

Kinetics of Methane Hydrate Formation & Dissociation Under Mars Relevant Conditions. S. R. Gainey¹, M. E. Elwood Madden, J. R. Leeman, B. M. Guttery. ¹University of Oklahoma, School of Geology and Geophysics, 100 E. Boyd St, Suite 710, Norman OK 73019, Gainey@ou.edu

Introduction: Spectral observations have indicated the presence of methane within the Martian atmosphere [1-3]. The methane source is not understood, but methane hydrate could be one of several potential sources. Gas hydrates, also known as clathrates, are crystalline solids that incorporate a gas molecule in cages of water molecules held by hydrogen bonds. Understanding the kinetics of methane hydrate formation and dissociation under Mars relevant conditions will allow the methane hydrate source hypothesis to be tested. However, methane hydrate formation and dissociation rates in the literature do not cover the appropriate range of pressure and temperature conditions. In this study methane hydrate formation rates at temperatures between 233 – 263 K and pressures 1.36 – 3.44 MPa were measured in the laboratory using the differential method proposed by [4]. Dissociation experiments were also conducted at 233 - 263 K and pressures ranging from 0.10 MPa – 2.54 using both depressurization and thermal heating to trigger dissociation. The kinetic data collected in this study will aid in the development of models of hydrate–ice systems on Earth and Mars.

Methods: The rate of methane hydrate formation was determined through cooling research grade methane within a vessel pressurized to the desired experimental conditions. Once the methane was in equilibrium with the desired thermal conditions of the freezer (marked by a stasis in pressure), the reacting vessel containing water ice was pressurized by opening a back flow regulator between the two vessels. The reacting vessel containing water ice was monitored with two thermo couples and one pressure transducer. Pressure and temperature data were recorded every 15 seconds in Labview. Applying the Van der Waals equation, the concentration of methane within the headspace was determined over time. Using the differential method proposed [4] the initial rate of reaction was determined and normalized for the surface area of the reacting boundary. Methane hydrate decomposition rates were determined by monitoring the increasing concentration of methane in the headspace while depressurizing the vessel or increasing the temperature of the freezer. The differential method was again used to determine the initial rate of dissociation.

Results: Initial rates of methane hydrate formation ranged from -1.20×10^{-3} to -9.07×10^{-4}

moles/m²s. All formation data indicated a rapid reaction of gas with ice within the first 100 seconds of pressurization forming a hydrate film at the gas-hydrate boundary, then significantly slowing due to diffusion (Figure 1) [2-5]. The data obtained in this study indicate that decreased temperatures coupled with higher pressures produce the most rapid hydrate formation (Figure 2). Initial rates of dissociation ranged from 1.03×10^{-3} to 2.55×10^{-5} moles/m²s. The release of methane was significantly more rapid during the first 500 second then slowed limited by diffusion. Lower pressure and higher temperature, moving the system away from the stability zone, produced the most rapid decomposition rates of methane clathrate.

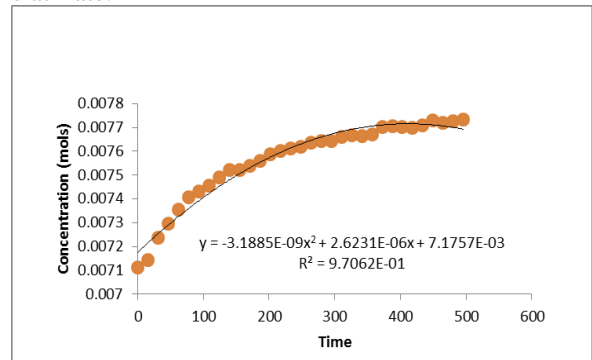


Figure 1: Concentration over time following pressure decrease to 1 atm, initiating dissociation. Methane increases within the head space, then slows at roughly five hundred seconds. The initial rate was determined by taking the derivative over five hundred second and setting time to zero.

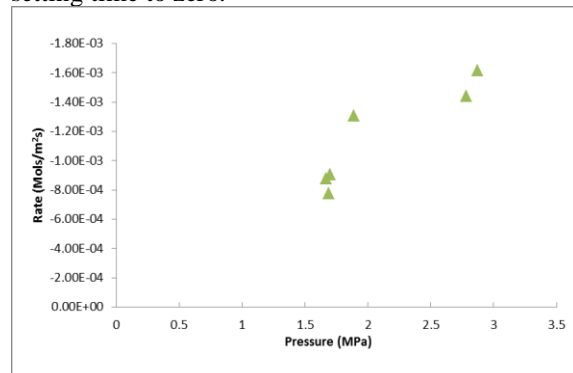


Figure 2: Formation kinetics, initial rate vs. pressure. The most rapid consumption of methane occurs at high pressure conditions. All experiments were conducted at ~ 250 K.

Discussion: The thermal effects on hydrate dissociation determined within this study will be used to evaluate whether the methane source hypothesis is feasible [6]. The known thermal effects of seasonal changes on and below the Martian surface will be utilized to determine the rate of dissociation of methane hydrate and the subsequent amount of methane released to the Martian atmosphere. These fluxes will be compared to those observed by [1-3].

Hydrate dissociation may also explain some geomorphic features on the Martian surface. The dissociation of methane hydrate may produce enough water and gas to account for outflow channels and chaotic terrain [7]. Rates determined may be utilized to determine the size of hydrate reservoirs required to produce such outflows.

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