

Fundamental Study of CO₂ Substitution in Methane Hydrates for Energy Production and Long Term Sequestration*

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Abstract

Due to increasing energy demands, the potential for use of gas hydrates as a future energy source is very important. Natural gas hydrates can be environmentally friendly because their high hydrogen/carbon ratio means that they emit less CO₂ during combustion than other heavier fossil fuels. Gas hydrates have a complex non-equilibrium nature with hydrate formers supplied from different phases, and each of these has a different composition and density. Hence, any change in chemical potential of the guest molecules due to change in concentration will lead to a new hydrate formation. Kinetic of hydrate formation has two physically well-defined stages. The first of these, nucleation, is the process in which the free energy benefit of the phase transition competes with the penalty of pushing aside initial phases to free up space for the hydrate crystals. This stage contains natural random elements related to molecular transport. When the size and shape of a hydrate particle reaches a size (critical size) in which the benefit of the phase transition exceed the push-work penalty reaches into the second stage of stable growth. Both of these processes are constrained by associated mass and heat transport. Formation of hydrate on a hydrate former/water interface rapidly leads to situations in which transport of mass through the hydrate film becomes rate limiting. Without hydrodynamic shear forces that break these films and open up for med mass supply of both hydrate former and water the onset of massive growth can be very slow.

The time for onset of massive growth is typically called induction time. A fast mechanism for replacing in situ CH₄ with CO₂ involves the formation of a new CO₂ hydrate from free water in the pores and injected CO₂, including the mixing of surfactants and a small amount of nitrogen (roughly 25 mole%) into CH₄ hydrate. The process will lead to a conversion from CH₄ hydrate to CO₂ hydrate while releasing CH₄ gas from the methane hydrate. Because adding surfactant to the injected CO₂ will reduce hydrate formation at the interface it should be possible to control the combined CH₄ production and CO₂ storage. Different types of surfactants are possible. Low molecular surfactants constructed on the basis of physical solvents for CO₂ are attractive because they enhance the interface thickness and dynamics without making very stable emulsions that could partly trap hydrate particles and clog pore space. But even alcohols will up-concentrate close to the water/non-polar interface. This is also the reason that methanol in small concentrations will actually act as a hydrate activator. It keeps the water/methane interface free of hydrate while at the same time reducing interface free energy and opening up for higher supersaturation below the methanol

enriched water interface where hydrate formation will not close the interface transport between methane and water. The small amount of N₂ should fill the small cavities of new CO₂ hydrate formation thereby stabilizing the structure. The main goal of this study is to better understand the role of surfactants in kinetic of hydrate formation and dissociation.

Reference Cited

OECD, 2017, Outlook for Natural Gas: World Energy Outlook 2017, OECD Publishing, Paris, 33 p. doi.org/10.1787/weo-2017-10-en

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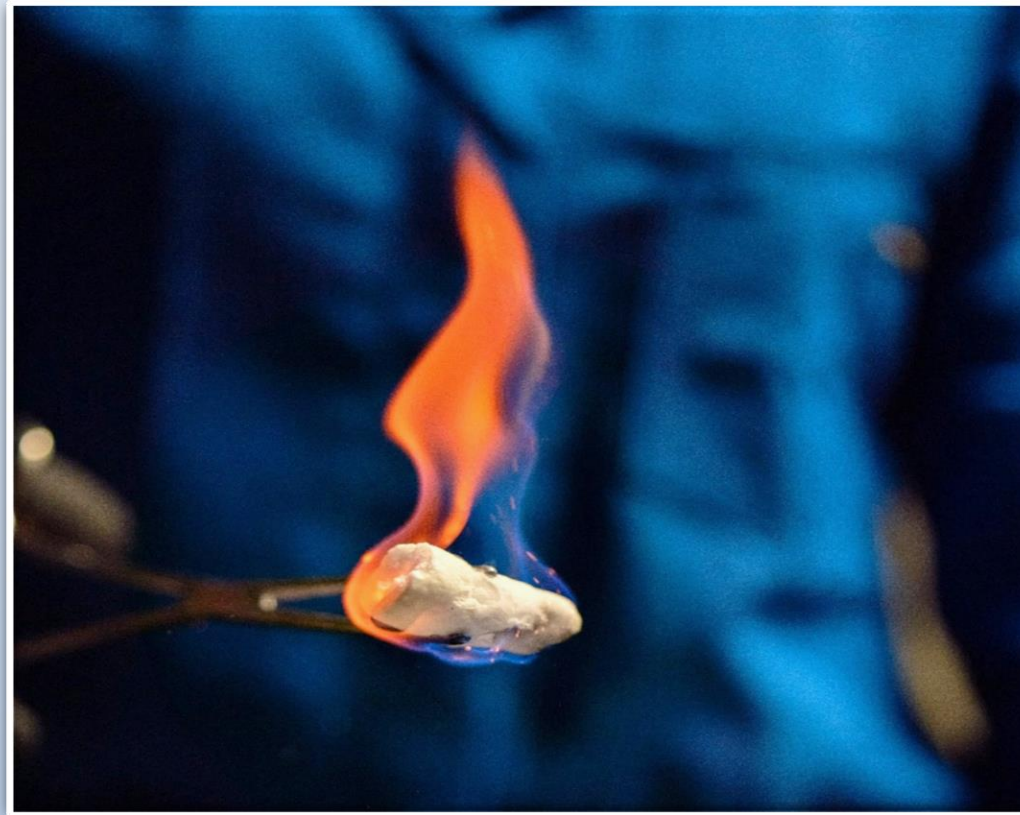
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<http://www.ruf.rice.edu/~hydrates/about.html> Website accessed September 2020.

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Fundamental Study of CO₂ Substitution in Methane Hydrates for Energy Production and Long Term Sequestration



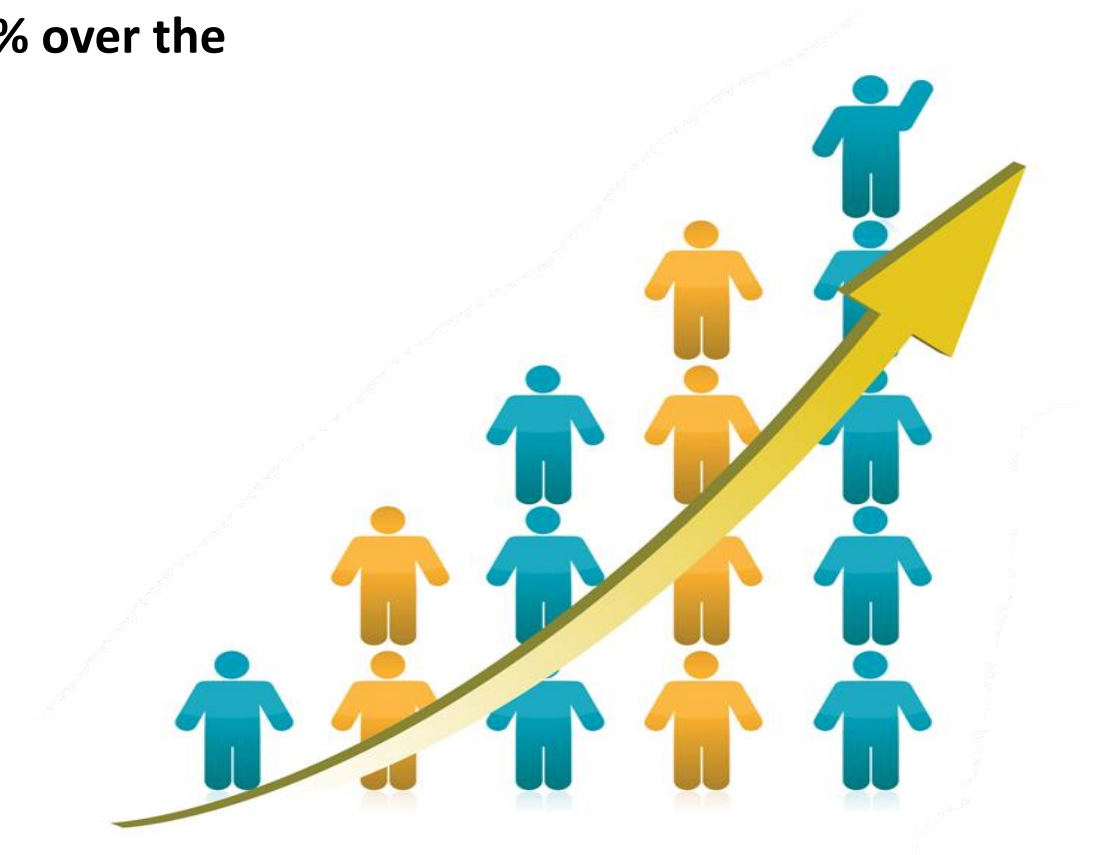
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University of California Irvine

Outline:

- ☐ Motivation
- ☐ Introduction
- ☐ Goal
- ☐ Concept
- ☐ Theoretical results
- ☐ Experimental setup
- ☐ Future work

Why do we care about energy?

- By 2040, global population will rise from 7 to 8 billion people.
- World energy demand is expected to increase by 50% over the next 20 years.

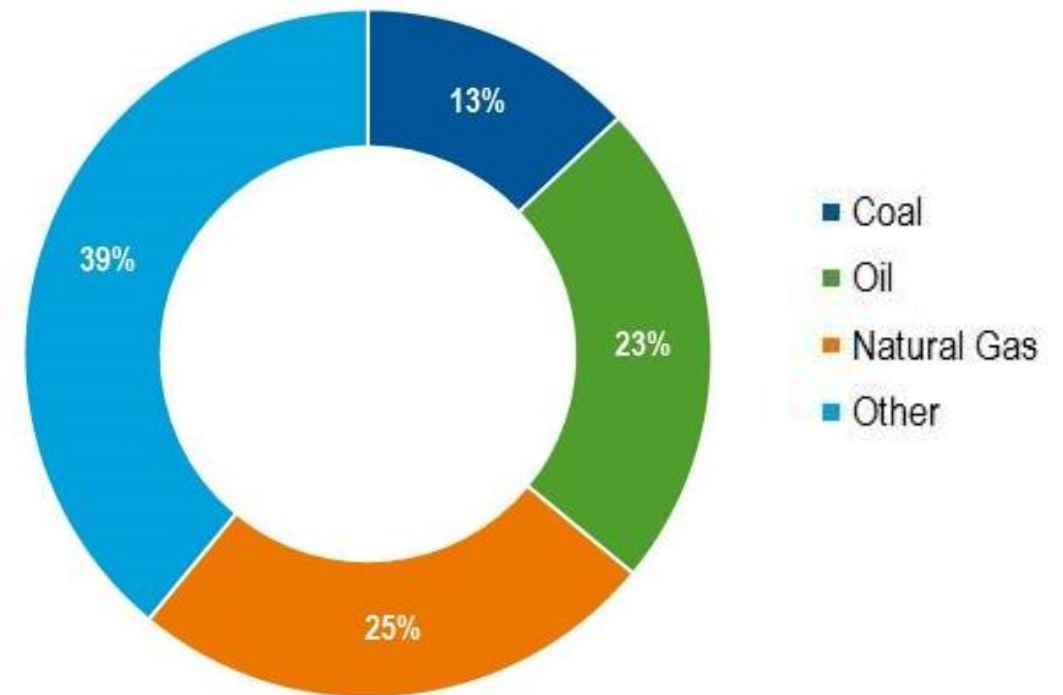


We Still Depend on Fossil Fuels

➤ Future

- Fossil fuels (coal, gas and oil) represent **61%** or maybe more of the global energy mix.
- Renewables and Nuclear energy can make up to **39%** of the global energy mix.
- But fossil fuels will remain our main source of energy for decades to come.

Estimated share of global energy demand 2040



Source: OECD/International Energy Agency, Outlook for natural Gas 2017.
There is no assurance that any forecast, Projection or estimate will be realized.

How does natural gas hydrate fit with clean energy?

Sources of fossil fuels:

➤ Coal:

Is an important energy source, but burning coal for electricity emits large quantities of carbon dioxide, and other potentially toxic pollutants.

➤ Oil:

Burning oil releases carbon into the atmosphere and causes air pollution, and also when crude oil leaks to the natural world, it destroys marine life and animal life.

➤ NGH/ Natural gas:

Natural gas hydrate are “Now” resources. They can be environmentally friendly because they emit less CO₂ release during combustion than other heavier fossil fuels. Gas hydrate is not the same as other natural gases (such as; conventional, shale gas and coalbed methane). NGH has been purified from pollutants as a part of its crystallization process.

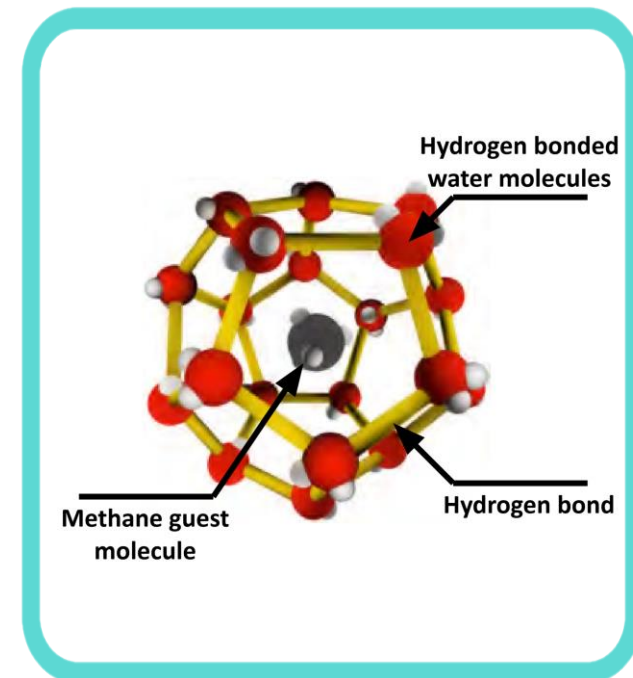
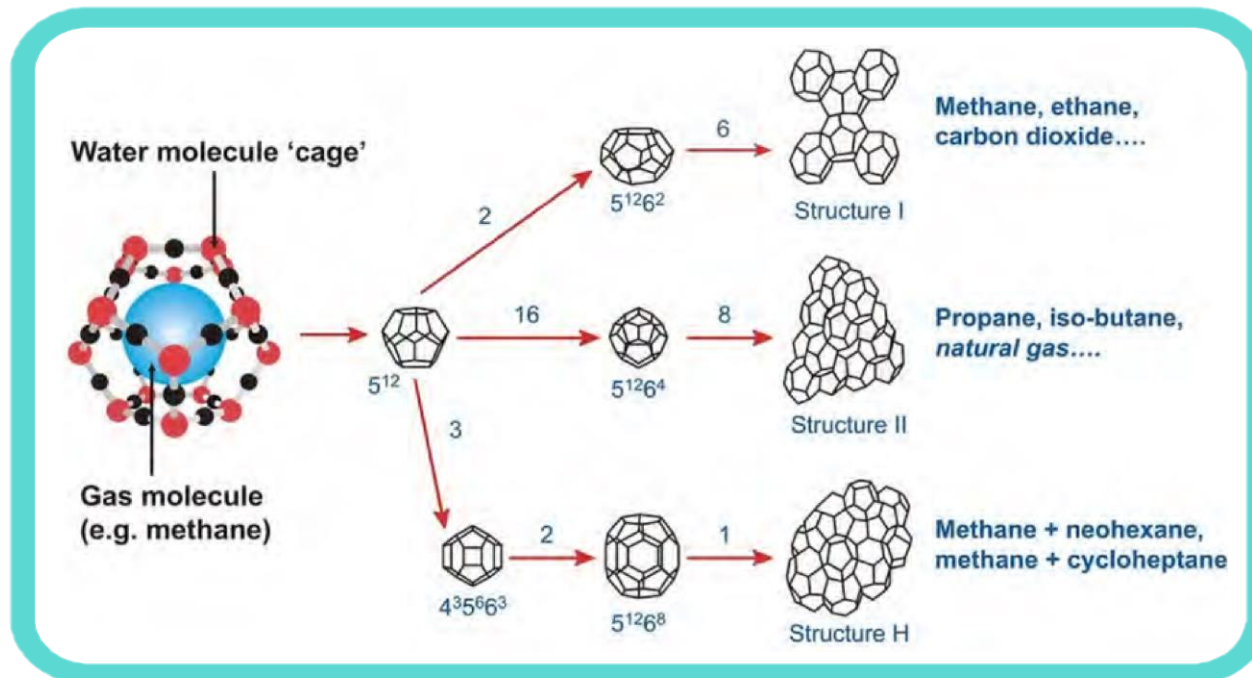
Introduction

What are hydrates?

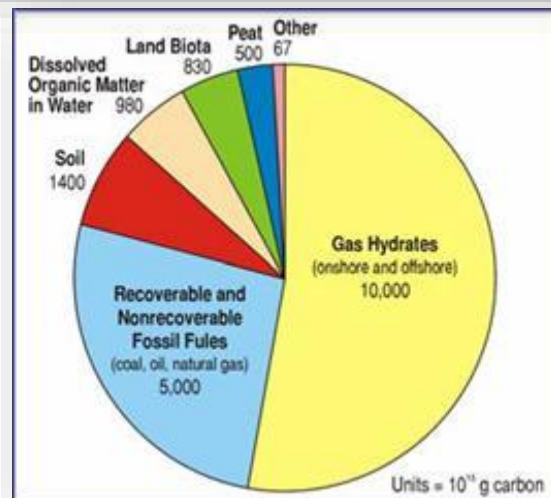
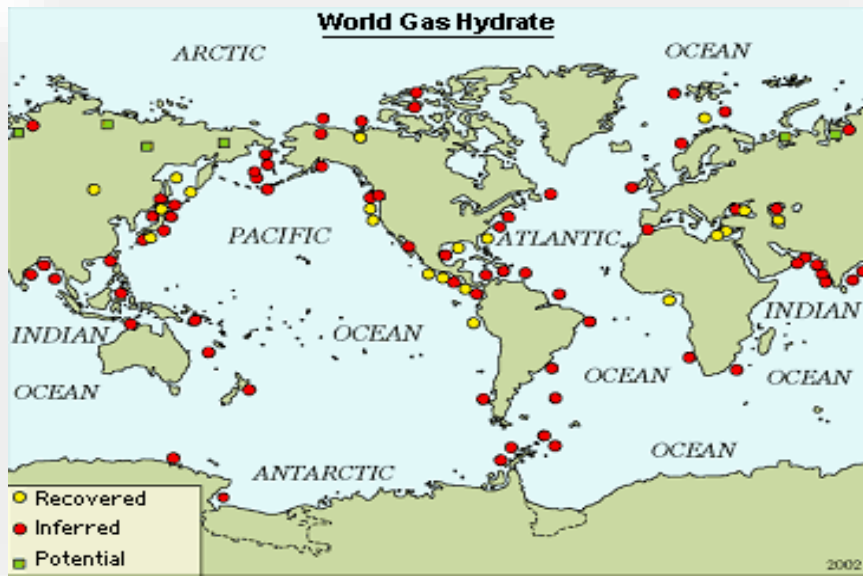
❖ A fairly rigid network of hydrogen bonded waters that enclathrate small molecules in cavities.

➤ Hydrate formation conditions

- Water
- Gas - CH₄, CO₂, H₂S and C₂H₆
- High Pressure
- Low Temperature



Where are gas hydrates found?



<http://www.ruf.rice.edu/~hydrates/about.html>

➤ A major energy resource

- Over 230 potential reserves have been found globally.
- At current consumption rates, that's enough to supply the entire world's demand for a 1,000 years or more.

➤ Methane hydrates contain more organic carbon than all known fossil fuels by at least a factor of 2.

What are methods of extraction of methane hydrate?

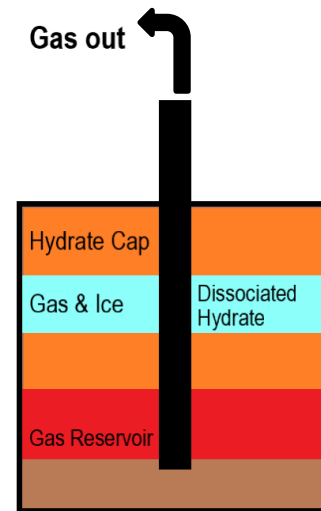
There are four methods for extraction of methane hydrate that have been studied extensively:

➤ Depressurization

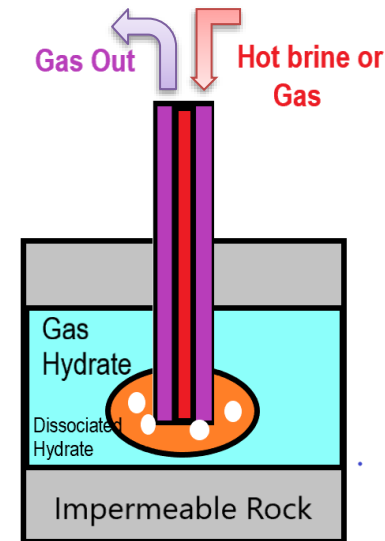
Hydrates dissociate with pressure. Absorbing energy and reducing reservoir temperature; this process requires heat, but available heat from the surrounding is limited, and may not be sufficient for commercial production rates.

➤ Heat injection

Hydrates dissociate with temperature. This process can be fast but it's very costly.



Depressurization



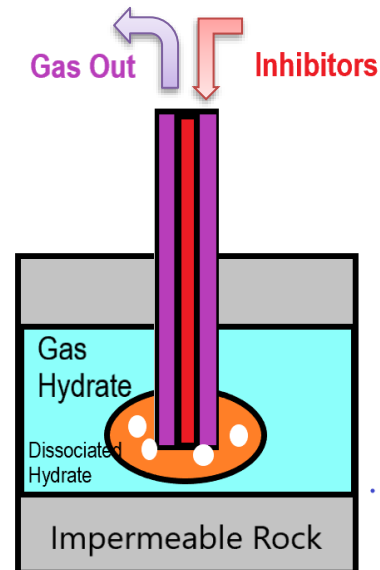
Heat injection

➤ Inhibitor injection

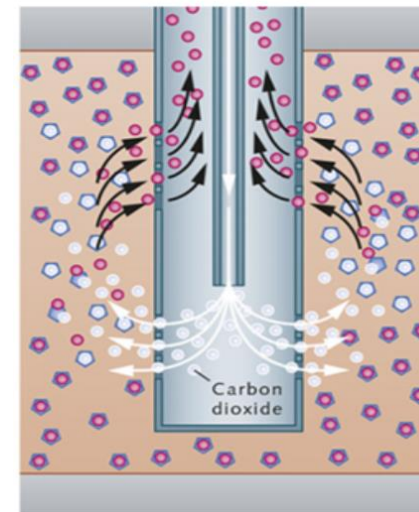
All chemicals that lead to lower chemical potential for liquid water will break hydrogen bonds and lead to dissociation. This process can be very fast, but it's also costly, in particular if the chemicals are water soluble and/or heavier than water.

➤ CO₂ injection

This process is very low cost because it's easy to get CO₂ from combustion, but it needs a special attention on formation rate of new hydrate and permeability.



Inhibitor injection



CO₂ injection

Concept

Gibbs Phase Rule

- ❖ Hydrates in nature and industry can normally not reach equilibrium, because there are too many co-existing phases.

No. Of deg. Of freedom \longrightarrow

$$\tau = N - \pi + 2$$

No. Of components No. Of Phases

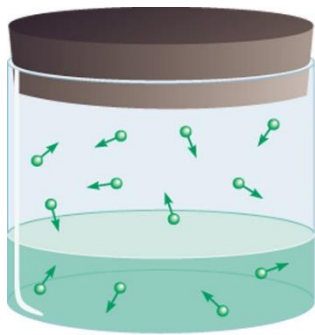
- Number of independent thermodynamic variables (temperature, pressure and masses in all phases)
- minus conservation laws
- minus conditions of equilibrium

If the system **can not reach true thermodynamic equilibrium**, then there is no rule that says chemical potential of hydrate formers is the same in all phases.

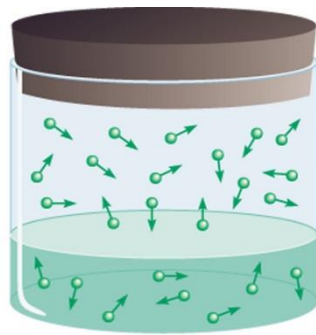
Active phases: hydrate, liquid water, gas, adsorbed phases on minerals and hydrate

First and second laws of thermodynamics

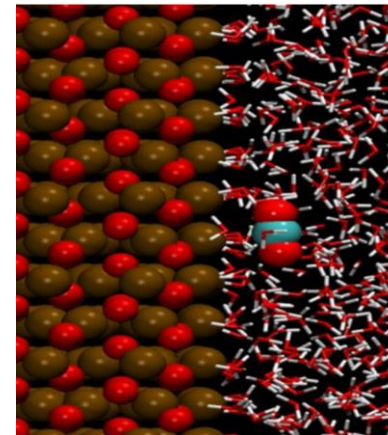
- ❖ Most stable hydrates form first from mixtures, under constraints of mass supply and heat release.
- ❖ CO_2 is sub critical and condenses/ adsorbs better on liquid water than CH_4 , N_2 and other supercritical components, as pre-stage to hydrate nucleation.
- ❖ Hydrate forms from many different phases – including towards mineral surfaces and from hydrate formers dissolved in liquid water. CO_2 adsorbs better on minerals than CH_4 and also dissolves better in water.



Solubility of CH_4 in water



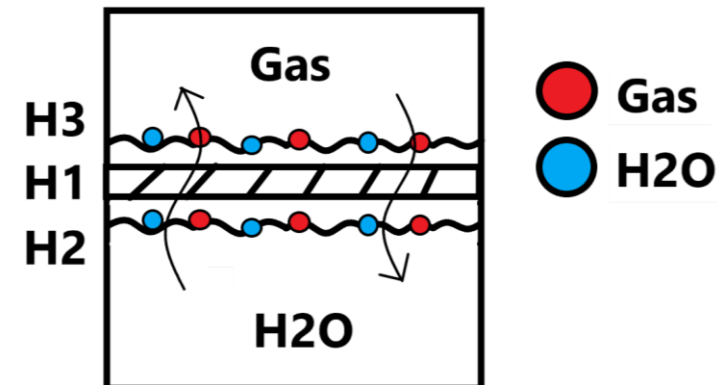
Solubility of CO_2 in water



CO_2 adsorbing onto mineral surface (Hematite) from water solution.

What is questionable about the model?

- 1) Heat transport through water is **substantially faster than mass transport** through water. Typically 2 – 3 orders of magnitudes.
- 2) An initial film of hydrate creates a barrier of mass transport from CO₂ phase towards water phase, but **hydrate can grow from dissolved CO₂** until stability limit (see earlier slides) of CO₂ concentration in water. This hydrate growth is mass transport limited (diffusion towards initial hydrate film) and **causes release of heat from below the initial hydrate film**. This can partly dissociate the hydrate film and lead to renewed direct contact between liquid water and CO₂.
- 3) **Growth** of hydrate based on transport through a hydrate film **is totally dominated by extremely slow diffusivity** of CO₂ (10⁻¹⁵ m²/s).



What is the difference between nucleation and induction time?

➤ Nucleation time

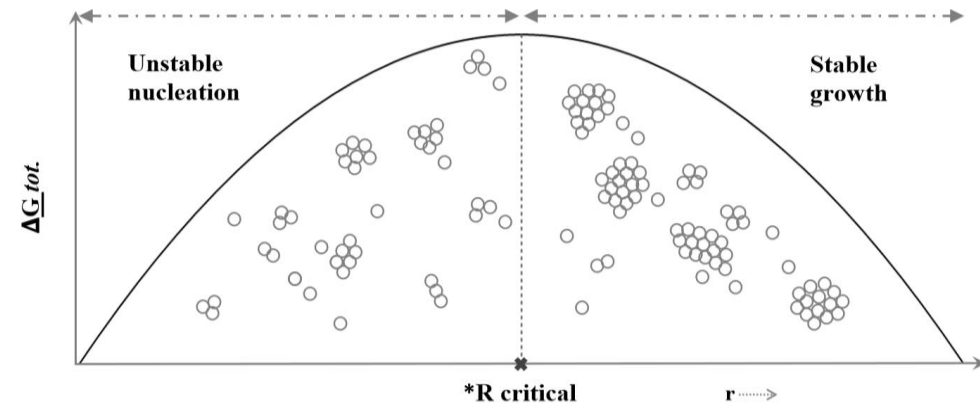
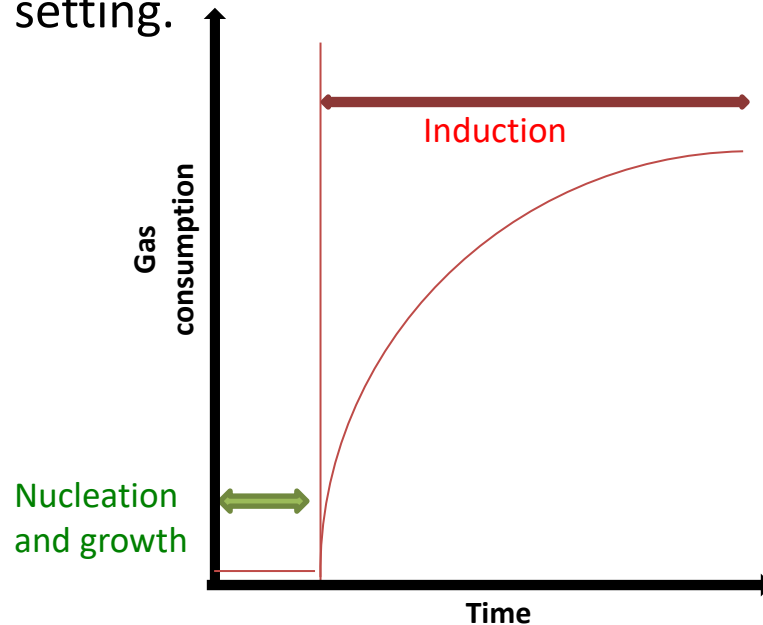
Is a nano scale phenomenon in time and volume scale. The time needed to create the first stable hydrate core.

➤ Growth

After nucleation, growth can be slowed down by reduced mass supply across hydrate.

➤ Induction time

“Onset of massive growth” (induction) is a result of various processes and individual for each unique setting.



What is the goal?

➤ Create CO₂ hydrate formation:

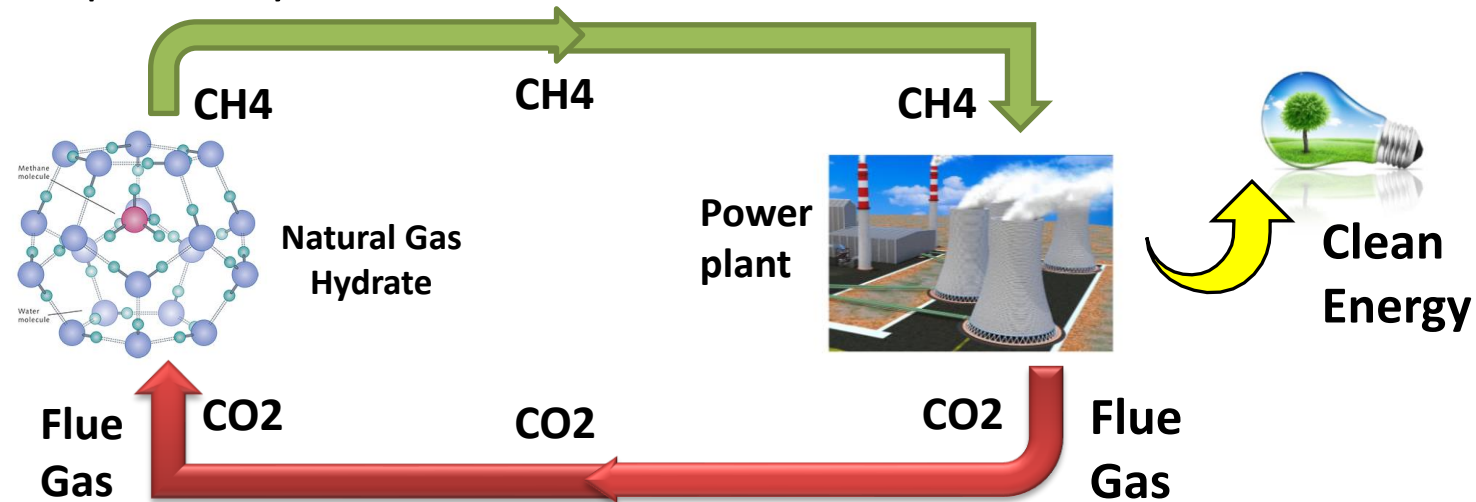
- Release heat through liquid water toward the in-situ methane hydrate.

➤ CH₄ hydrate dissociation:

- Heat from new formation assists in dissociating the methane hydrate.

➤ Advantages:

- The best situation is for safe long-term storage of CO₂.
- Release of natural gas hydrate for energy.
- Solid structure is replaced by another solid.



Conversion mechanisms:

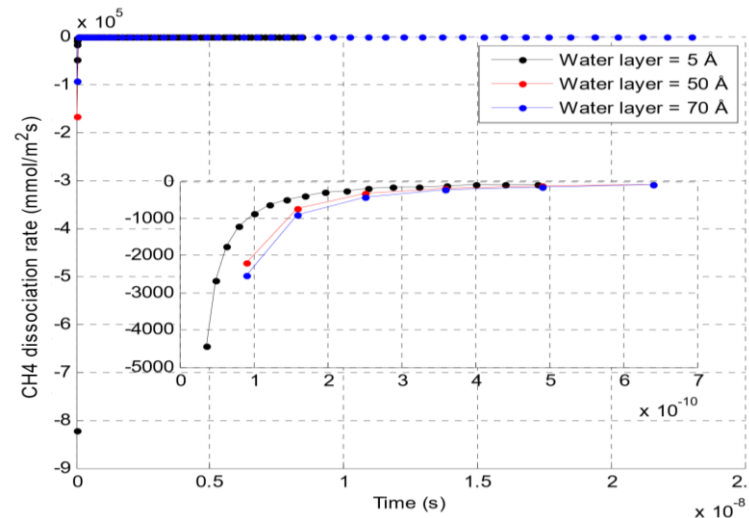
➤ Solid state conversion

Is very slow, with diffusivity coefficient in the order of 10^{-15} m²/s. Only proven for temperatures below 0.

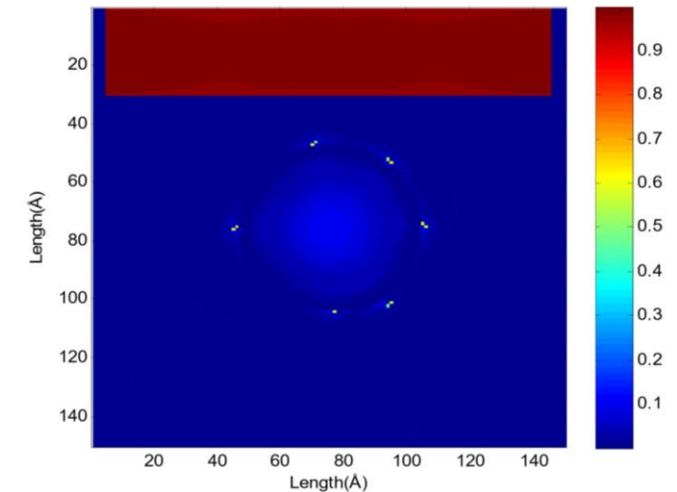
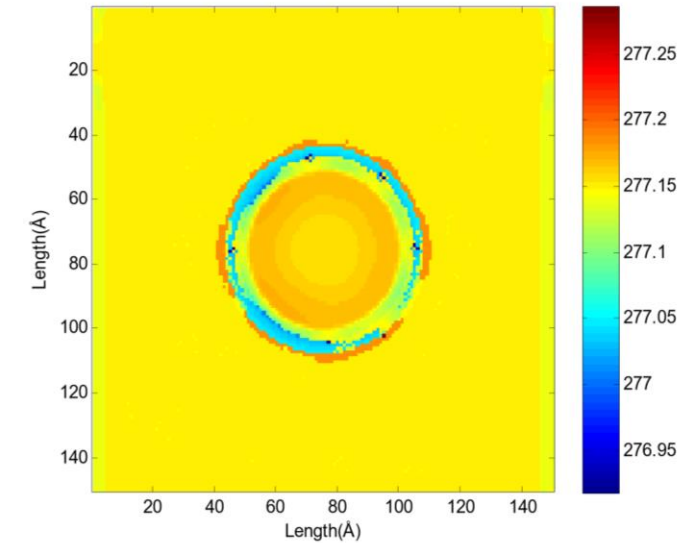
➤ New CO₂ hydrate formation

This mechanism is much faster and in the rate order of liquid water transport, but requires advance theory to investigate dynamic couplings between mass and heat transport.

With only 0.5 nm free water that curve is reorganization to interface around solid hydrate and then a very slow solid state conversion. For the two other the fast mechanism works as long as there is available free water. The more free water – the longer the fast mechanism.

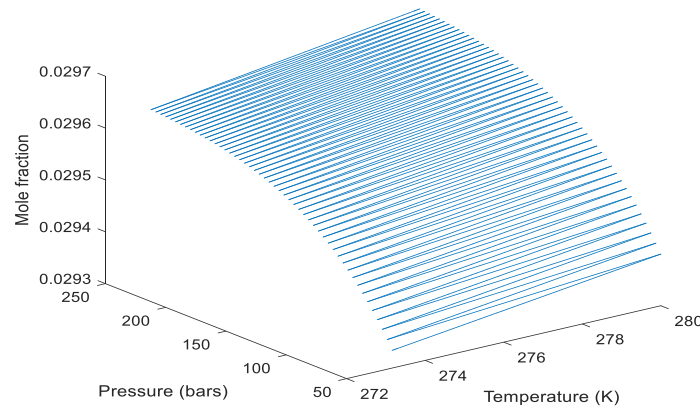


Theoretical Results

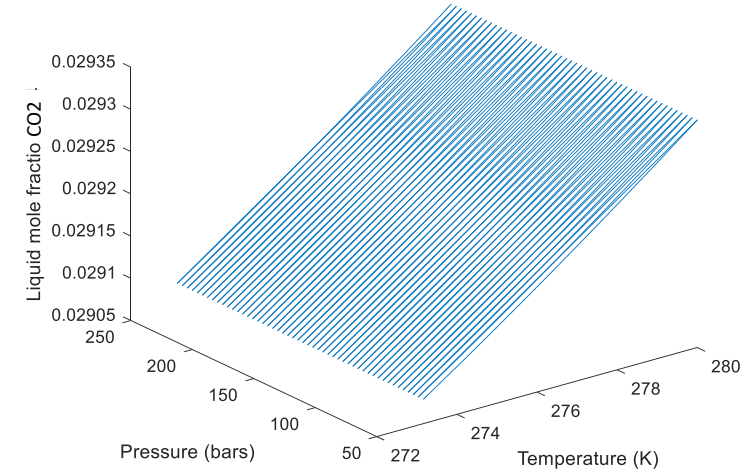


Hydrate growth from dissolved CO₂ in water phase

These curves are calculated solubility of CO₂ in liquid water based on equal chemical potential for CO₂ in gas and in the liquid water phase



These curves are for equilibrium between CO₂ hydrate and liquid water containing given mole-fractions of CO₂ in the water surrounding the hydrate



For every specific T and P hydrate can grow from the mole-fraction of the solubility curve (left) down to the mole-fraction of hydrate stability limit (right).

The very small pressure dependency on the right hand curve is due to equilibrium between two condensed phases. The molar volume for water in the Poynting correction for liquid water is 18 cm³/mole and the corresponding Poynting correction for water in hydrate is proportional to a molar volume of 22 cm³/mole.

Poynting corrections are small and impact gets even smaller since they almost cancel each other.

➤ Hydrate stability limit (right curve on previous slide):

$$\mu_{H_2O}^{(aq)} = \mu_{H_2O}^{(Pure, liq)}(T, P_0) + \bar{v}_{H_2O}^{(pure liquid)}(P - P_0) + RT \ln(x_{H_2O} \gamma_{H_2O}) = \mu_{H_2O}^{(hydrate)} = \mu_{H_2O}^{(0, H)}(T, P_0) + \bar{v}_{H_2O}^{(0, H)}(P - P_0) - RT \sum_{i=1}^n \nu_i \ln[1 + \sum_{j=1}^{n_{guest}} h_{ij}]$$

This equation is fairly general classical thermodynamics. And as well known pressure dependency between condensed phases (and solid) is very limited pressure dependent. 0 indicates reference pressure 1 bar.

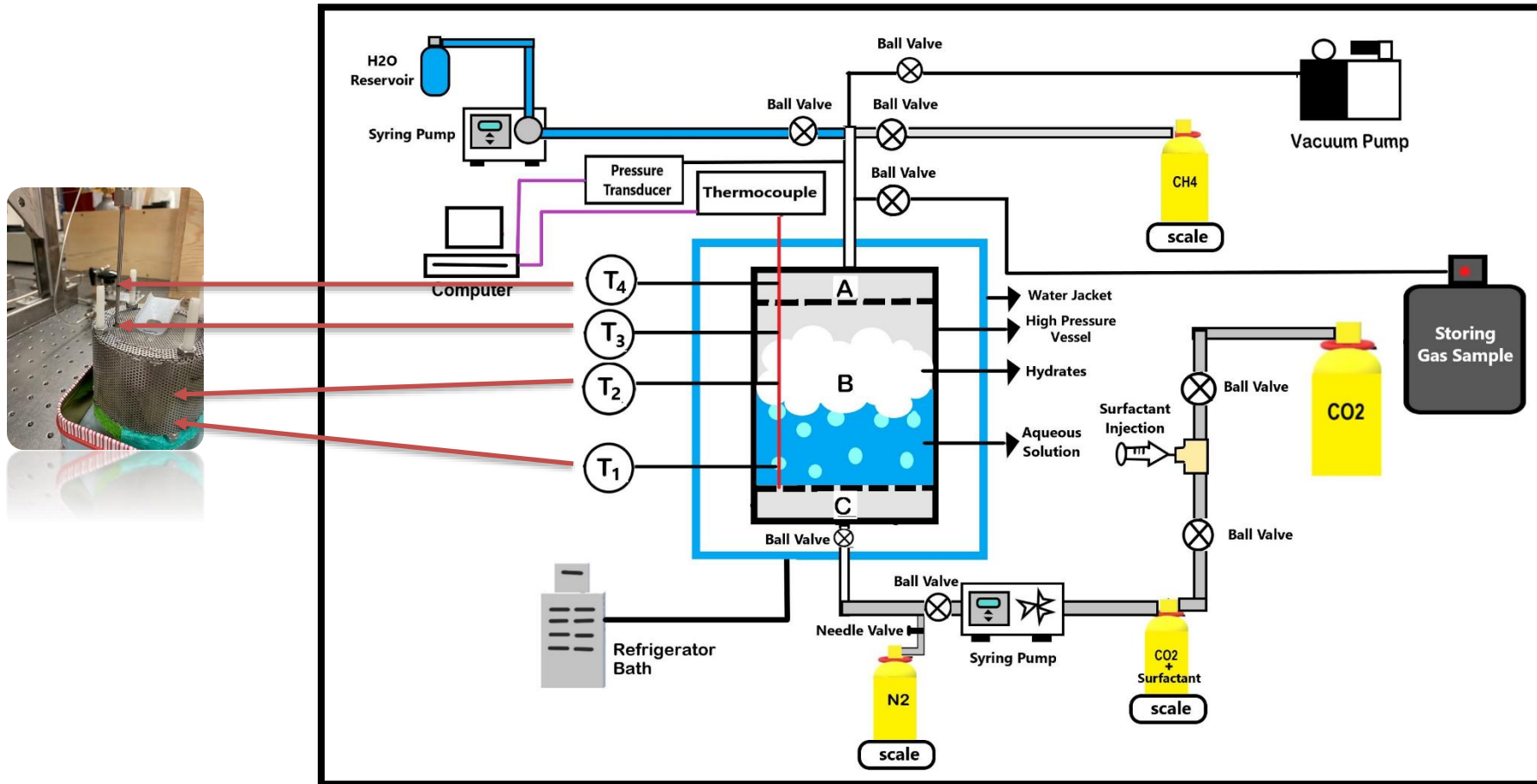
➤ Solubility Henry's law (left curve on previous slide):

$$y_{CO_2} \phi_{CO_2}(T, P, \vec{y}) P = x_{CO_2} \gamma_{CO_2}^{\infty} f_{CO_2}^{\infty}(T, P_0) Poynting^{\infty} \longrightarrow e^{\int_{P_0}^P \frac{v}{RT} dp}$$

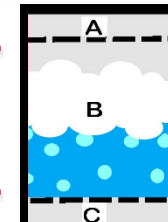
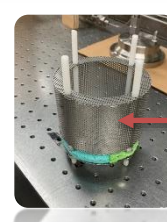
$$x_{CO_2} = y_{CO_2} \phi_{CO_2}(T, P, \vec{y}) \frac{P}{H(T)} \frac{1}{Poynting^{\infty}} \approx 1.56$$

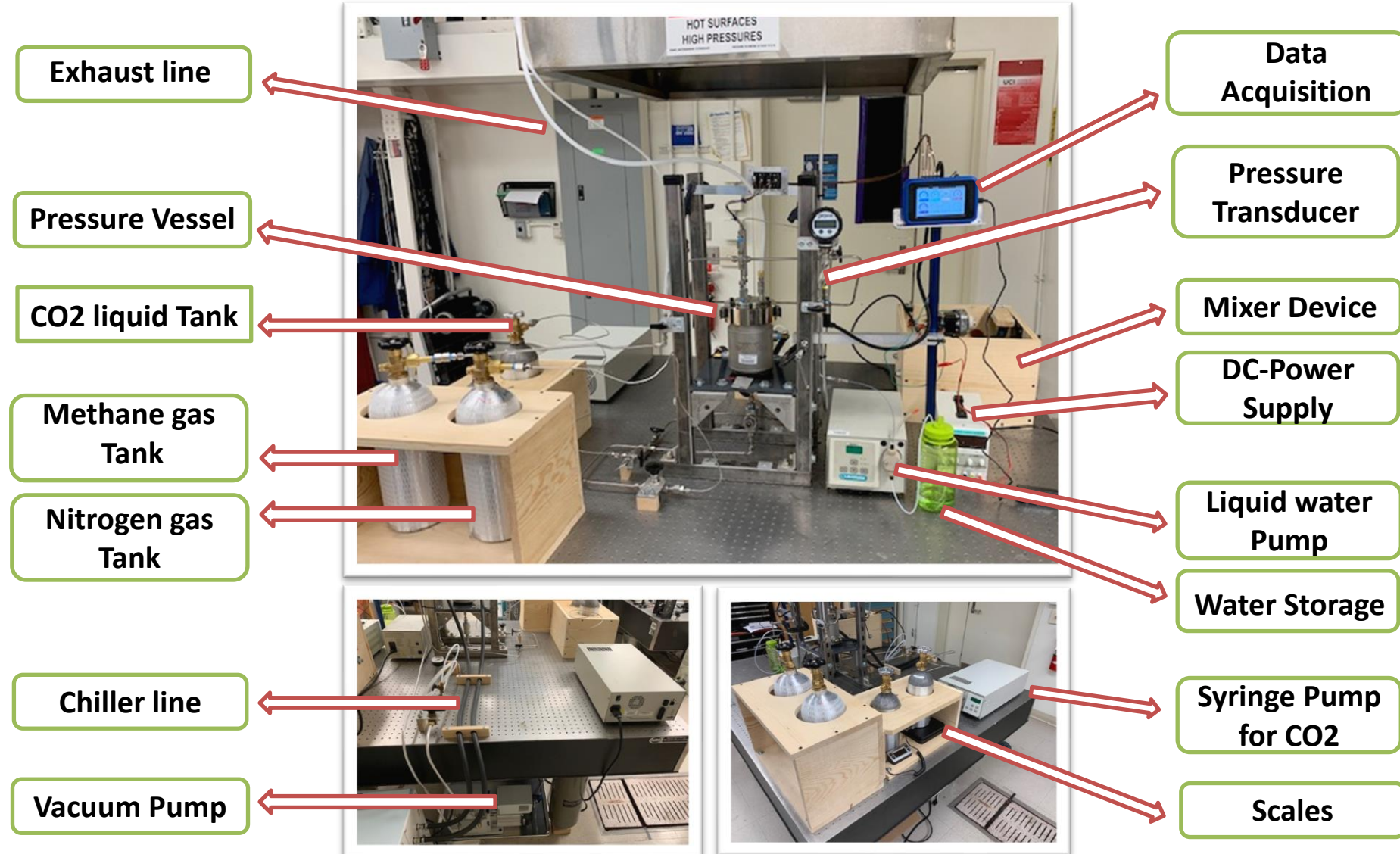
2-D Schematic

Experimental Setup



Basket: 200grams
+
Glass beads:
472grams

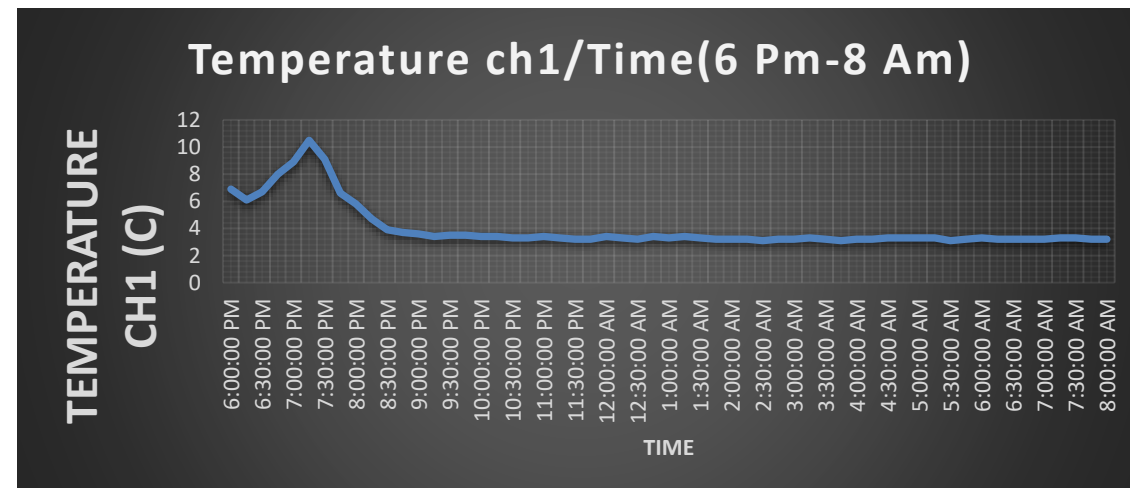
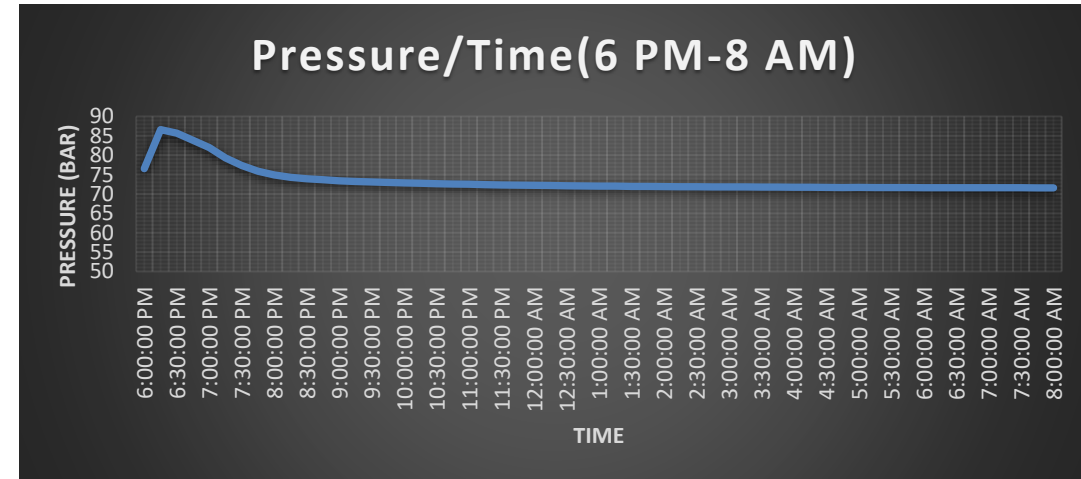




Results:

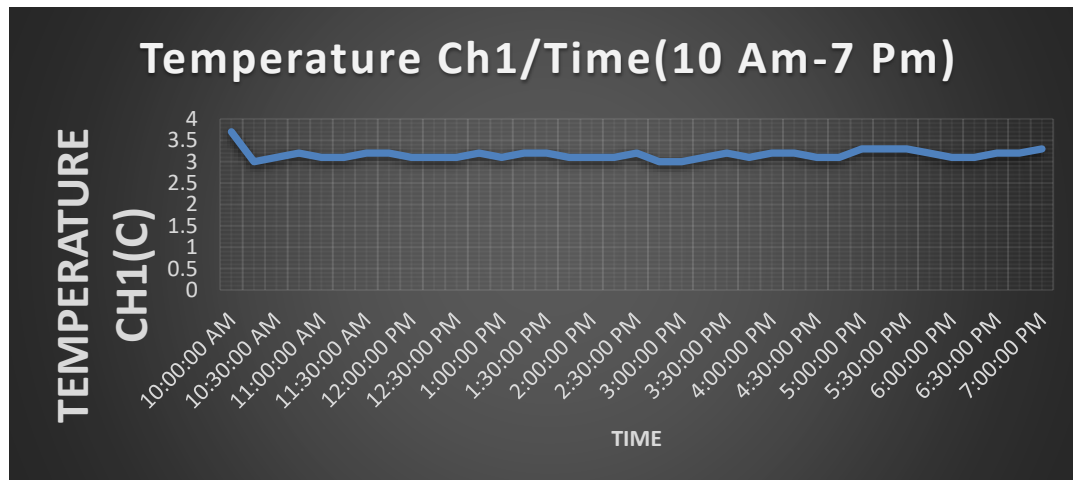
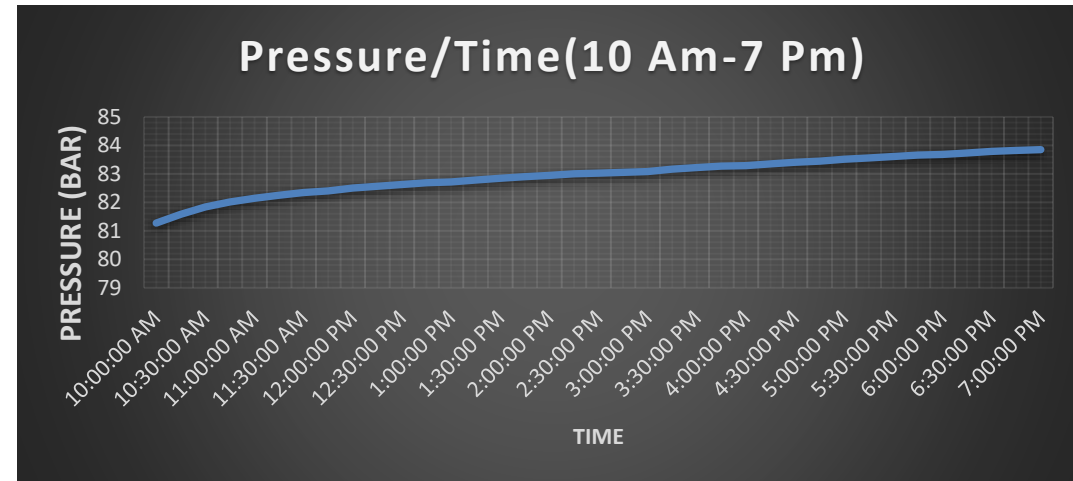
➤ Methane Hydrate Formation

- Pressure/Time (6pm-8am)
Pressure drop by hydrate formation was 5.8 bar.
- Temperature/Time (6pm-8am) increased by 2C (max. peak temperature) at 7pm due to methane hydrate formation.



➤ Conversion Mechanism by CO₂ Hydrate

- Pressure/Time (10am-7pm)
Pressure drop by
temperature was 0.12 bar.
Pressure increased 2.63 bar
by substitution of CO₂ into
the methane hydrate.
- Temperature/Time
(10am-7pm)



Future Work

- ☐ Refining CH₄ hydrate preparation to maximize the fraction of CH₄ trapped as real hydrate and minimize hydrate trapped gas bubbles and hydrate trapped liquid water spots.
- ☐ Quantify mass balances.
- ☐ Refine procedures for emptying vessel quickly from CH₄, and quickly filling with CO₂.
- ☐ Testing and verification of reproducibility.
- ☐ Addition of limited amounts of N₂ (not more than 25% by volume).
- ☐ Adding limited amounts of surfactant.

Acknowledgements

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Questions

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