Abstract 1418

## CO<sub>2</sub> Clathrate Dissociation Rates Below the Freezing Point of Water

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Introductio	on	Initial Rates		Change of Reaction Mechanism		
Gas hydrate clathrates are cage-like struc- tures of water molecules surrounding a gas molecule such as carbon dioxide or methane. $CO_2$ clathrate is structure I, indi- cating 5.75 H2O molecules : 1 $CO_2$ . Clath-	l (VDa) 2 pilonique (VDa) 2 pi	<ul> <li>-The initial rate of dissociation shows little change between 1 atm and 4.4 atm.</li> <li>-When pressures are reduced to 0.003 atm, the CO<sub>2</sub> hydrate sublimates, and the rate accelerates by one order of magnitude.</li> <li>-Blackburn et al. [7] concluded that this sublimation process is heat limited.</li> </ul>	-Initial rates of reaction me ing gas mus -Calculation of	al rates of dissociation produce a thin film of ice, capping the hydrate. The eaction mechanism then changes to a diffusion limited process, as escap- ig gas must pass through the overlying ice (Figure 3). culation of diffusion coefficients for the reaction rate is ongoing.		
save their exceptional thermal expansivity	-1 CO2 minutes construction of the second se	However, in experiments at higher pressures the initial rate is a first order reaction, limited by the kinetics of hydrate dissociation.		Atmospheric CH <sub>4</sub>		
and conductivity. Hydrates are stable at	bo -2			Unconfined Reservoir	Confined Reservoir	
tions making them likely to form in many	-3- H <sub>2</sub> O gas	Initial Rates of Hydrate Dissociation		Hydrate Dissociation	Slow CH <sub>4</sub> diffusion through overlying ice Water Ice	
environments throughout the solar	-4			Gas Hydrate	Gas Hydrate	

system. Clathrates have been suggested sources of methane in the Martian atmosphere [1,2,3,4], and subsurface water and

250 300 Temperature (K)

200

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.

## Methods

The goal of this work is to measure the rate of clathrate formation and dissociation below 273K.

- -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 to react with the gas in the headspace.
- -A small gas reservoir was cooled within the freezer so that gas entering the reactor chamber is at thermal equilibrium with the ice in the reactor.
- -Pressure and temperature measurements were taken every 15 seconds and recorded in LabView.
- -The gas was released into the reactor and hydrate was formed.
- -The amount of gas present throughout the experiment was calculated using the Van der Waal's equation to account for intermolecular attraction. -Parallel experiments below atmospheric pressure were conducted in the

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(hPa)	<b>(K)</b>	(mol m <sup>-2</sup> s <sup>-1</sup> )	
4460	250	3.69 x 10 <sup>-4</sup>	
1013	250	3.47 x 10 <sup>-4</sup>	
3	250	3.00 x 10 <sup>-3</sup>	[7]

A comparison of rates above and below Earth 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.

At low-pressure conditions within the Andromeda chamber, the headspace is significantly undersaturated with respect to water vapor, which may lead to sublimation of the hydrate [7], rather than dissociation and release of only the gas component, as observed at higher pressures.





![](_page_0_Figure_20.jpeg)

Fig.3 - Gas released during hydrate dissociation shows a change of reaction mechanism from inital surface dissociation to a diffusion limited rated.

## **Future Work**

-Complete a similar series of experiments for methane clathrate. -Produce data for a larger pressure range. -Use gas consumption data to determine an approximate diffusion coefficient.

-Model the moving boundary system with a Stefan problem like solution.

Mars environment chamber (Andromeda chamber) at the University of Arkansas. This chamber has been previously described [6], and the results are reported in detail in a previous abstract [7].

![](_page_0_Picture_26.jpeg)

![](_page_0_Figure_28.jpeg)

Fig.4 - Preliminary analysis indicates it may be possible to use a graphical estimate of the diffusion coefficient via pressure decay during formation based on a method outlined by Sheikha et al. [8]

> $D = Estimated Diffusion Coefficient [ <math>m^2s^{-1}$ ] b = slope of best fit line [dimensionless . = Height of gas zone [m]  $M = Molar mass of gas [kg kmol^{-1}]$  $K_h = Henry's Constant [ Pa m<sup>3</sup> kg<sup>-1</sup>]$ Z = Gas compressibility [ dimensionless ] R = Universal Gas Constant [ J kmol<sup>-1</sup> K<sup>-1</sup>]T = Temperature [K]

> > Conclusions

Fig.1 - Physical system is placed into commercial freezer to reach experimental temperatures. The National Instruments ADC system is visible to the left. Chilled gas from the reserve tank passes through the regulator to the reactor. Pressure decay is observed during hydrate formation and pressure builds during hydrate dissociation.

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-Hydrate dissocation rates can be determined by change in temperature and pressure conditions of the system. -Reaction mechanism changes with time as hydrate becomes capped by ice and the process becomes diffusion limited -Low pressure and humidity conditions result in an order of magnitude faster dissociation rate which appears to be heat transfer limited. -Significant impacts on modeling carbon fluxes [9] (See poster #1705)

![](_page_0_Picture_35.jpeg)

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