

THE STABILITY OF SULFATE-BEARING WATERS ON MARS. V. Chevrier¹, J.D. Chittenden¹, D.W.G. Sears¹, ¹W.M. Keck Laboratory for Space Simulations, Arkansas Center for Space and Planetary Sciences, 202 Old Museum Building, University of Arkansas, Fayetteville, AR 72701, USA <vchevie@uark.edu, jchitte@uark.edu, dsears@uark.edu>.

Introduction: Liquid water is known to be unstable on the surface of Mars, but the surface conditions are nevertheless close to the triple point of water. Thus under appropriate conditions, liquid water could form and remain at least metastable for a certain time [1]. Various observations of geological features, such as recently formed gullies, support this hypothesis [2].

In order to test the possibility of liquid water being present on the surface of Mars, experiments have been conducted using the Andromeda simulation chamber that allows the measurement of evaporation rates for water under various conditions. The goal is to investigate and focus on the features specific to Mars that could allow liquid water to form. Here we provide a brief review of the theory behind evaporation of water and ice, illustrated by experiments involving sulfate-bearing waters.

Experimental setup: The atmosphere is first evacuated from the chamber by lowering the pressure to less than 0.09 mbar. The chamber is then filled with pure CO₂ to atmospheric pressure, and cooled below 0°C using a methanol/dry-ice slurry circulated around the chamber. Once filled, the chamber is opened and the sample is placed on a top loading Ainsworth analytical balance. The platform supporting the balance set-up is lowered into the chamber. The lid is lowered and sealed, and the pressure is dropped to 6 mbar. As soon as the pressure is 6 mbar, the data are logged. These include mass, temperature (of the chamber and the sample), and pressure. The pressure is kept between 5 and 7 mbar during the whole experiment. The sample consists of water containing 20 wt% MgSO₄.

Results and discussion:

Pure water: The evaporation of pure liquid / water ice has discussed previously [3]. It appears that under Martian conditions, the evaporation rate of water, water ice and brine solutions agrees well with the Ingersoll equation [4]:

$$E = 0.612 \Delta \eta \rho_{\text{atm}} D \left[\frac{\frac{\Delta \rho}{\rho} g}{\nu^2} \right]^{\frac{1}{3}}$$

where E is the evaporation rate in mm/h, $\Delta \eta$ is the concentration difference at the surface of the sample and at distance, ρ_{atm} is the atmospheric density, D is the diffusion coefficient for water in CO₂ (1.4×10^{-3}

m²/s), g is acceleration due to gravity (3.75 m/s²), and ν is the kinematic viscosity of CO₂ (6.93×10^{-4} m²/s). The term $\Delta \eta$ is calculated from:

$$\Delta \eta = (P_{\text{H}_2\text{O}} M_{\text{CO}_2}) / (P_{\text{atm}} M_{\text{H}_2\text{O}})$$

$P_{\text{H}_2\text{O}}$ is the saturation vapor pressure of water on the surface of the sample and P_{atm} is the pressure in the chamber. M_{CO_2} and $M_{\text{H}_2\text{O}}$ are the molar masses for CO₂ and water. Finally the term $\Delta \rho / \rho$ is defined by:

$$\frac{\Delta \rho}{\rho} = \frac{P_{\text{H}_2\text{O}} (M_{\text{CO}_2} - M_{\text{H}_2\text{O}})}{P_{\text{atm}} M_{\text{CO}_2} - P_{\text{H}_2\text{O}} (M_{\text{CO}_2} - M_{\text{H}_2\text{O}})}$$

The saturation vapor pressure of water is calculated using a fit equation of the form:

$$P_{\text{H}_2\text{O}} = -A/T + B$$

Brine experiments: Evaporation of NaCl and CaCl₂-bearing brines has been previously investigated [5]. Liquid chloride brines show a lower evaporation rate than pure water, resulting mainly from the much lower temperature of the eutectic point. But there is also a diminution of the evaporation rate that results from the interactions between ions and water that decrease its activity. This is particularly evidenced in highly concentrated brines. Therefore the Ingersoll equation is modified first by dividing the evaporation rate by the density of the brine, and by modifying the saturation vapor pressure as follows:

$$P_{\text{H}_2\text{O}}(\text{br}) = a_{\text{H}_2\text{O}} \times P_{\text{H}_2\text{O}} = \Phi_{\text{H}_2\text{O}} \times C_{\text{H}_2\text{O}} \times P_{\text{H}_2\text{O}}$$

Where $P_{\text{H}_2\text{O}}(\text{br})$ is the saturation vapor pressure for the brine, $a_{\text{H}_2\text{O}}$ is the activity of water, which decomposes into $C_{\text{H}_2\text{O}}$ the concentration of water, and $\Phi_{\text{H}_2\text{O}}$ the osmotic or activity coefficient of water. If the salt present a low charge and thus a low interaction, the activity of water remain very close to 1.

However, most studies have shown the presence of abundant MgSO₄ salts on the surface of Mars [6], suggesting that the brines on Mars contained high sulfate abundances. In this case ions are more highly charged than for NaCl solutions. Ionic interactions will be stronger, which in turn will strongly influence the activity of water.

The activity of water can be evaluated through the specific ion interaction model SIT [7]. This model accounts for electrostatic, non-specific, long-range interactions, as described by the Debye-Hückel theory, but includes a term of short-range non-electrostatic interactions which become effective at very high concentrations. In this case, the activity of water in the presence

of a salt $N_{v+}X_{v-}$ is calculated through the following equation:

$$\text{Log}(a_{H_2O}) = \frac{-\Phi_{H_2O} \sum_k m_k}{\ln(10) \times 55.10}$$

This equation takes into account the abundance of all ions of molalities m_k . The osmotic coefficient itself is calculated as follows:

$$1 - \Phi = \frac{A \ln(10) |z_+ z_-|}{I_m (Ba_j)^3} \left[\frac{1 + Ba_j \sqrt{I_m} - 2 \log(1 + Ba_j \sqrt{I_m})}{1 + Ba_j \sqrt{I_m}} \right]$$

$$- \ln(10) \varepsilon_{(N,X)} m_{NX} \left(\frac{v_+ v_-}{v_+ + v_-} \right)$$

A and B are temperature dependant constants, a_j is the effective diameter of the hydrated ion, m_{NX} is the molality of the salt, z_+ and z_- are the charges of the ions and v_+ , v_- are the number of ions in the salt formula. $\varepsilon_{(N,X)}$ is the specific ion interaction coefficient, and I_m is the ionic strength and is calculated as:

$$I_m = \frac{1}{2} |z_+ z_-| m_{NX} (v_+ + v_-)$$

Therefore depending on the value of $\varepsilon_{(N,X)}$, the activity of water can be strongly reduced if the brine is concentrated (Fig. 1). Fig. 1 shows that activity can be decreased to 0.5 for solutions of 3.5 mol/kg which is the maximum value corresponding to saturation at ambient temperature.

Fig. 2 shows the results of the present experiments, in which 20 wt% $MgSO_4$ is allowed to evaporate at about 269 K under martian conditions. The rate of evaporation is much lower than predicted by the Ingersoll equation, but fits the data assuming $\varepsilon_{(N,X)}$ of 1.0. indeed the pure Ingersoll equation gives about 4.4 mm/h whereas the modified equation including the water activity gives about 2.8 mm/h.

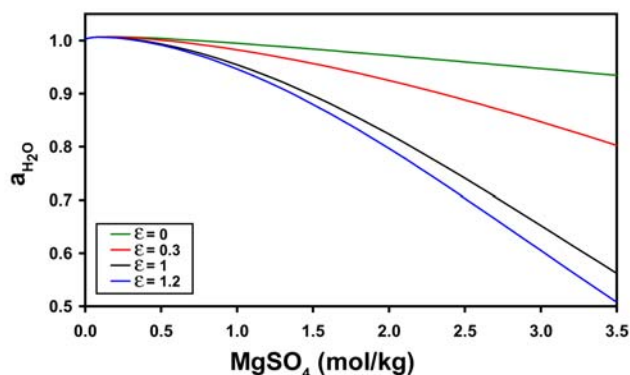


Figure 1. Theoretical (SIT model) activity of water as a function of the concentration of $MgSO_4$ for different values of specific ion interaction coefficient $\varepsilon_{(N,X)}$.

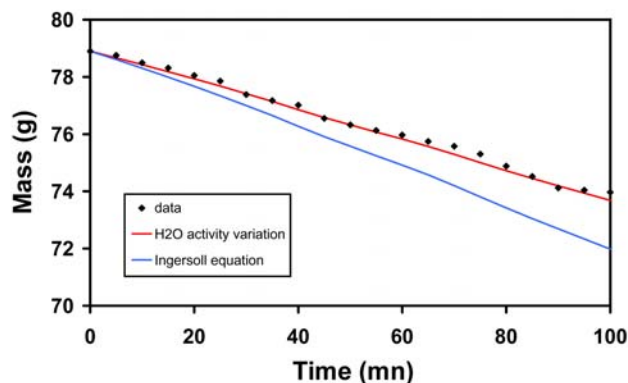


Figure 2. Evaporation curves for liquid brine containing initially 20 wt% $MgSO_4$ (black diamonds). The blue curve is calculated from the Ingersoll equation including pressure and temperature variations as measured during the experiment. The red curve includes the variation of water activity during evaporation.

Conclusions: Various experiments have been conducted to investigate the evaporation of water under Martian conditions. All verify the Ingersoll equation, providing a theoretical basis for model of liquid / ice water evaporation on Mars. The present work demonstrates the importance of changes in activity due to solute ion interactions. In the future, we will explore the effect of a variety of conditions, including the effects of soil layers, brines, wind conditions, and illumination.

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