

EXPERIMENTAL INVESTIGATION OF ADSORPTION KINETICS IN MONTMORILLONITE: IMPLICATIONS FOR DIURNAL VARIATIONS OF MARTIAN ATMOSPHERIC WATER. H. N. Farris¹, V. F. Chevrier¹, D. Kennington¹, and K. L. Bryson², ¹Arkansas Center for Space and Planetary Sciences, University of Arkansas, 346 ½ N. Arkansas Ave., Fayetteville, AR 72701, hnfarris@uark.edu, ²Department of Physics, Virginia Commonwealth University, Richmond, VA 23220.

Introduction: The stability of ice on Mars is affected by factors such as latitude and depth, as well as the thermal properties of the regolith, thus ice is unstable in equatorial regions at geologically short timescales [1]. Concentrations of water in equatorial regions may be attributed to water-rich minerals like sulfates [2], metastable water ice [3] and clays [1].

Variations in Martian orbital parameters have resulted in large-scale transport of this equatorial water towards the poles. The distribution of ice is governed by thermodynamics and kinetics. Kinetics is largely dependent on the adsorptive and diffusive properties of regolith [5], which are studied through simulation experiments on regolith analogs such as montmorillonite. Previous measurements were limited to constant temperature [6], despite kinetics of adsorption being largely dependent on temperature. This could create local accumulations of water vapor potentially leading to liquids. Moreover, numerical models of water ice stability [7] often require kinetic parameters that are lacking for Mars relevant materials.

Methodology: Clay minerals, like montmorillonite, were chosen for experimentation as they are usually excellent adsorbents and could be present in various regions on the Martian surface. Samples of montmorillonite (Panther Creek, CO) were first ground and sieved to $<63\mu\text{m}$ and dried by baking in a vacuum oven at $102 \pm 1^\circ\text{C}$ and 35 mbar for one day. The sample was then removed from the oven, sealed in a desiccator and cooled to -20°C in a freezer to eliminate any remaining moisture. The regolith was then deposited into petri dishes (15 cm diameter) in layers 1-2 mm thick.

The chamber was evacuated to the <0.09 mbar and then filled with CO_2 gas to atmospheric pressure, while a methanol/dry ice slurry was flowed through the cooling coils to chill the chamber to below 0°C . Then the chamber was opened, the sample placed atop a balance, a humidity buffer (saturated salt solution) was added, and the chamber was reclosed and evacuated to 7 mbar. A continuous flow of CO_2 while pumping was used to maintain the desired relative humidity inside the chamber.

The experiment was then run for 4-8 hours, the time necessary for the sample to reach saturation. During this time, mass, pressure, temperature, and humidity data were recorded every minute. Finally,

once the experiment was terminated, the sample was heated in the vacuum oven and measuring the mass difference determined the amount of water absorbed.

Mass-loss curves (Fig. 1) show the increase of adsorbed water over time. They all have a similar shape with an initial slope at $t = 0$ and eventually reach a plateau after a certain amount of time, which varies depending on the material. A polynomial fit to the data yields the adsorption kinetic constant, k_a .

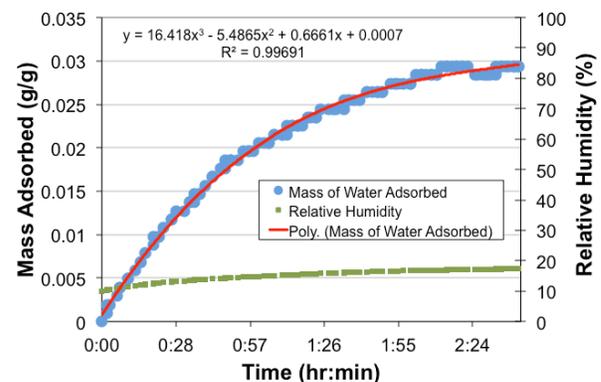


Figure 1 Mass loss curve of water adsorbed onto montmorillonite under Martian simulated conditions at about 3 C and 15% relative humidity. The sample reached equilibrium after ~ 2.7 hrs.

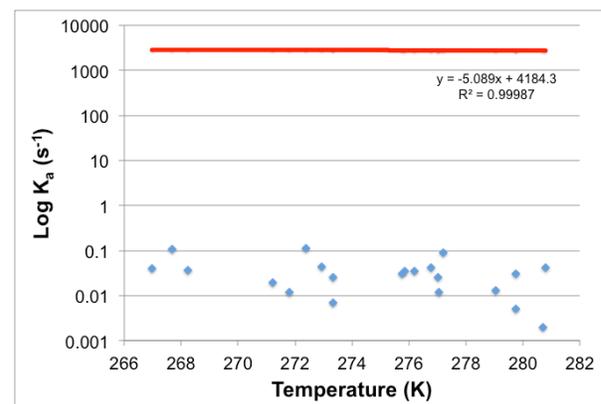


Figure 2 Adsorption kinetic constant of montmorillonite as a function of temperature showing comparison between experimental values (blue dots) and expected theoretical value (red line)

Approach: Adsorption of gases onto surfaces is usually described by the Langmuir isotherm:

$$\frac{1}{\theta} = 1 + \frac{1}{\alpha P} \quad (1)$$

where P is the partial pressure of water. α is the Langmuir adsorption constant, and θ is the percentage of the area covered by water molecules:

$$\theta = \frac{m_a}{\rho_{H_2O} A_S l} \quad (2)$$

where m_a is the mass of the adsorbed water (g/g), A_S is the effective grain size area, l is the monolayer thickness, and ρ_{H_2O} is the density of water. Knowing the effective surface area of the samples, it is possible to determine the amount of surface covered as a function of time and by obtaining a fit to the data in Fig. 1 and determine k_a and k_d , the kinetic constants of adsorption and desorption, from the following expression [6]:

$$\theta = \frac{k_a}{k_a + k_d} [1 - e^{-(k_a + k_d)t}] \quad (3)$$

k_a can be determined from the slope of the adsorption kinetic curve at $t = 0$ since the derivative of equation (4) ($d\theta/dt$ reduces). Then the desorption constant, k_d , can be determined from the plateau portion (equal to $k_a/(k_a + k_d)$, i.e. (4) at $t = \infty$) or a complete fit of the kinetic curve, but only so far for monolayers (i.e. Langmuir).

It is still unclear if there exists intrinsic properties of the water that affect the adsorption process:

$$k_a' = p k_a = \frac{p}{\sqrt{2\pi MRT}} C \quad (4)$$

where p is atmospheric water vapor, M is the molecular mass of water, R is the ideal gas constant, and C is the sticking coefficient:

$$C = C_0 e^{\left(\frac{-\Delta E_a}{RT}\right)} \quad (5)$$

where C_0 is a constant dependent on type of adsorbate and E_a is an energy.

Discussion: The aforementioned approach is only true for low pressures, because at higher pressures multiple molecular layers of water are adsorbed, and therefore is better described by the BET isotherm, which is the Langmuir expression adjusted for multiple water molecule layers [5]:

$$\frac{p'}{v(1-p')} = \frac{1}{v_m c} + \frac{p'(c-1)}{v_m c} \quad (6)$$

where p' is the measured pressure divided by the saturation pressure of the adsorbate (i.e. the relative humidity), v is the volume of the adsorbed gas, v_m is the monolayer adsorbed gas volume, and c is the BET constant.

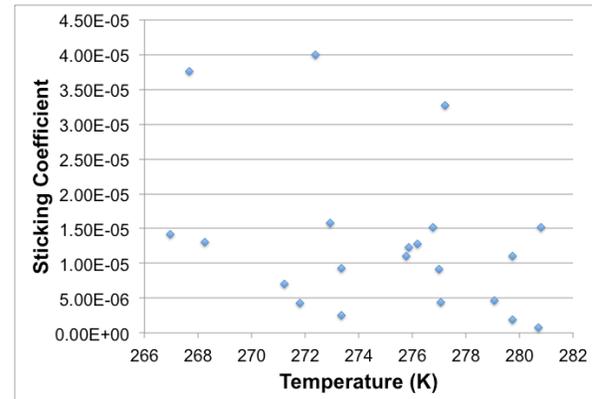


Figure 3 Sticking coefficient, C_s , of montmorillonite as a function of temperature.

The sticking coefficient is an intrinsic property that exists between the adsorbing liquid and the adsorbate, which can account for the discrepancy seen between the experimental and theoretical values of k_a (Fig. 2). However, in order to better isolate the affects of the sticking coefficient, the desorption kinetic constant, k_d , must be calculated:

$$k_d = \nu e^{\left(\frac{-\Delta H_d}{RT}\right)} \quad (7)$$

where ν is a frequency and ΔH_d is an enthalpy. In the case for multilayers of desorbed water, the BET isotherm must be employed, requiring an entirely new approach than that used for adsorbed water. The desorption kinetic constants for montmorillonite are currently being determined by modeling the data using both the Langmuir and BET approach in Origin 9.1.

References: [1] Chevrier, V.F. et al. (2008) *Icarus*, 196, 459-476. [2] Jakosky, B.M. et al. (2005) *Icarus*, 175, 58-67. [3] Chevrier, V.F. et al. (2007) *GRL*, 34. [4] Poulet, F. et al. (2005) *Nature*, 481, 623-627. [5] Brunauer, S. et al. (1938) *J. Am. Chem. Soc.*, 60, 308-319. [6] Beck, P. et al. (2010) *JGR* 115. [7] Rivera-Valentin, E. G. (2012) Doctoral Dissertation, University of Arkansas.