

# Study of Thermodynamics and Kinetics of Carbon Dioxide Hydrate

## Formation and Dissociation

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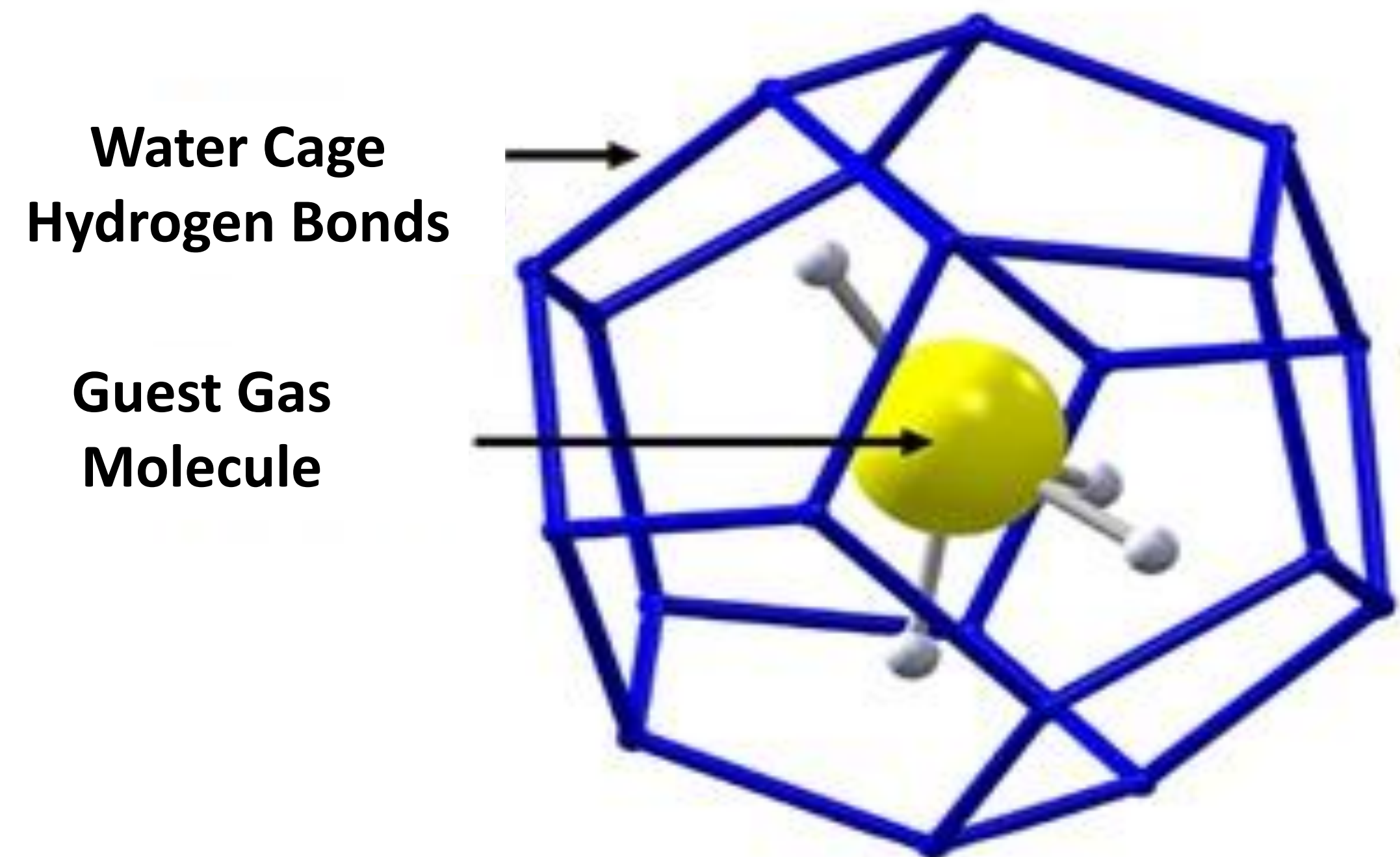


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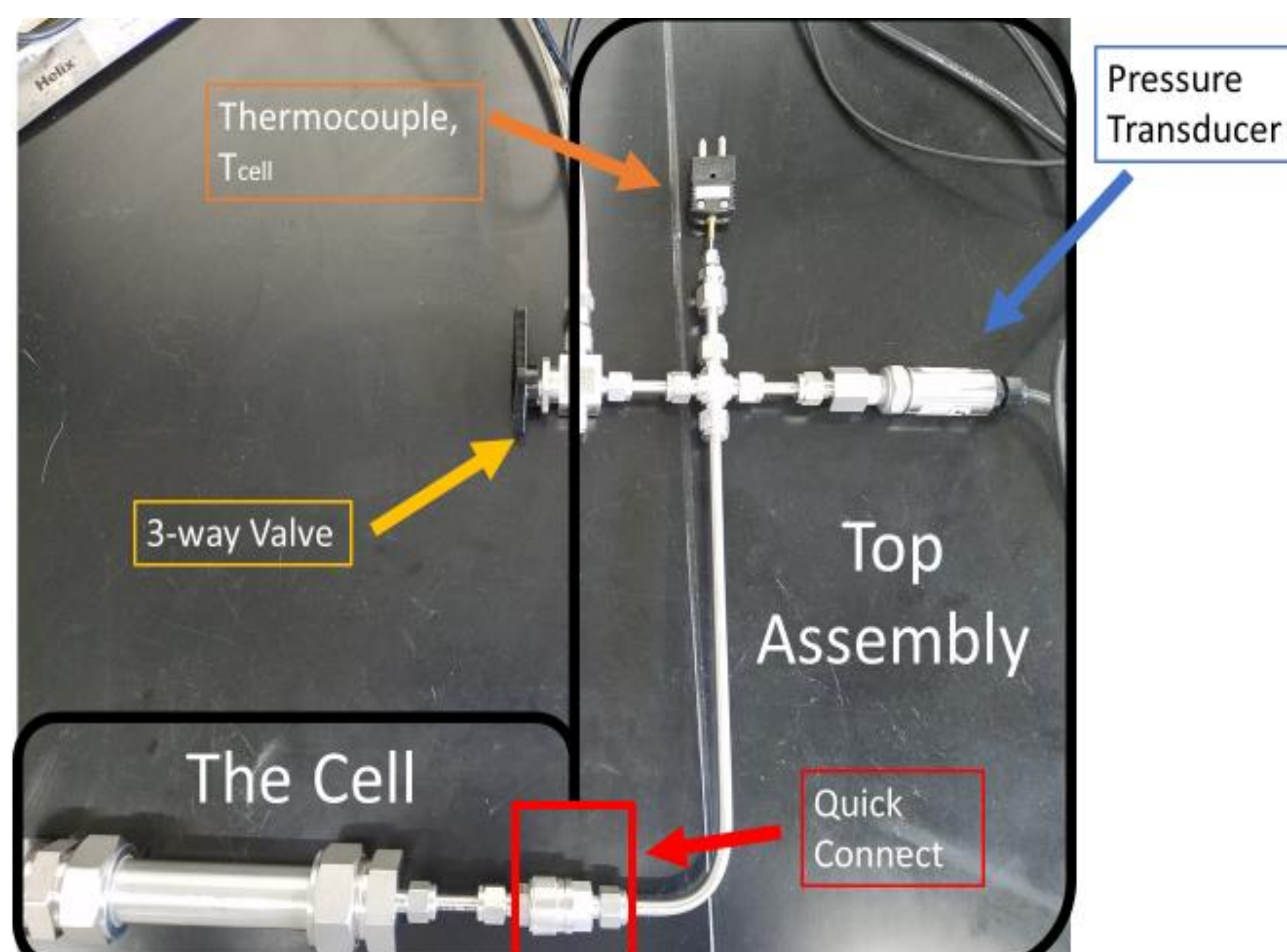
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### Introduction

Gas hydrates form when a water cage traps a guest gas molecule. Carbon dioxide (CO<sub>2</sub>) hydrates form at low temperatures and high pressures and are of interest for their carbon storage potential to mitigate CO<sub>2</sub> emissions. There are over 700,000 trillion ft<sup>3</sup> of naturally occurring methane in hydrates in marine and permafrost environments all over the world. Sequestering CO<sub>2</sub> as gas hydrates in conjunction with methane extraction from methane hydrate reserves could be used to stabilize the seafloor during the extraction. During this study, a small volume (~79 mL) reactor was built to monitor the conditions of CO<sub>2</sub> hydrates as they formed in 12-15 mL of deionized water, salt water solution, or sodium dodecyl sulfate solution in the presence or absence of sand.



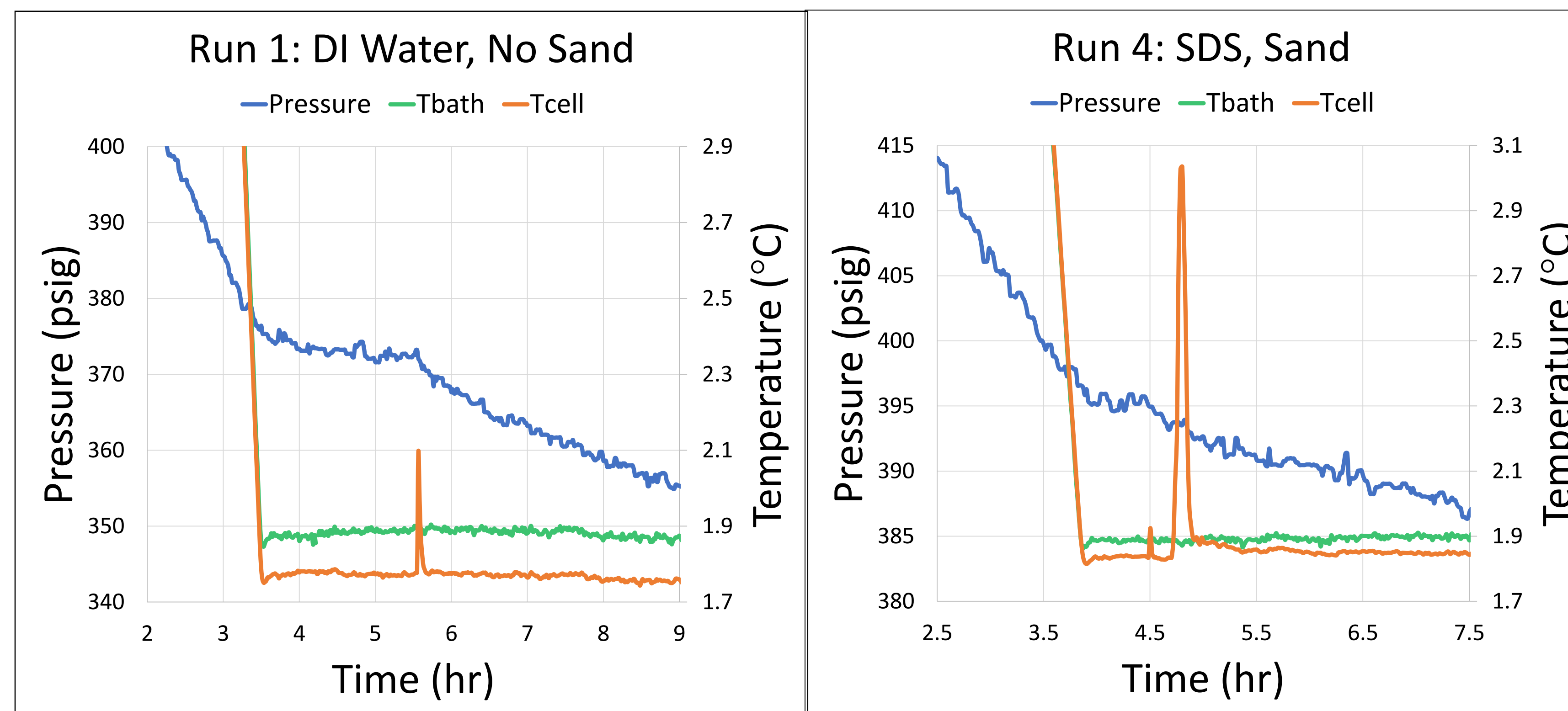
### The Reactor



### Methodology

For each trial, the reactor was filled with solution at room temperature (23-29°C) and then pressurized to 450-475 psig before being placed in a 2°C cooling bath. Over a minimum of four days, system pressure and temperature were continuously recorded. For half of the experiments, ~16 mL of the reactor was filled with sand to simulate ocean floor conditions.

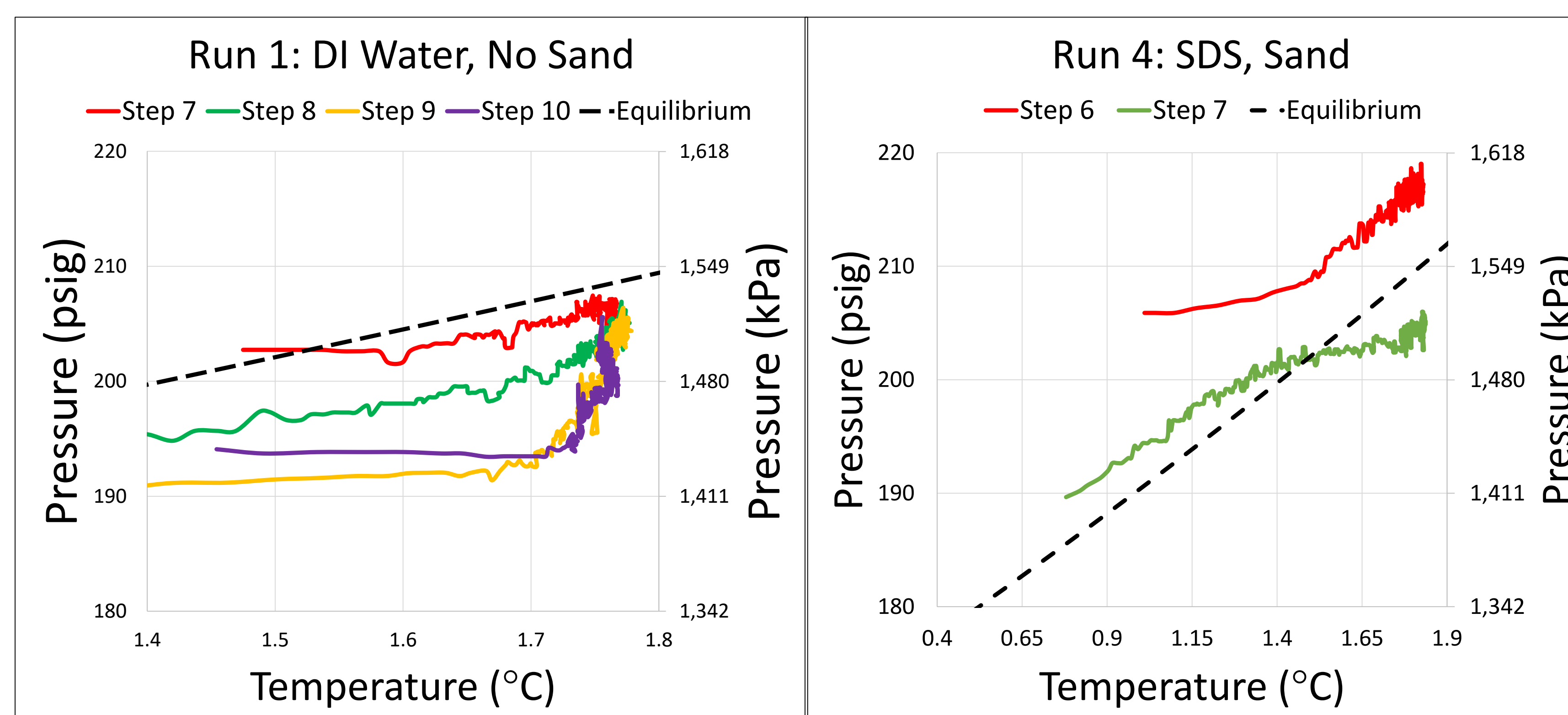
### Formation



The first sign of hydrate formation in Run 1 where at 5 ½ hours a 0.3°C spike aligns with a change in the rate of pressure drop.

Run 4's hydrate formation starts when a 0.1°C spike and pressure drop occur simultaneously, followed by a 1.2°C spike and 2<sup>nd</sup> pressure drop.

### Dissociation



The key steps during Run 1's depressurization, where the cell pressure traced equilibrium (dotted) along a similar slope.

During Run 4's dissociation, step 6 tracks just higher than predicted, but step 7 is unusual as it crosses the predicted equilibrium line.

### Results

| Run | Solution                     | Sand    | Induction Time (hr) | Overall ΔP (psi) (solubility + hydrates) |
|-----|------------------------------|---------|---------------------|--|
| 1   | Deionized (DI) Water         | No Sand | 1.9                 | 105                                      |
| 2   | Salt Water (Instant Ocean)   | Sand    | 18.9*               | 73                                       |
| 3   | DI Water                     | Sand    | 17.0*               | 103                                      |
| 4   | Sodium Dodecyl Sulfate (SDS) | Sand    | 0.6                 | 73                                       |
| 5   | Salt Water (Instant Ocean)   | No Sand | 10.2                | 127                                      |
| 6   | SDS                          | No Sand | 18.1*               | 135                                      |

### Conclusions

- CO<sub>2</sub> hydrates do form in all conditions tested
- Sand inhibits the conversion of gas into gas hydrates
- Induction time for salt water were the longest on average
- Conversion data requires deep understanding of CO<sub>2</sub> solubility under different pressure and temperature conditions
- Overall, these results suggest that techniques to encourage hydrate formation would benefit this approach to large scale marine CO<sub>2</sub> sequestration

### Future Work

- Duplicate the set of runs for repeatability and trend analysis
- Develop a model for the solubility of CO<sub>2</sub> in water under changing pressure and temperature conditions
- Form gas hydrates with mixed gases, specifically methane and CO<sub>2</sub>

### Acknowledgements

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