

**CO<sub>2</sub> CLATHRATE DISSOCIATION RATES BELOW THE FREEZING POINT OF WATER.** J.R. Lee-man<sup>1</sup>, D.G. Blackburn<sup>2</sup>, M.E. Elwood Madden<sup>1</sup>, R. Ulrich<sup>2</sup>, and V. Chevrier<sup>2</sup>. <sup>1</sup>School of Geology and Geophysics, University of Oklahoma, 100 E. Boyd, Norman, OK 73019, melwood@ou.edu, <sup>2</sup>Arkansas Center for Space and Planetary Science, University of Arkansas, Fayetteville, AR 72701, dgblackb@uark.edu

**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.

**Methods:** A device has been constructed at the University of Oklahoma to measure the rate of clathrate formation and dissociation by monitoring pressure and temperature conditions inside a reactor cooled within a commercial freezer. A small gas reservoir was also cooled within the freezer so 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 in Labview.

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 [6], and the results are reported in detail in another abstract [7].

**Results:** 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.

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, rather than dissociation and release of only the gas component, as observed at higher pressures.

Pressure (MPa)	Temperature (K)	Rate (molm <sup>-2</sup> s <sup>-1</sup> )
4.46x 10 <sup>-1</sup>	250	3.69x 10 <sup>-4</sup>
1.01x 10 <sup>-1</sup>	250	3.47 x 10 <sup>-4</sup>
3.00x 10 <sup>-4</sup>	250	3.00 x 10 <sup>-3</sup>

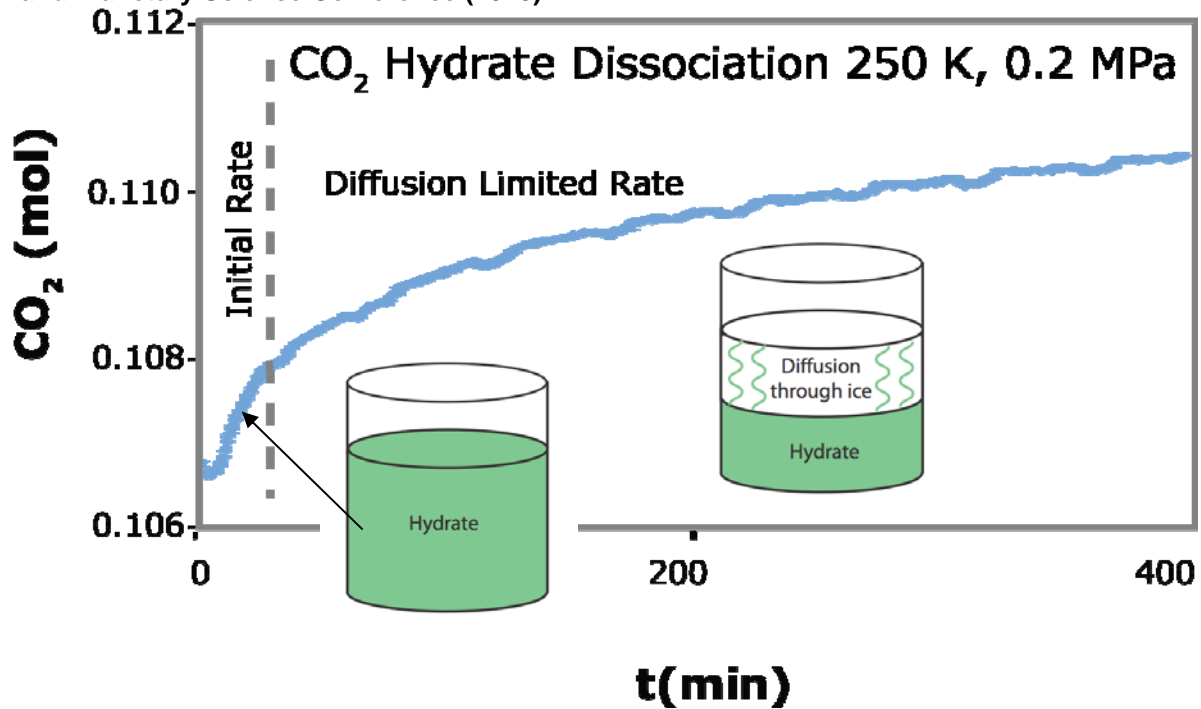
**Table 1.** Observed rates of dissociation at various pressure conditions.

**Discussion:** 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.

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).

The calculation of a reaction rate during the diffusion-limited period of dissociation is non-trivial. The diffusion coefficient at a specific location changes with the moving ice/hydrate boundary. Gas is released from the clathrate creating a sub-gradient in the opposite direction to the dominant diffusion gradient. Detailed discussion of this mechanism is left to future studies.

**Conclusions:** 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].



**Figure 1.** CO<sub>2</sub> flux over time during a dissociation experiment. The dissociation reaction mechanism changes from a first order initial rate to a diffusion-limited rate as the experiment proceeds.

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