

EXPERIMENTAL STUDY OF THE KINETICS OF CO₂ HYDRATE DISSOCIATION UNDER SIMULATED MARTIAN CONDITIONS. D.G. Blackburn¹, R. Ulrich¹, M.E. Elwood Madden², J.R. Leeman², and V.F. Chevrier¹. ¹Arkansas Center for Space and Planetary Science, University of Arkansas, Fayetteville, AR 72701, dgbblackb@uark.edu, ²School of Geology and Geophysics, University of Oklahoma, 100 E. Boyd, Norman, OK 73019, melwood@ou.edu

Introduction: The composition of the martian polar caps has long been debated with a consensus opinion that the north is composed predominately of water ice and the south a combination of solid CO₂ and water ice [1]. Smythe and Miller [2] suggested that the polar caps may be composed of at least some CO₂ hydrate, aka. clathrate, or compound gas hydrates [3, 4, 5, 6, 7]. Durham [8] predicted that a martian ice cap composed of hydrate will melt less readily than a cap of pure water ice, as the thermal conductivity of hydrate is lower. Gas hydrate has not yet been detected on Mars [1], but this can be explained by the infrared spectral similarities between it and pure water ice [9]. With the likelihood of CO₂ hydrate in the polar caps of Mars, knowledge of the kinetics of its phase changes becomes important because it will affect the mass balance of CO₂ and H₂O. Kinetics of hydrates under martian conditions is a relatively unexplored field [3, 4, 9], and the lack of sufficient laboratory data in this area motivated this work.

Procedure: CO₂ hydrate was formed for the purpose of measuring its kinetics under simulated Martian conditions.

Hydrate Production. CO₂ hydrate was formed following the technique of Stern et al [10]. Ultra-pure water was frozen and crushed using a food processor within a freezer at 253 K to prevent melting. Approximately 100 g of crushed ice was placed within a pre-cooled Parr pressure vessel and pressurized to 4100 kPa with CO₂ gas. The pressure vessel was allowed to warm slowly over the course of several hours through the ice melting point. As the ice melts, it converts to CO₂ hydrate, buffering the temperature at 275 K. Following conversion to hydrate the temperature continues to rise. Once the vessel reached 280K, it was placed within a freezer and cooled to <263K. The vessel was then allowed to warm through another cycle to 280K. This process was repeated 3-4 times until no buffering effect was discernible in the temperature profile as the vessel warmed, indicating the ice had completely transformed into hydrate. The vessel was then cooled to 253K prior to harvesting the gas hydrate. Hydrate samples were removed from the vessel immediately after depressurization and placed in liquid nitrogen to minimize decomposition. Samples were observed to be homogenous and fizzed and popped during transfer from the vessel, indicating they were composed of CO₂ hydrate.

Experimental. The hydrate samples were removed from the liquid nitrogen storage vessel an hour before the run and placed in a freezer set to 263K, which is in the anomalous hydrate stability zone at atmospheric pressure (Fig 4). Once the samples warmed to this new temperature, they were then placed in an open polystyrene cylinder on a mass balance in our chamber simulating the Martian environment (6 mbar CO₂ atmosphere and 263K) and allowed to dissociate. The martian environment was produced using the same planetary simulation chamber described in Sears and Moore [11]. Water humidity and mass loss rates were recorded, using a hygrometer and a precision mass balance, respectively. From the humidity and mass loss rates, the loss rate for water and carbon dioxide were derived. Three thermocouples recorded temperatures, two of the hydrate sample and one the atmosphere inside the chamber.

Results: The dissociation rates of five hydrate samples have been measured to date. Figures 1, 2, and 3 give the results from one example in which the temperature of the chamber and atmosphere were set to 263 K.

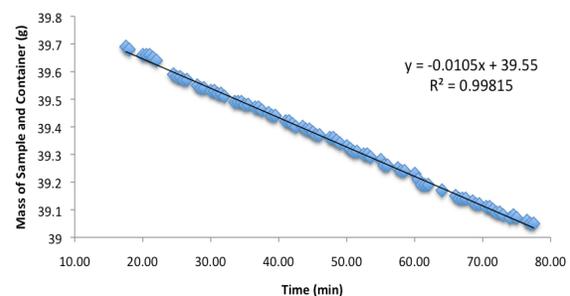


Figure 1. The mass loss rate vs. time of CO₂ hydrates under Martian conditions, 6 mbar and 263K

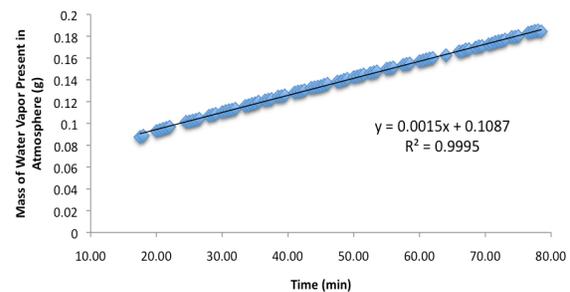


Figure 2. The grams of water vapor present in the atmosphere vs. time, determined from the partial pressure of water vapor in the chamber as given by the hygrometer

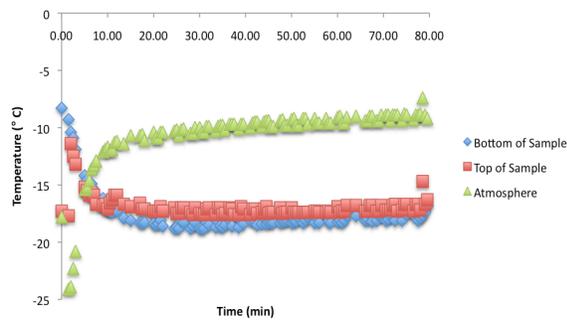


Figure 3. Temperatures during the run. Thermocouple 1 was touching the bottom of the sample, and thermocouple 2 was placed on the top. Thermocouple 3 records the temperature of the atmosphere. The chamber reached martian surface pressure at 5 minutes into the run.

When the sample is corrected for surface area, the resulting evaporation rate is $8.25 \times 10^{-6} \text{ g cm}^{-2} \text{ s}^{-1}$, which amounts to a loss rate of $7.07 \times 10^{-6} \text{ g cm}^{-2} \text{ s}^{-1}$ for CO_2 and $1.18 \times 10^{-6} \text{ g cm}^{-2} \text{ s}^{-1}$ for H_2O .

Discussion: The ideal hydration number for CO_2 hydrate is 5.75, which translates into a mass ratio of water to CO_2 of 2.35. The mass ratio of the H_2O : CO_2 released from the sample described in the Results section is 0.67, which means that CO_2 loss from the sample is dominant. This information implies that two processes are occurring simultaneously and that the first is principal: (1) the hydrate is recrystallizing into hexagonal ice, allowing CO_2 to escape, and (2) the remaining hexagonal ice is sublimating.

Given that the hydrate sample cooled to 255 K during the run and remained at that temperature in relation to the 263 K of the atmosphere, a heat transfer limited process is implied. Most models of hydrate dissociation assume a heat transfer limited process, but these models are typically under high-pressure conditions applicable to hydrate dissociation in industrial pipelines where the temperature is raised above the solidus [9].

The possibility also remains that the process is mass transfer limited, since CO_2 is diffusing into a CO_2 atmosphere and must also diffuse through a small layer of hexagonal or porous ice formed on the surface of the sample. The activity of water is also known to affect dissociation rates of hydrates as well [12], and previous studies of CO_2 hydrate transition to ice have found the process to be diffusion-limited [3, 4]. Further testing by varying atmospheric compositions and by altering incident radiation on the sample will be needed to establish the exact controlling mechanism, and what intermediary solid phases are formed.

The conditions of this experiment are within the temperature bounds for the well-established anomalous self-preservation regime of CO_2 hydrate at 1 bar in which hydrate can remain stable weeks outside of its thermodynamic stability zone [3, 9, 13, 14]. Preliminary indications are that this anomalous behavior does not extend into lower pressures (6 millibars) as would be found on the martian surface.

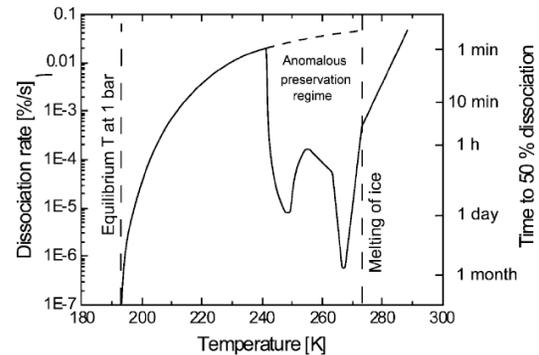


Figure 4. Dissociation kinetics at 1 bar of methane hydrate from Stern et al [14]. CO_2 hydrate exhibits similar behavior.

Conclusion: Hydrate transformation into ice under low-pressure conditions appears to be heat-transfer limited from early experimental results. This could have profound implications for the mass-balance of CO_2 in the martian polar caps. Further experiments will help to refine the controlling mechanism for carbon dioxide hydrate dissociation at martian conditions, and the results could also be applied to methane hydrates, a suggested source for martian methane [12,15].

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