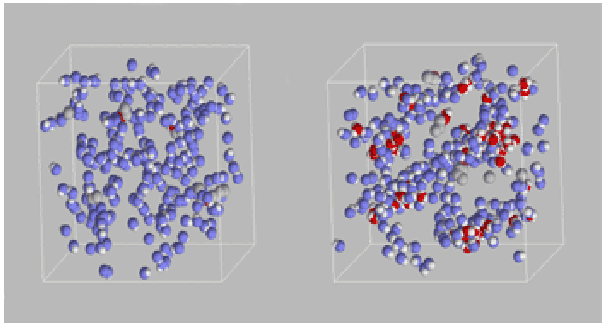
Approaches for Property Calculation

- ***Experimental Measurements.***

- ***Thermodynamic Modeling at the Continuum Scale.***

$$P = f(N, V, T)$$

- ***Computational Simulations at the Molecular Scale:***
    - ***Molecular Dynamics, Monte Carlo, Ab Initio, etc.***



Example: Gas Hydrates

Question

Hydrate P-T equilibrium conditions?

Answer through:

- ***Computational Simulations using the Monte Carlo approach.***
- ***Thermodynamic Modeling (for equilibrium conditions).***
  - ***Van der Waals and Platteeuw Theory (1959) and subsequent modifications.***
- ***Experimental Measurements.***
  - ***PVT, etc.***

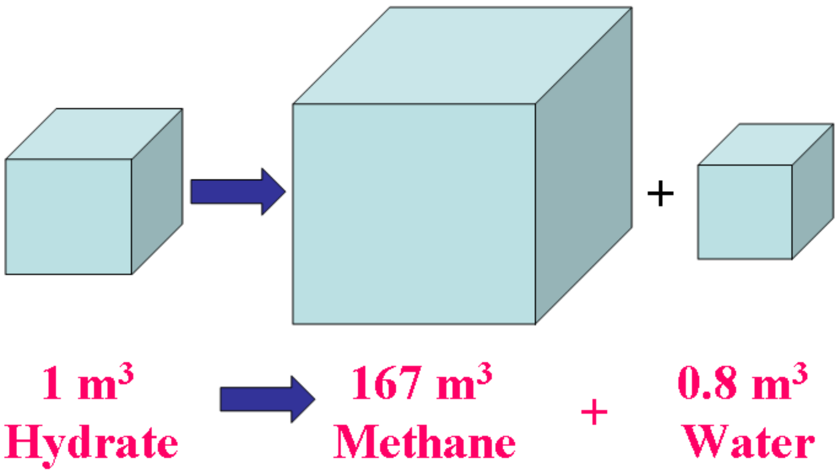
Topic of Interest to this study!

Gas Storage and Transport

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

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

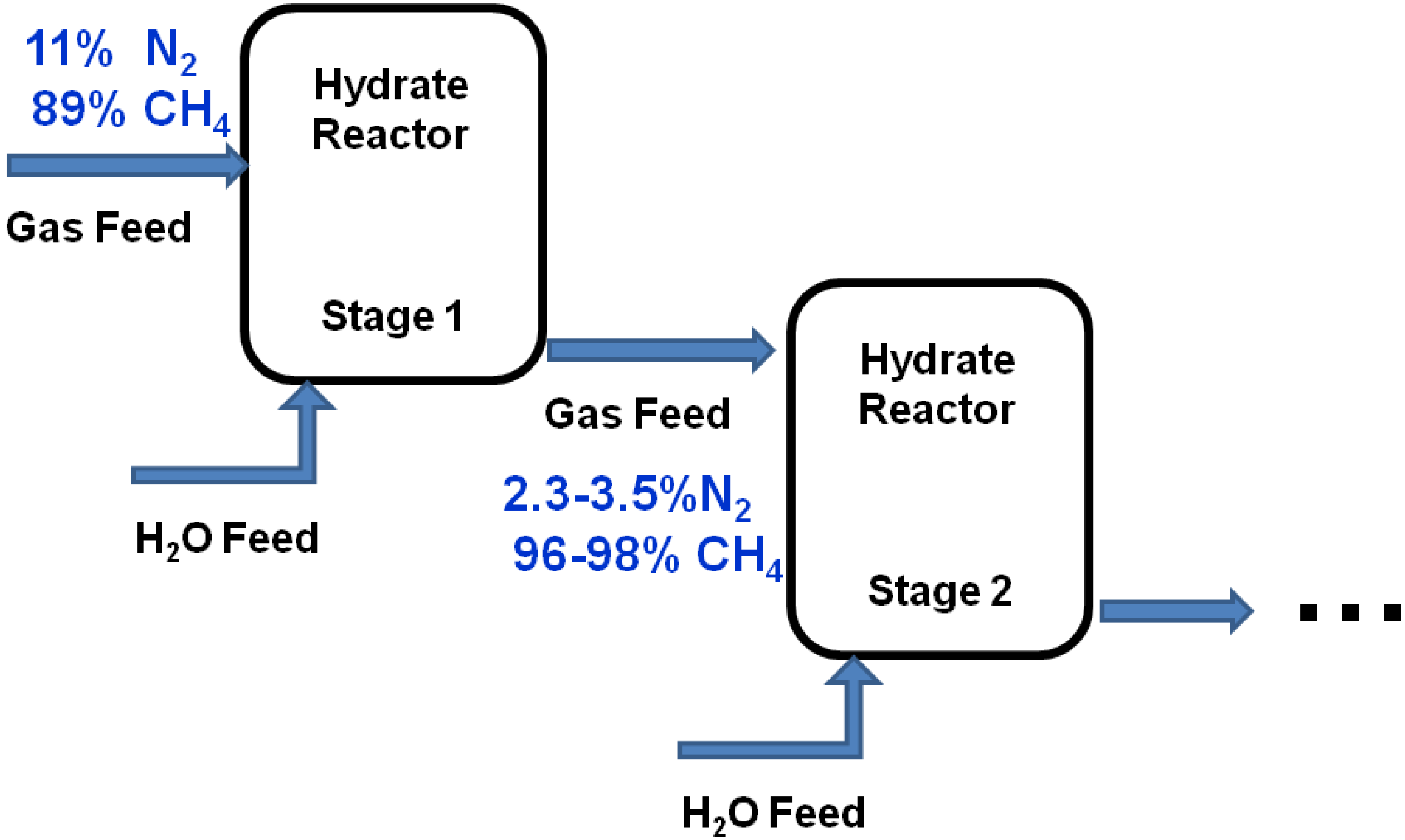
- **Transport stranded CH_4 gas.**
- **Transport gas into slurries.**
- **Store Hydrogen.**
- **Store CO_2 in CO_2-hydrate pellets.**
- **…**



Significant Potential in Future Applications !!!

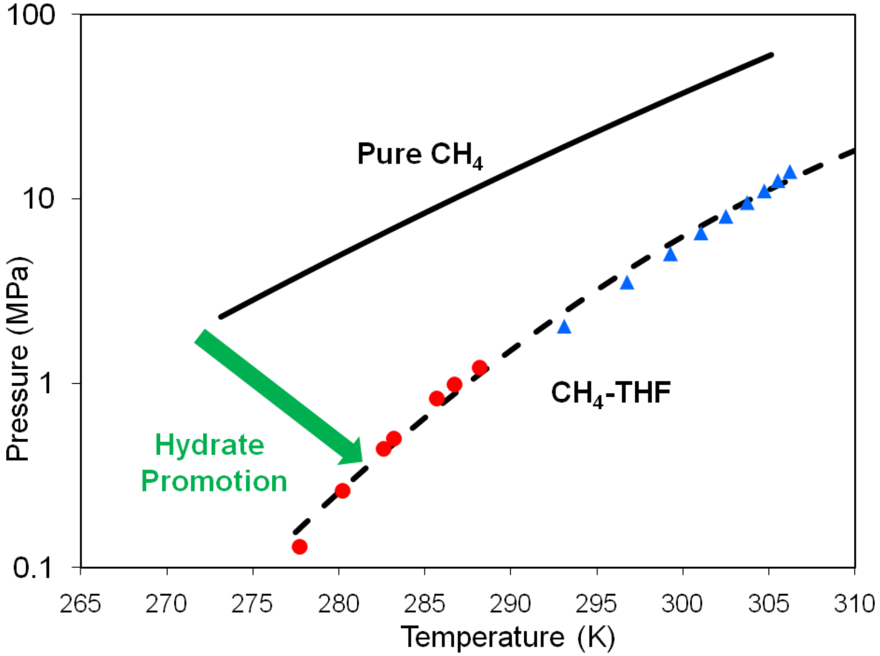
Gas Mixture Separation

N_2–CH_4 binary mixture separation using the hydrate approach

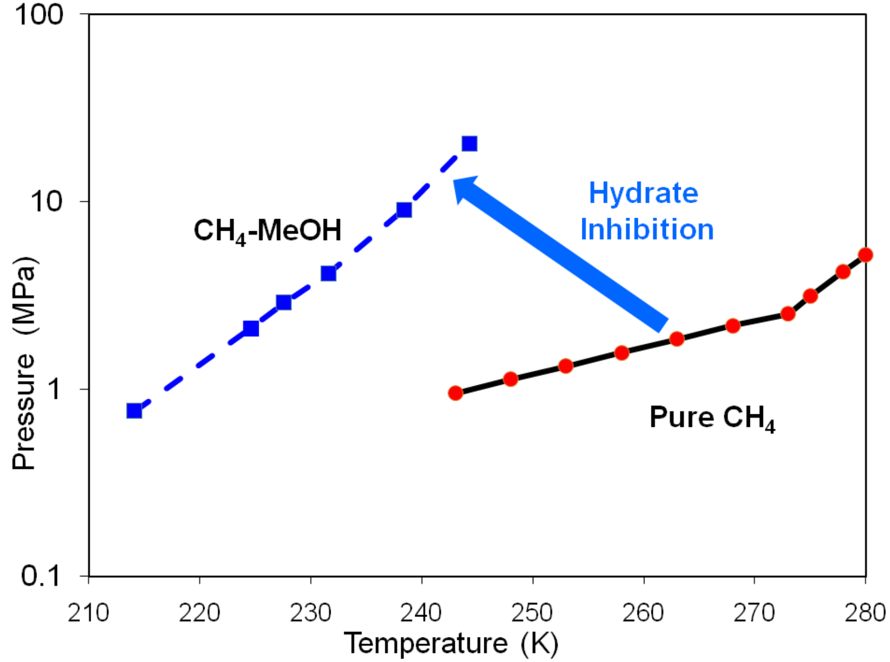


Effect of Additives

An additive can promote hydrate formation (e.g., THF) or inhibit hydrate formation (e.g., MeOH).



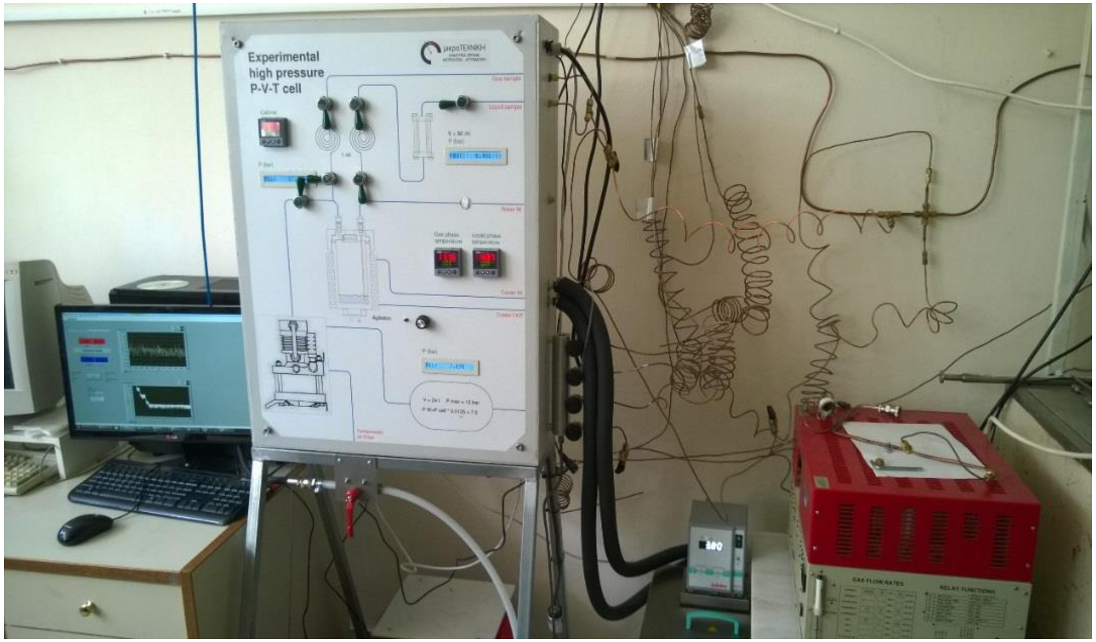
Gas Storage and Transport
Separation Technology



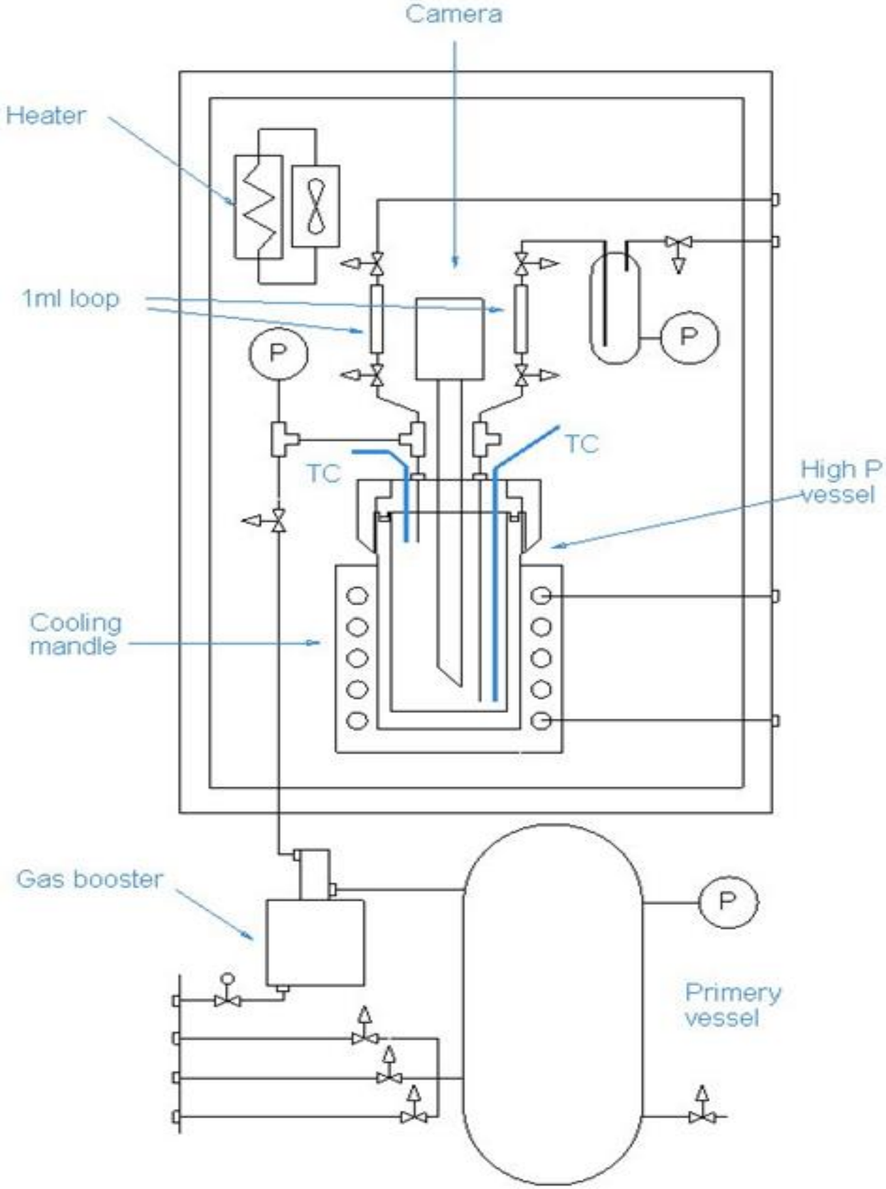
Flow Assurance/Safety

Ionic Liquids can function as both promoters or inhibitors!

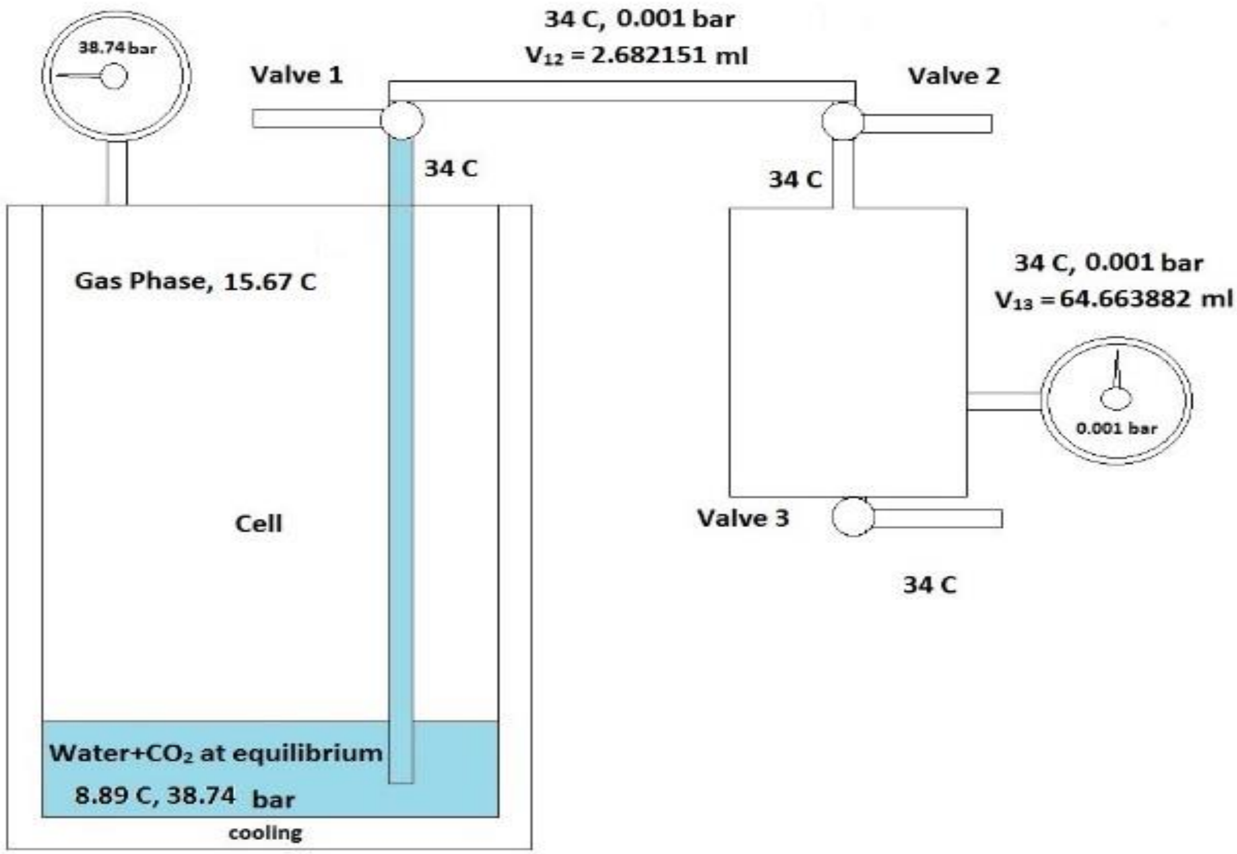
Experimental Device



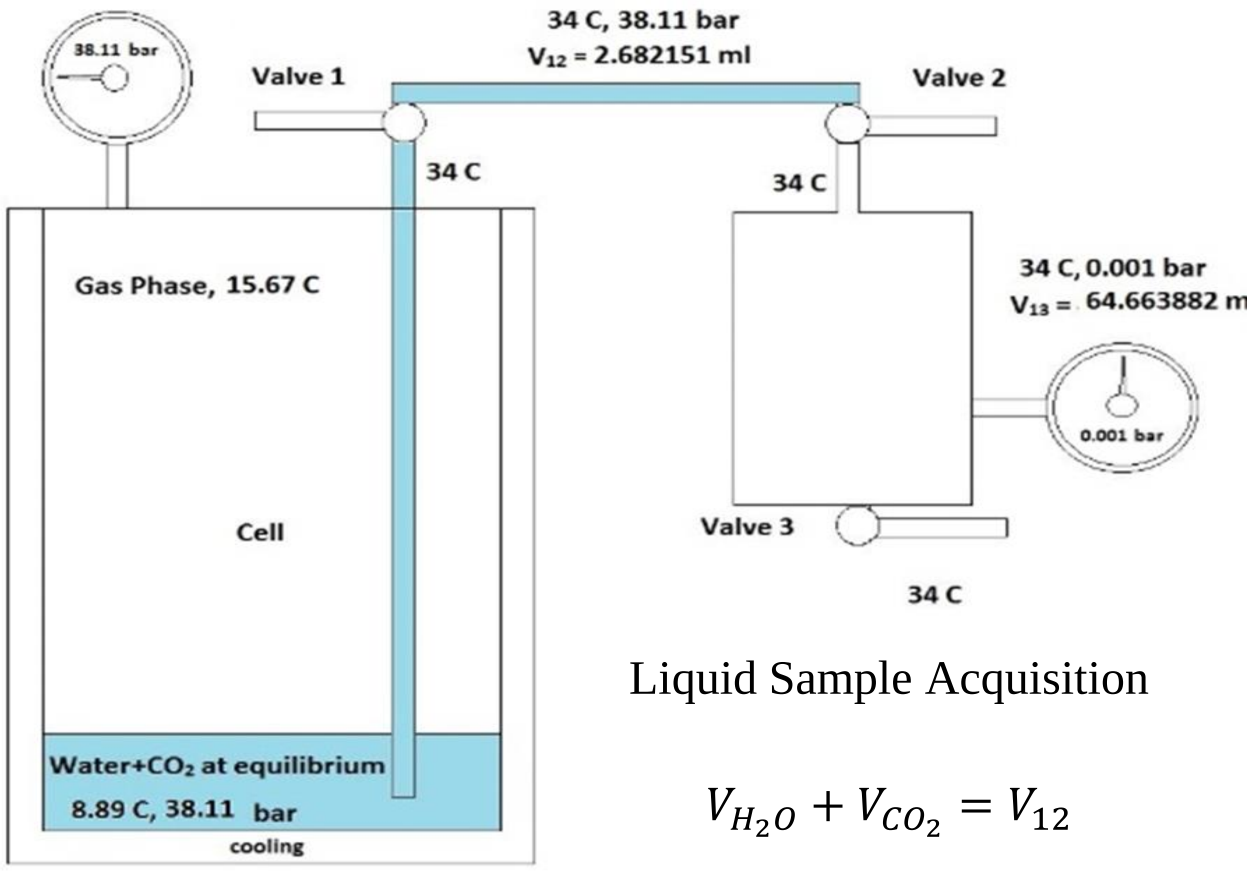
1. Preparation manifold
2. Thermostated air cabinet
3. PVT cell
4. Pressure relief cell for liquid sampling
5. Electronics and monitoring
6. Julabo temperature control system
7. Gas chromatograph



Solubility Calculation

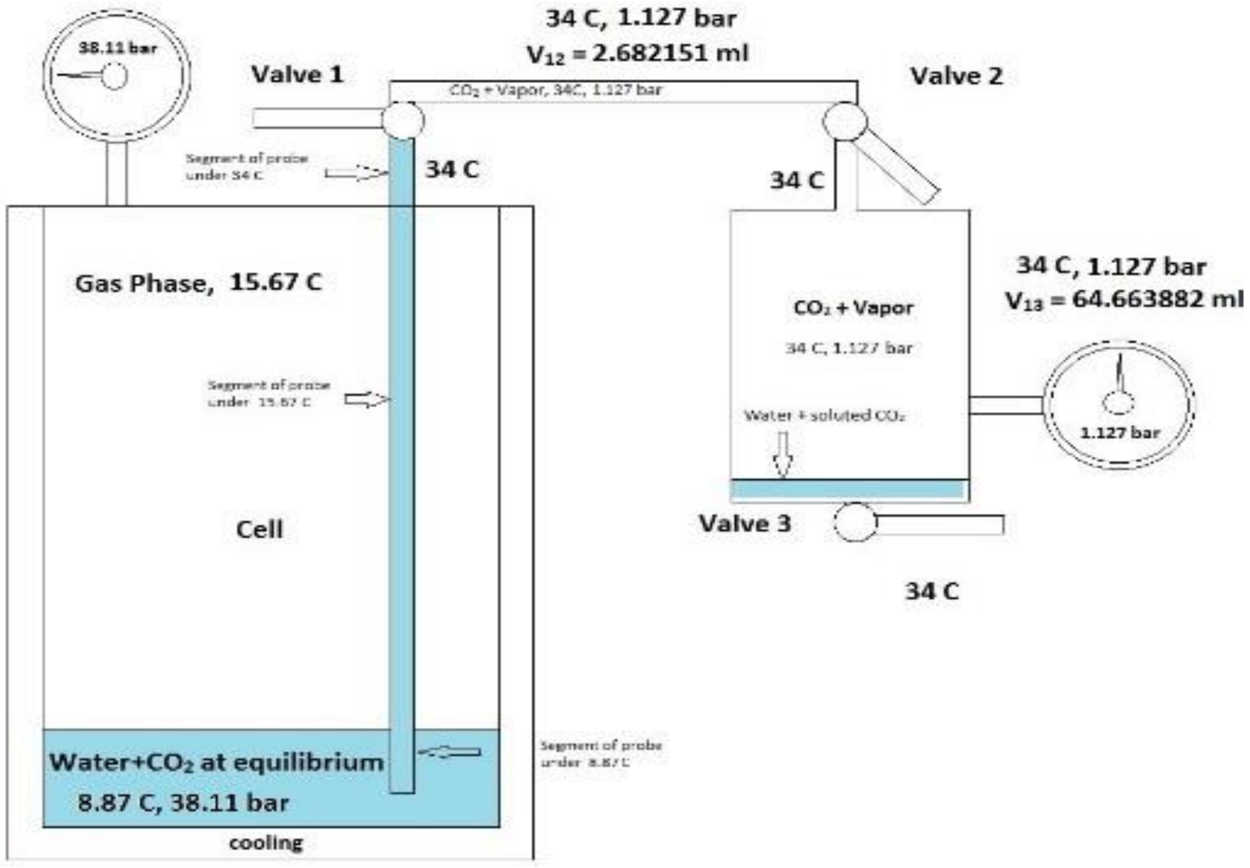


System at Equilibrium point



Liquid Sample Acquisition

$$V_{H_2O} + V_{CO_2} = V_{12}$$



Expansion to pressure relief cell

Solubility Equations

Liquid Sample Acquisition

$$V_{H_2O} + V_{CO_2} = V_{12}$$

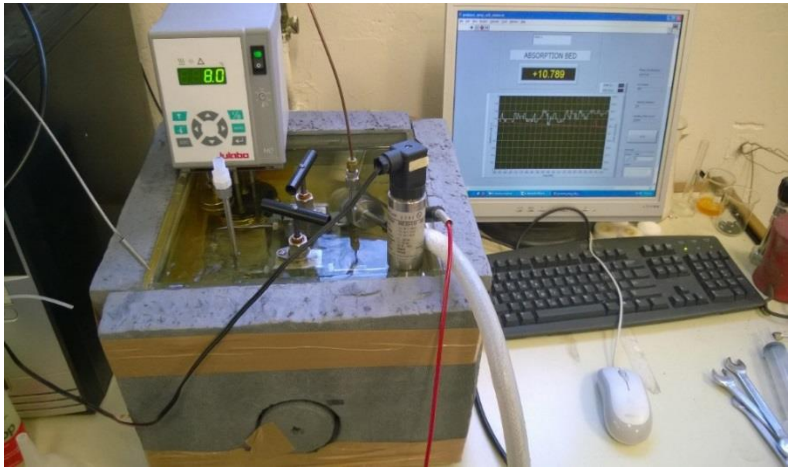
- $$V_{CO_2} = \left[\frac{(P - P_g)\cdot(V - V_{H_2O})}{R\cdot T} + \frac{\rho\cdot V_{H_2O}}{\frac{18}{1000}}\cdot\left(\frac{moles_{\ CO_2}}{moles_{\ H_2O}}\right)\right]\cdot \tilde{V}_{CO_2}$$

- $$n_{CO_2} = \frac{(P - P_g)\cdot(V - V_{H_2O})}{R\cdot T} + \frac{\rho\cdot V_{H_2O}}{\frac{18}{1000}}\cdot\left(\frac{moles_{\ CO_2}}{moles_{\ H_2O}}\right)$$

- $$X_{CO_2} = \frac{n_{\ CO_2}}{n_{\ H_2O} + n_{\ CO_2}}$$

Bed Cell

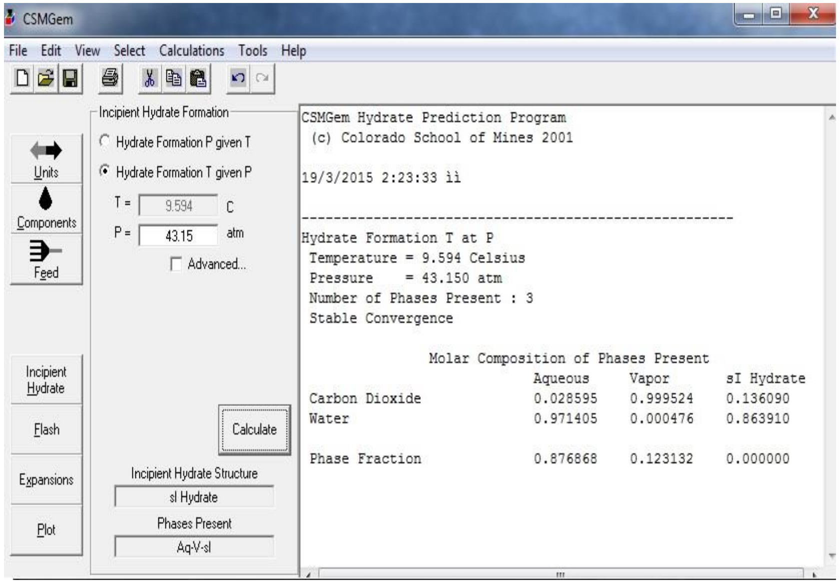
1. Equilibrium view cell
2. Pressure Transducer
3. Thermostatic bath
4. Electronics and monitoring



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

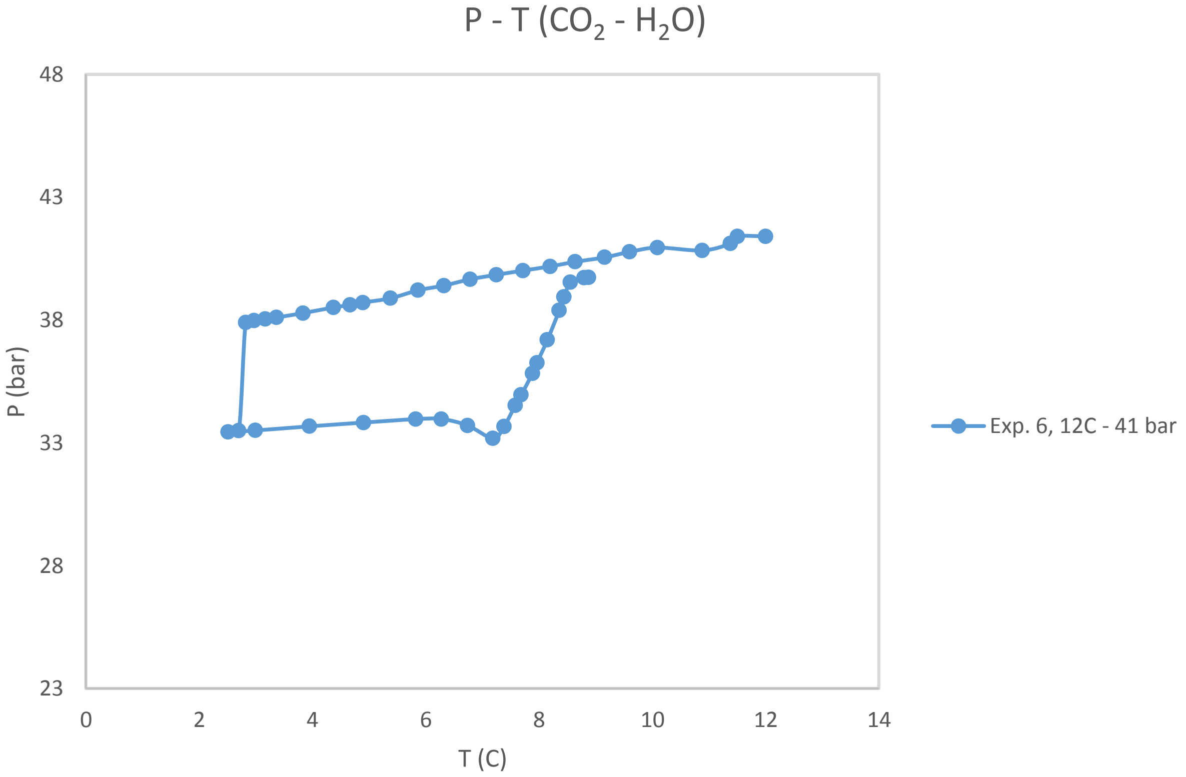


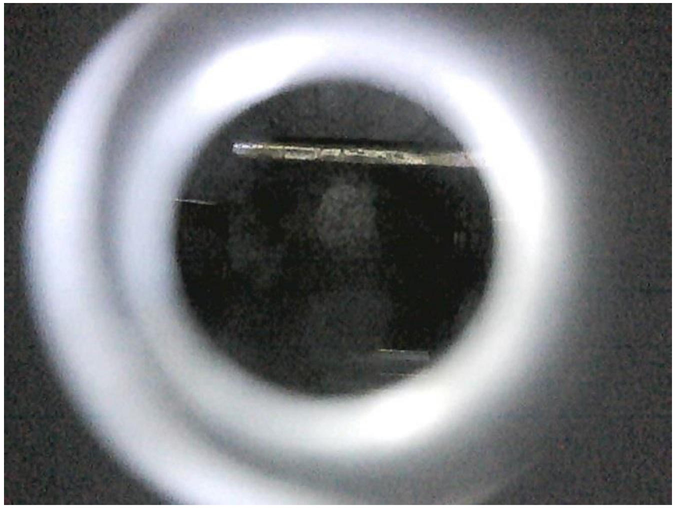
Results

Carbon Dioxide

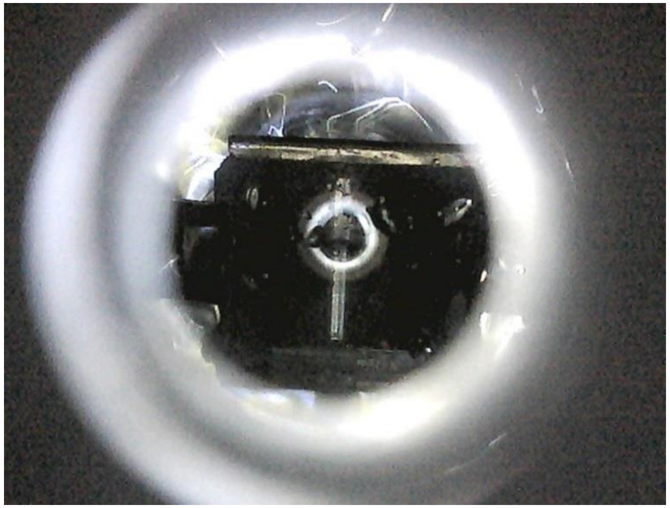
Typical Clathrate P-T diagram

- Isochoric cooling
- Metastability limit – Hydrate formation
- Isochoric heating
- Hydrate Dissociaton
- Equilibrium point – Hydrate dissociation completed



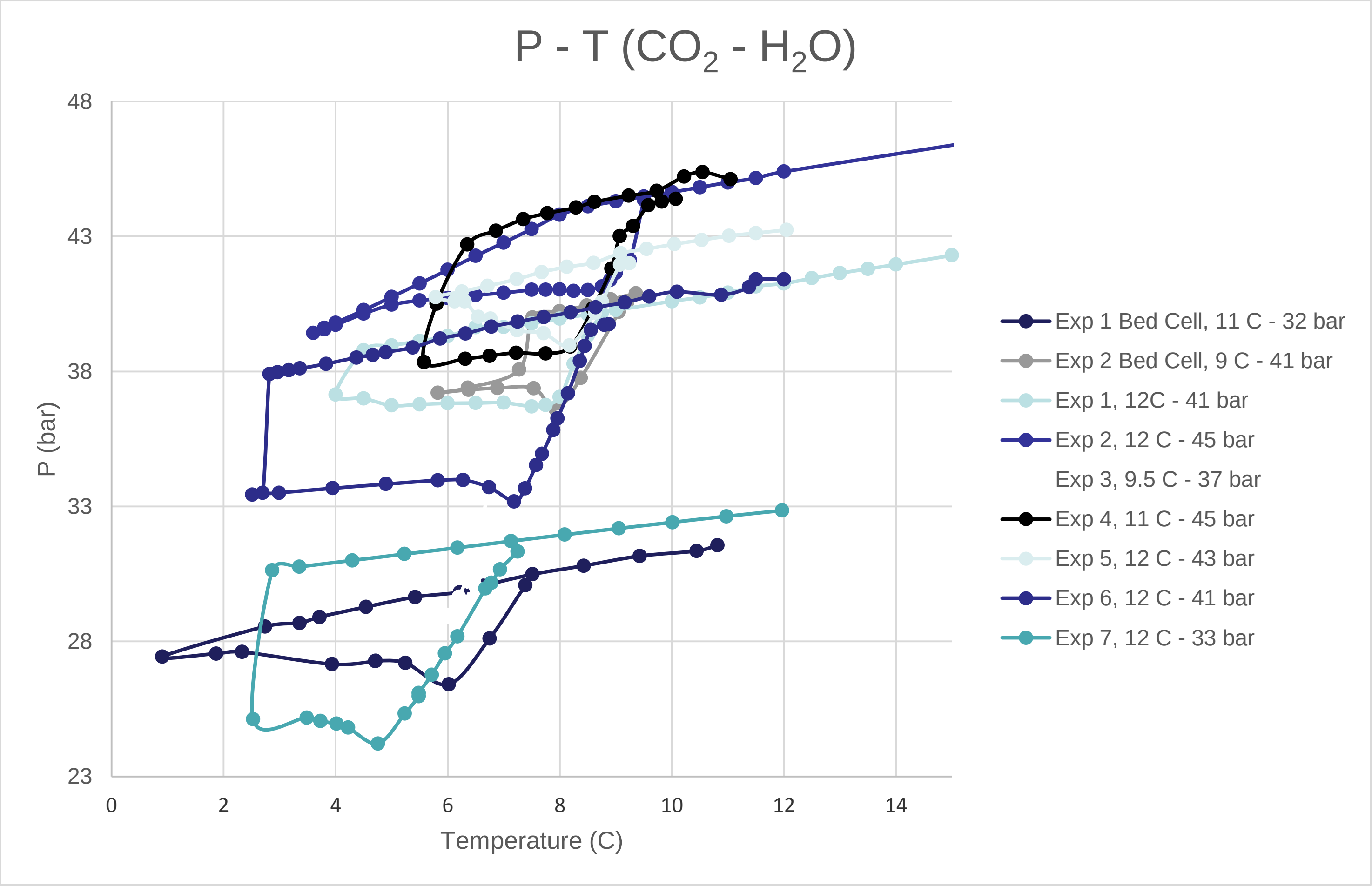


Carbon Dioxide Hydrate formed

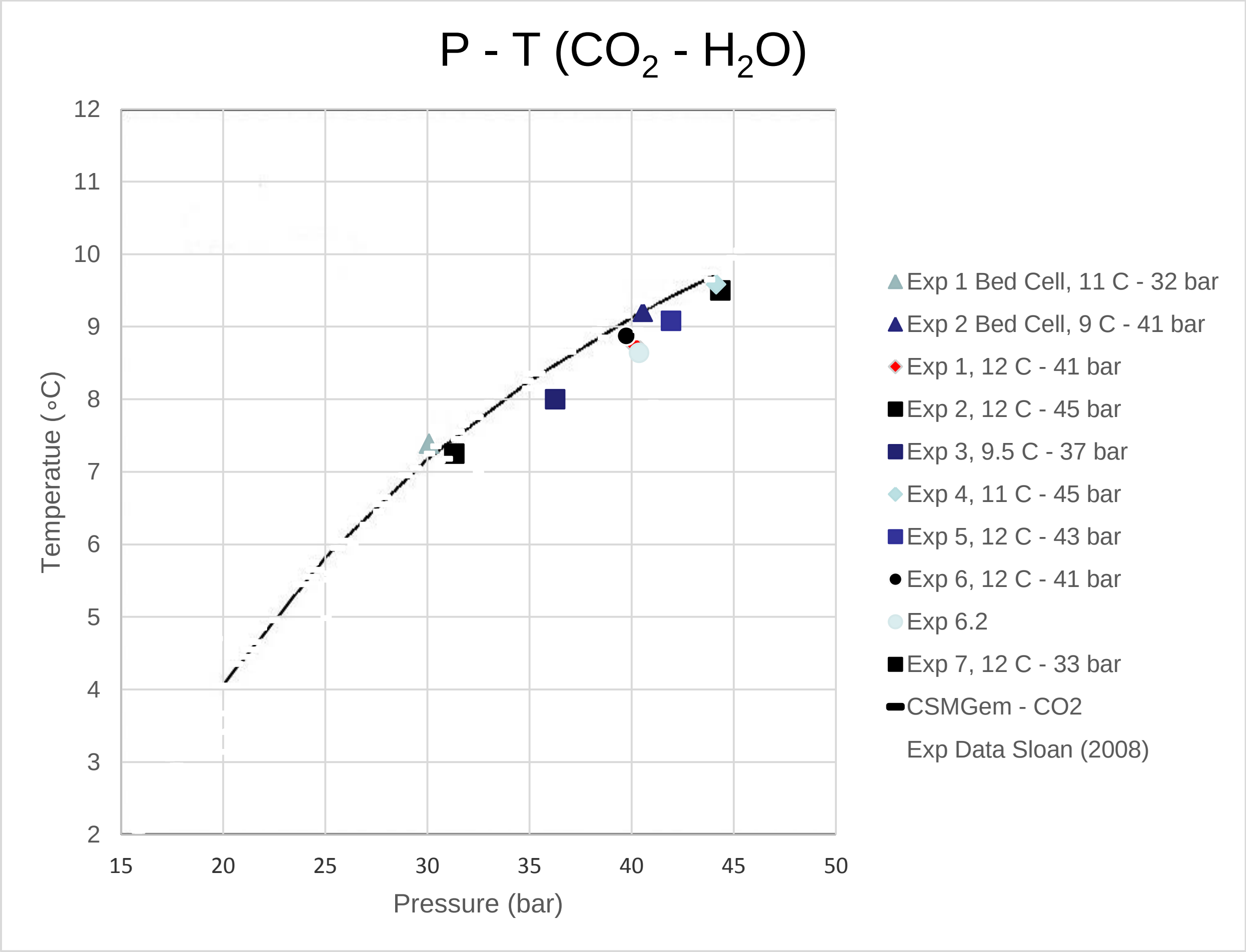


Equilibrium point

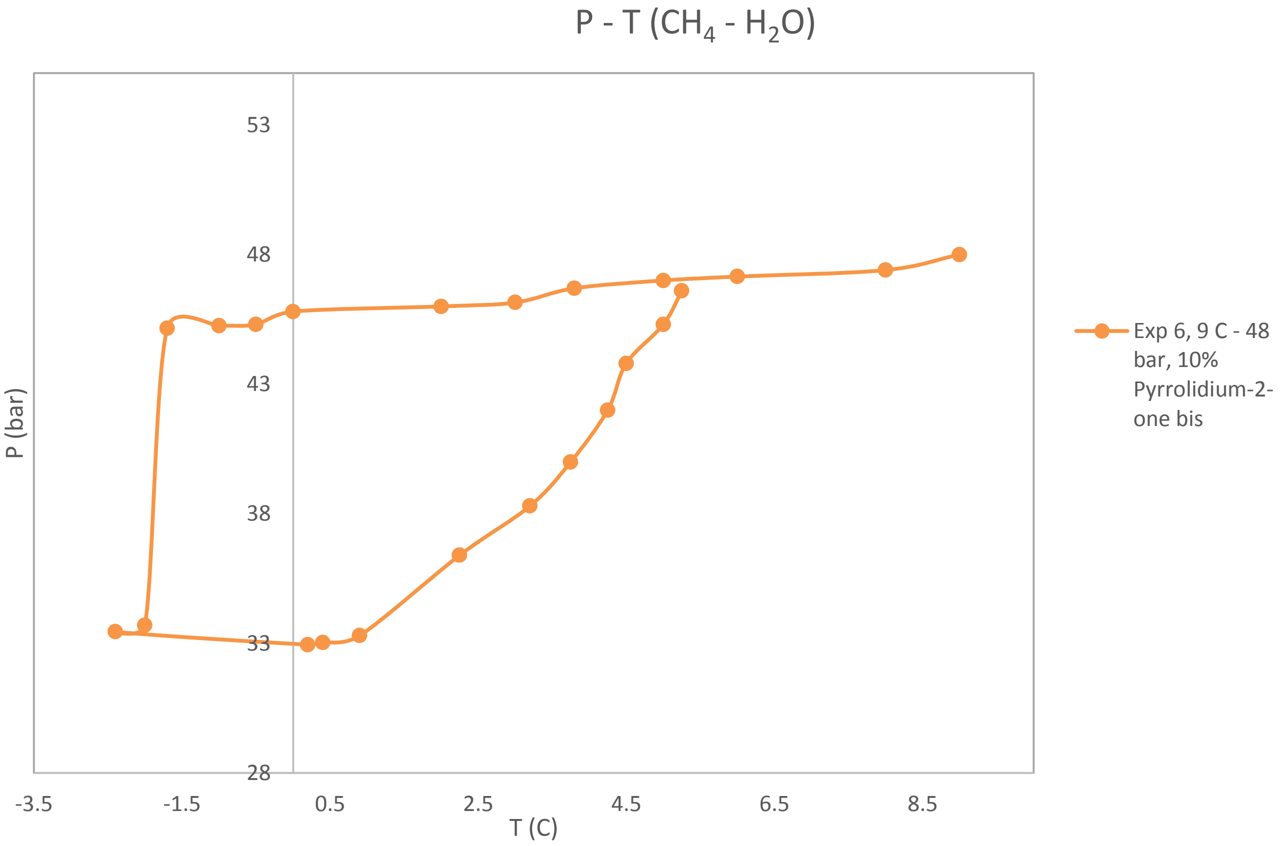
Experiments conducted with Carbon Dioxide and Water



Carbon Dioxide equilibrium points

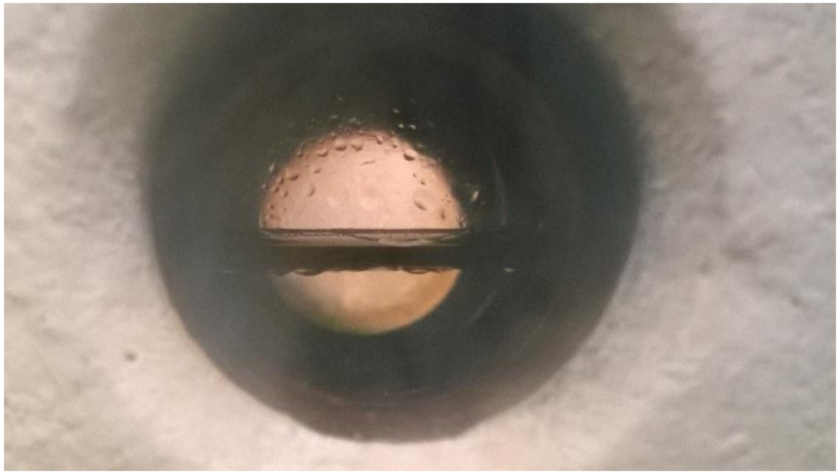


Methane



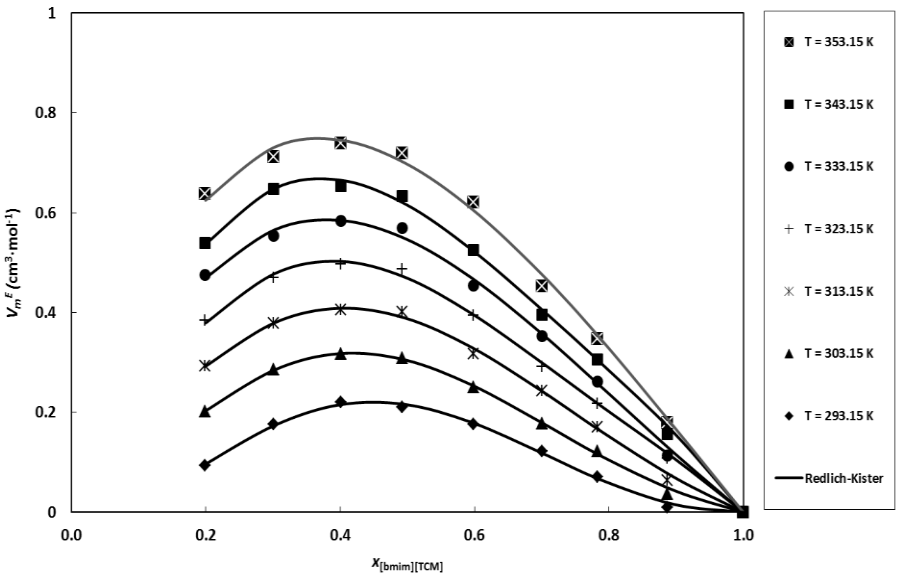
P - T (CH_4 - H_2O)
53
48
43
38
33
28
-3.5
-1.5
0.5
2.5
4.5
6.5
8.5
T (C)
P (bar)
Exp 6, 9 C - 48 bar, 10% Pyrrolidium-2-one bis

Methane Hydrate formed

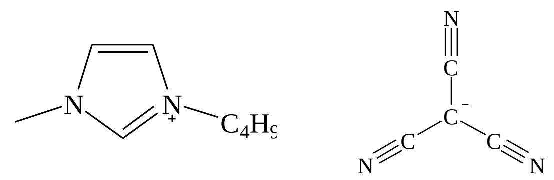


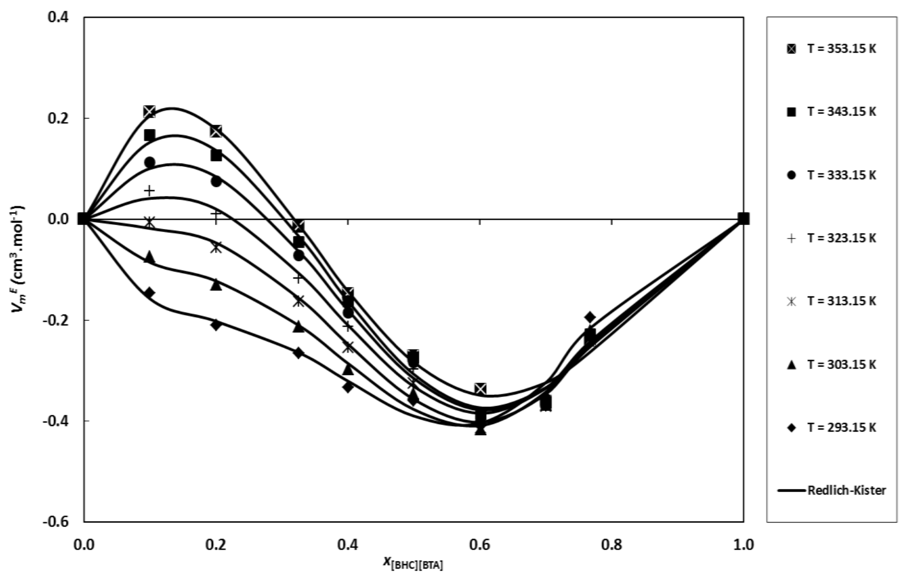
Near Equilibrium point

Excess molar volume of IL/H_2O binary systems

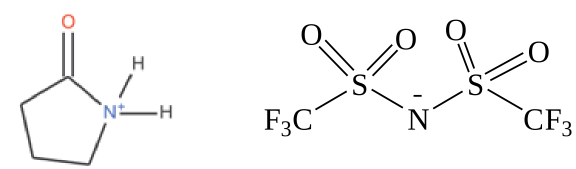


1-butyl-3-methyl-imidazolium tricyanomethanide

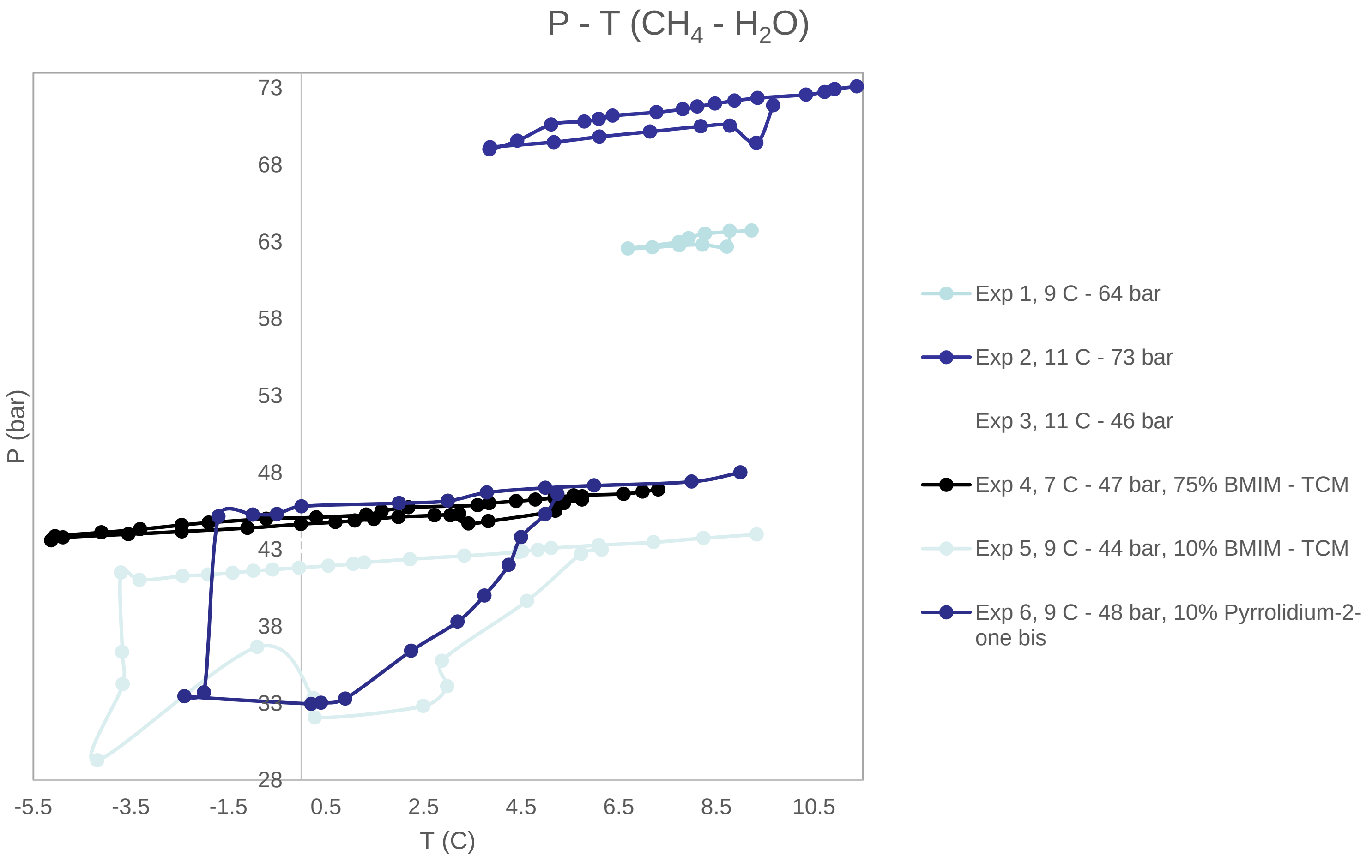


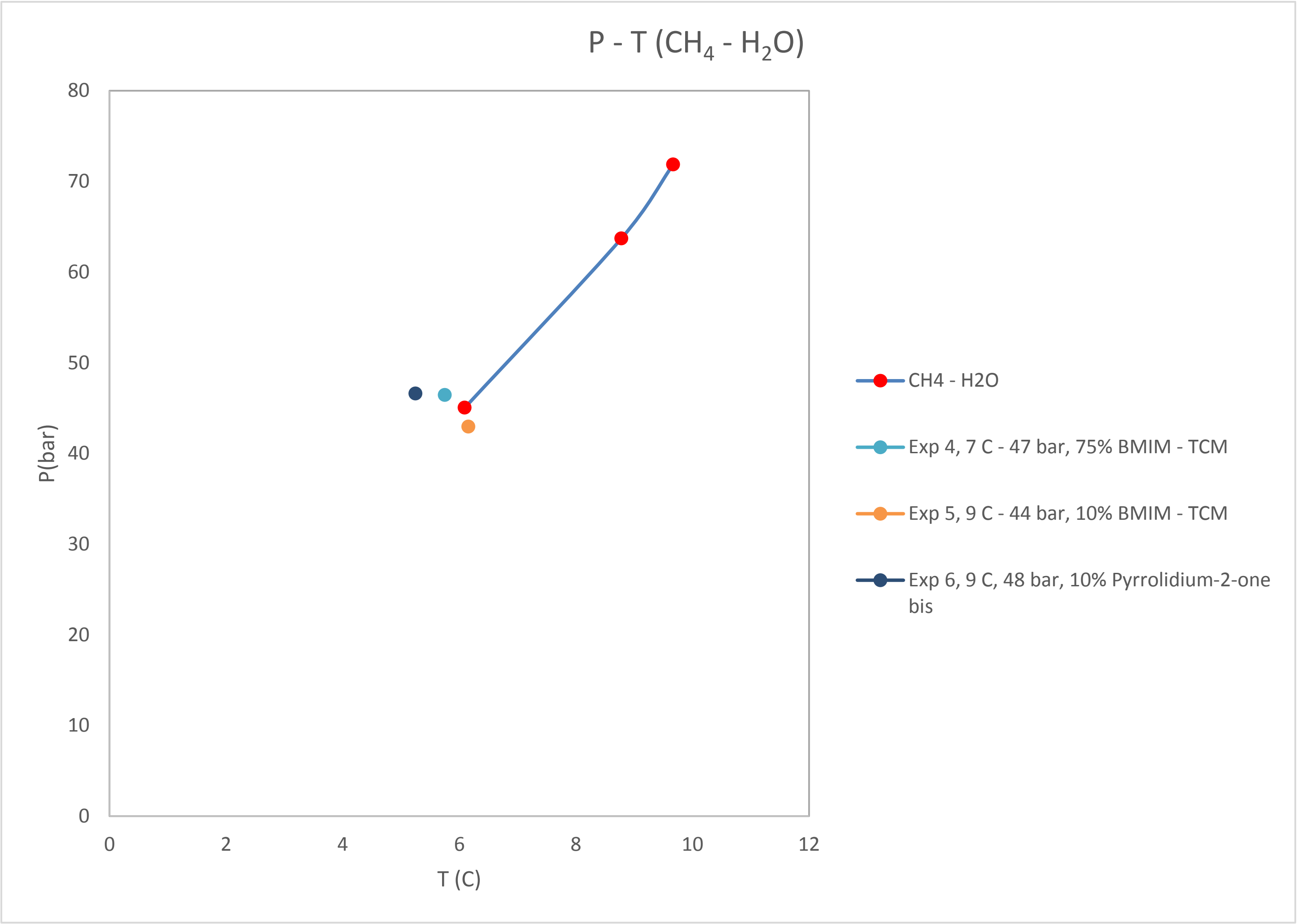


Pyrrolidium-2-one bis(trifluoromethylsulfonyl)imide



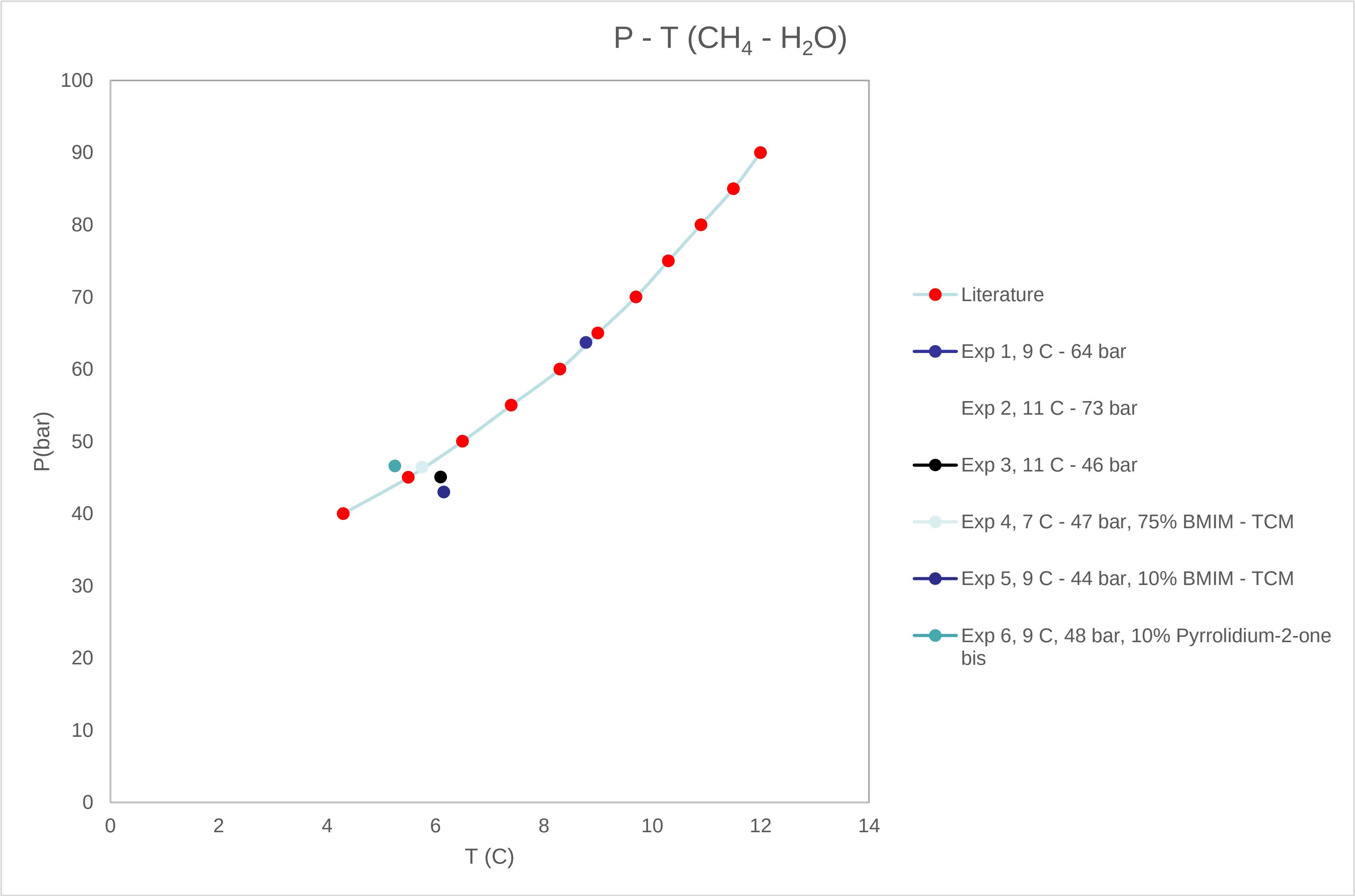
Experiments conducted with Methane and Water





How examined Ionic Liquids shift equilibrium point, compared to Methane – Water systems

Methane equilibrium points



Thank you!