

# CO<sub>2</sub> Clathrate Formation and Dissociation Rates Below 273K

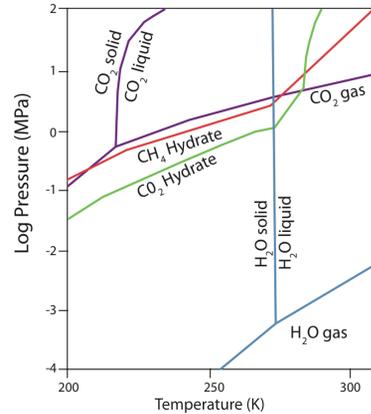
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## Introduction

Gas hydrate clathrates are cage-like structures of water molecules surrounding a gas molecule such as carbon dioxide or methane. CO<sub>2</sub> clathrate is structure I, indicating 5.75 H<sub>2</sub>O molecules : 1 CO<sub>2</sub>.

Clathrates have properties similar to water ice, save their exceptional thermal expansivity and conductivity. Hydrates are stable at low temperature, modest pressure conditions making them likely to form in many environments throughout the solar system. Clathrates have been suggested sources of methane in the Martian atmosphere [1,2,3,4], and subsurface water and carbon reservoirs [5]. However, experimental data is needed to better understand reaction mechanisms and constrain the rates of the hydrate formation and dissociation processes. This will lead to predictions of gas fluxes between subsurface aquifers, hydrate reservoirs, and planetary atmospheres within models of carbon reservoirs on Mars and other planets.



## Reaction Mechanism

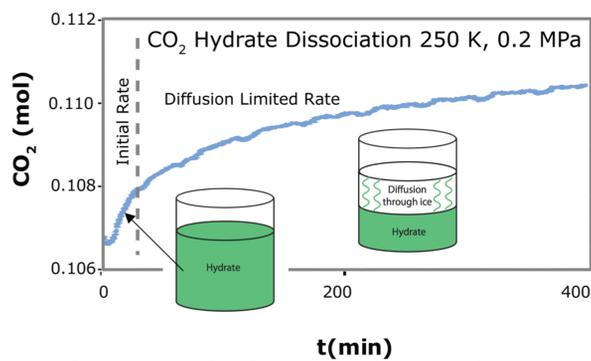


Figure 1 - As gas hydrate dissociated the reaction mechanism changes from an initial rate (kinetically controlled) to a diffusion limited rate.

## Experimental Apparatus

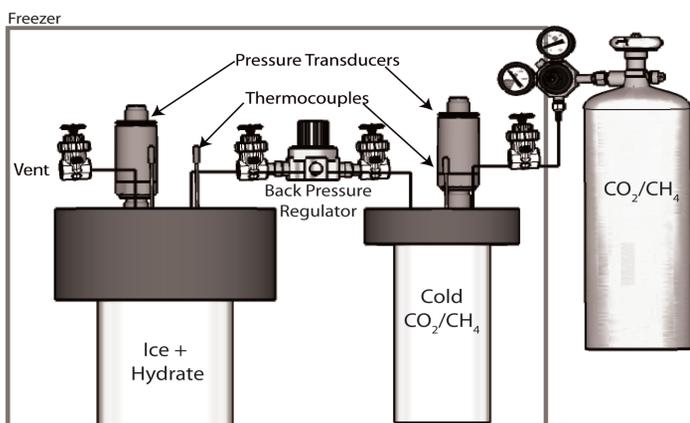


Figure 2 - Experimental apparatus developed at the University of Oklahoma to study the initial rates of formation and dissociation of various types of gas hydrates.



## Initial Rates

Experiment Type	Pressure [MPa]	Temperature [K]	Rate [mol m <sup>-2</sup> s <sup>-1</sup> ]
Dissociation	4.46x10 <sup>-1</sup>	250	3.69x10 <sup>-4</sup>
Dissociation	1.01x10 <sup>-1</sup>	250	3.47x10 <sup>-4</sup>
Dissociation*	3.00x10 <sup>-4</sup>	250	3.00x10 <sup>-3</sup>
Dissociation	1.01x10 <sup>-1</sup>	260	6.32x10 <sup>-5</sup>
Dissociation	1.01x10 <sup>-1</sup>	260	2.53x10 <sup>-4</sup>
Formation	7.52x10 <sup>-1</sup>	250	2.08x10 <sup>-4</sup>
Formation	7.52x10 <sup>-1</sup>	250	2.35x10 <sup>-4</sup>
Formation	7.52x10 <sup>-1</sup>	250	9.04x10 <sup>-5</sup>
Formation	5.93x10 <sup>-1</sup>	250	9.60x10 <sup>-5</sup>
Formation	8.96x10 <sup>-1</sup>	260	1.26x10 <sup>-4</sup>
Formation	8.96x10 <sup>-1</sup>	260	3.15x10 <sup>-4</sup>

Table 1 - Rates of hydrate dissociation/formation experimentally determined at the University of Oklahoma and University of Arkansas\*[7].

A comparison of rates above and below atmospheric pressure suggest that the rate of dissociation changes significantly with pressure (Table 1). However, the relative humidity of the headspace may also play a role in the hydrate dissociation mechanism.

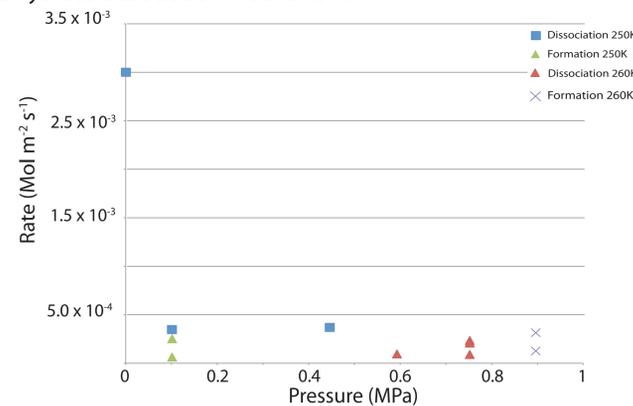


Figure 3 - Results of hydrate dissociation experiments at 250K and 260K. Low pressure experiments (3.0x10<sup>-4</sup> MPa) conducted at the University of Arkansas indicate sublimation effects.

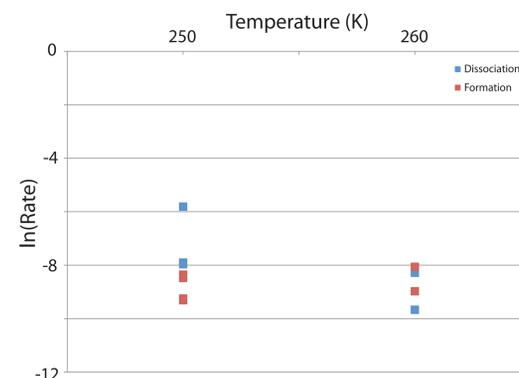


Figure 4 - Formation rates of hydrate increase with temperature while dissociation rates decrease with temperature. This is likely due to the self-preservation mechanism of gas hydrates as they dissociate below the freezing temperature of water ice. Anomalous slow dissociation rates have been observed in many studies and have been attributed to the formation of a water ice shell through which gas must diffuse in order for dissociation to continue. Within this regime, dissociation rates are assumed to be diffusion-limited.

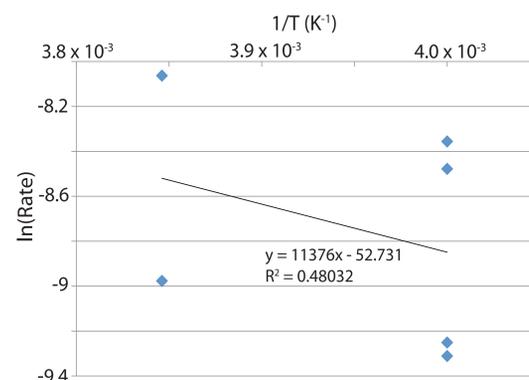


Figure 5 - Arrhenius Plot of CO<sub>2</sub> hydrate formation rates. An activation energy of 94586J can be determined with reasonable confidence from experiments conducted at OU at 250K and 260K.

## Methods

A device has been constructed to measure the rate of clathrate formation and dissociation by monitoring pressure and temperature conditions inside a reactor chamber cooled in a commercial freezer. A small gas reservoir was also cooled to ensure that gas entering the reactor chamber is at thermal equilibrium with the ice in the reactor. The amount of gas present throughout the experiment was calculated using the Van der Waal's equation to account for intermolecular attraction. Pressure and temperature measurements were taken every 15 seconds and recorded with Labview/National Instruments equipment. A container of water, open only at the top was placed inside the reactor chamber and frozen before pressurization, leaving the top of the ice cylinder open and free to react with the gas in the headspace. In this arrangement the gas is reacting with a known surface area of ice, allowing surface area normalized rates to be measured. This geometry will also facilitate future work on diffusion rates during hydrate formation.

Parallel experiments below atmospheric pressure were conducted in the Mars environment chamber (Andromeda chamber) at the University of Arkansas. This chamber has been previously described [4], and the results are reported in detail in another abstract [6].

## Diffusion Coefficient Solution

Determining diffusion coefficients through gas hydrate and/or ice is a non-trivial task involving a moving ice/hydrate boundary as well as solid state diffusion ahead of the boundary. Experimentally determined diffusion coefficients from the literature vary by several orders of magnitude (give examples and references, maybe a table). In addition, most previous work has assumed a steady state boundary which may bias the solution. Current work on this project includes evaluating the diffusion-controlled rate data collected within the context of a moving boundary Stephan Task to determine if iterative forward modeling using varying diffusion coefficients can be used to constrain diffusion coefficients in ice and hydrate. However, time series measurements of CO<sub>2</sub> concentration and ice hydrate boundary position are needed to fully determine the diffusion coefficient.

## Conclusions

The rate of dissociation shows little change between 1 atm and 4.4 atm (Table 1). When pressures are reduced to 0.003 atm, the CO<sub>2</sub> hydrate is sublimating, and the rate accelerates by one order of magnitude. During formation an activation energy of 94.6kJ/mol was calculated.

Blackburn et al. [8] concluded that this sublimation process is heat limited. However, in experiments at higher pressures the initial rate is a first order reaction, limited by the kinetics of hydrate dissociation. After an initial 'film' of hydrate has dissociated to ice, the reaction mechanism changes to a diffusion limited process, as escaping gas must pass through the overlying ice (Figure 1).

CO<sub>2</sub> clathrate dissociation rate is determined by several factors which change with the pressure and temperature conditions of the system. The reaction mechanism also changes with time as hydrate becomes 'capped' by ice generated during earlier clathrate dissociation (Figure 1). At lower pressures and humidity, the hydrate sublimates at a rate one order of magnitude faster and heat transfer is the primary limiting agent. These changes in mechanism and rate have significant implications for modeling carbon fluxes on Mars and other planetary bodies[9].

## References

- [1] Mumma M.J. et al. (2009) Science,323,1041-1045. [2] Chastain B.K. and Chevrier V.(2007) Planet. Space Sci.,55,1246-1256. [3] Elwood Madden M. E. (2007)GRL,11, L11202. [4] Formisano V. et al. (2004) Science,306,1758-1761. [5] Hoffman, N. (2000) Icarus 146,326-342. [6] Blackburn D.G. et al.(2010) LPSC XXXI, Abstract.[7]Sears D.W.G. and Moore S.R.(2005) GRL, 32 L16202. [8]Blackburn D.G. et al.(2009) LPSC XXXX, Abstract#1341.[9]Root M. et al.(2010) LPSC XXXI



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