

LOW TEMPERATURE AQUEOUS PERCHLORATE SOLUTIONS ON THE SURFACE OF MARS.

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Introduction: Although there has been no direct evidence for liquid water on the surface of Mars, indirect evidence comes from recent gully formation, which suggests the presence of liquid water processes near the surface [1, 2]. However, pure water is unstable in its liquid form due to the low pressures and temperatures associated with the Martian surface, so water is likely to be kept frozen and sublimating, or evaporating and boiling, if liquid [3]. Brines or salt-rich solutions composed of NaCl or CaCl₂ have been suggested since they are known to lower the freezing point and evaporation rates [4, 5].

Recent results from NASA's polar lander Phoenix have suggested the presence of perchlorates in the soil surrounding the landing site [6]. It is likely that these ions associate with either sodium or magnesium [7]. Very little is known regarding the behavior of these salts in solution, especially at low temperatures. Through evaporation experiments and geochemical modeling, we have studied the stability of perchlorates in a simulated Martian environment.

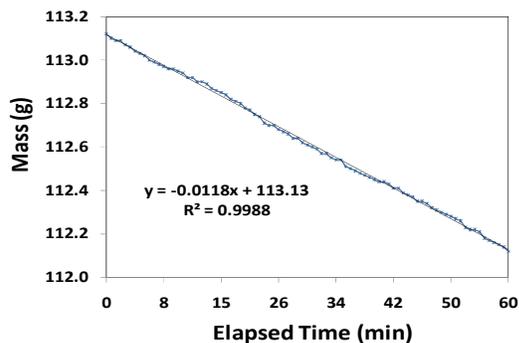


Figure 1. Mass loss of 55 wt% NaClO₄ at 265 K. A regression equation gives the slope of mass loss rate, which is then used to calculate the evaporation rate.

Experimental: Experiments were performed in a Martian simulation chamber using previously described methods [8]. Samples of NaClO₄ or Mg(ClO₄)₂ solutions at various concentrations (~20 to 50 wt%) are placed into a chilled CO₂ atmosphere (~263 K), which is then pumped down to Martian pressure (7 mbar). Using a precision balance, the mass loss rate was then measured (Fig. 1) and converted into evaporation rate using the following formula:

$$E = \frac{\Delta m / \Delta t}{\rho_{sol} S}$$

where $\Delta m / \Delta t$ is the mass loss rate, S is the surface area of the sample and ρ_{sol} is the density of the solution.

Results: At temperatures between 256 and 269 K, evaporation rates of sodium perchlorate (Fig. 2A) range from 0.07 mm h⁻¹ (55 wt% concentration at 258 K) to 0.49 mm h⁻¹ (20 wt% concentration at 266 K). As seen in previous studies, evaporation rate is dependent on both temperature and concentration of the solution [4, 8]. For instance, the evaporation rate of a 55 wt% solution ranges from 0.07 to 0.19 mm h⁻¹ over a temperature range of 11 K. The evaporation rate is also dependent on perchlorate concentration: at 266 K, the 20 wt% sodium perchlorate evaporates at 0.49 mm h⁻¹, while the 55 wt% evaporates at 0.14 mm h⁻¹.

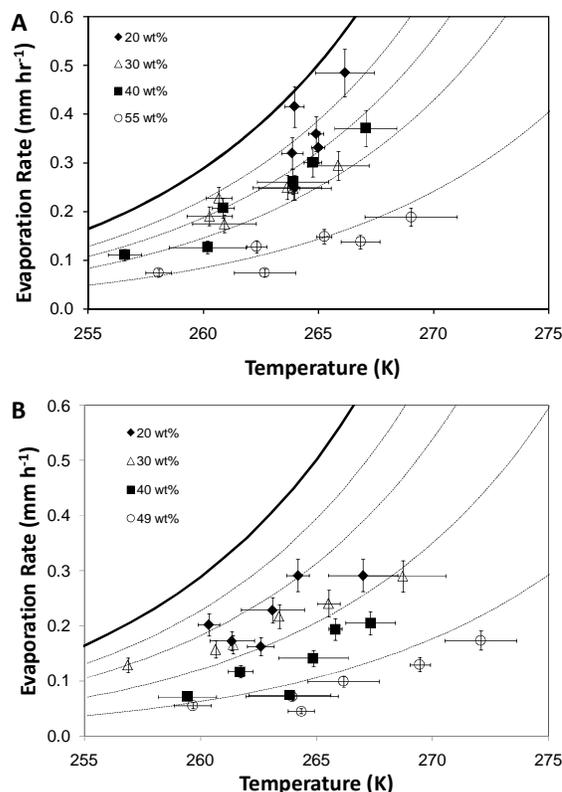


Figure 2. Evaporation rate of NaClO₄ (A) and Mg(ClO₄)₂ (B) as a function of sample temperature and concentration. Dashed lines are theoretical evaporation rates for each concentration, calculated from the Ingersoll (1970) equation and Pitzer model. The solid line is for pure water.

Magnesium perchlorate behaves in a similar manner (Fig. 2B). Evaporation rates range from 0.29 mm h⁻¹ (20 wt% at 267 K) to 0.06 mm h⁻¹ (49 wt% at 260 K). Again, evaporation rates are dependent on both temperature and concentration. For instance, at 264 K, the 20 wt% magnesium perchlorate evaporates at 0.29 mm h⁻¹, while a 49 wt% solution

evaporates at 0.07 mm h^{-1} . In addition, temperature plays a suppressive role as seen in the 49 wt%: evaporates rates range from 0.17 mm h^{-1} (272 K) to 0.06 mm h^{-1} (260 K).

Experimental evaporation rates are slightly lower in magnesium perchlorate than for sodium perchlorate. This is due to the fact that activity of water is lower in magnesium perchlorate solutions, as demonstrated by the Pitzer model [9].

Discussion: Thermodynamics of Sodium Perchlorate. Few data are available from low-temperature sodium perchlorate solutions. From data collected from various sources [9, 10], and calculating the corresponding thermodynamic parameters, the phase diagram was produced (Fig. 3A). Only three hydrous phases are known: NaClO_4 (anhydrous), $\text{NaClO}_4 \cdot \text{H}_2\text{O}$ and $\text{NaClO}_4 \cdot 2\text{H}_2\text{O}$. The dissolution of the mono-hydrate phase into liquid water at room temperature is highly endothermic. This phenomenon is quite unusual when compared with other salts. The eutectic temperature was determined to be 236 K at a concentration of 52 wt%.

In an attempt to obtain saturation at the low temperatures that we are running our experiments, we super-saturated the sodium perchlorate to 65 wt% at room temperature. When mass was measured, sample temperature was $272 \pm 2 \text{ K}$, and showed no mass loss. However, the sodium perchlorate crystallized out of solution. Although it is unknown by direct measurement, the phase diagram dictates this is the mono-hydrate phase. Spectral analysis will be performed on the crystallized sodium perchlorate in hopes of learning more about the hydrated states [11].

Magnesium Perchlorate. Less is known about the low-temperature properties of magnesium perchlorate $\text{Mg}(\text{ClO}_4)_2$. It is extremely exothermic when dissolved in water, and has a saturation concentration of 49 wt% at room temperature. Calculated eutectic temperature was found to be 200 K at 43.7 wt% (fig. 3B), very close to previous measurements [12]. At low temperature, magnesium perchlorate has only one hydrate, $\text{Mg}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$. This hydrate is apparently stable up to $\sim 420 \text{ K}$, where this hexahydrate melts into water and $\text{Mg}(\text{ClO}_4)_2 \cdot 3\text{H}_2\text{O}$ [13, 14]. Thus the deliquescence property suggested before for magnesium perchlorate may not be valid on Mars, since temperatures remains too low for the trihydrate phase to form.

Conclusions: The evaporation rates of magnesium and sodium perchlorates are generally quite similar, although slightly lower for magnesium, due to lower water activity (due to stronger ionic interactions with Mg^{2+} and ClO_4^-). As previously demonstrated, the main control on the evaporation rate remains the temperature [8]. However, thermodynamic calculations show that magnesium

perchlorate remains liquid at much lower temperatures (down to 200 K). In these conditions, the combination of a larger stability field for liquid and lower resulting evaporation rates suggest that magnesium perchlorate should be the dominant liquid phase at the Phoenix landing site. Further work will establish the behavior of both salts under their liquid and solid state at the Phoenix landing site, as soon as the data become available.

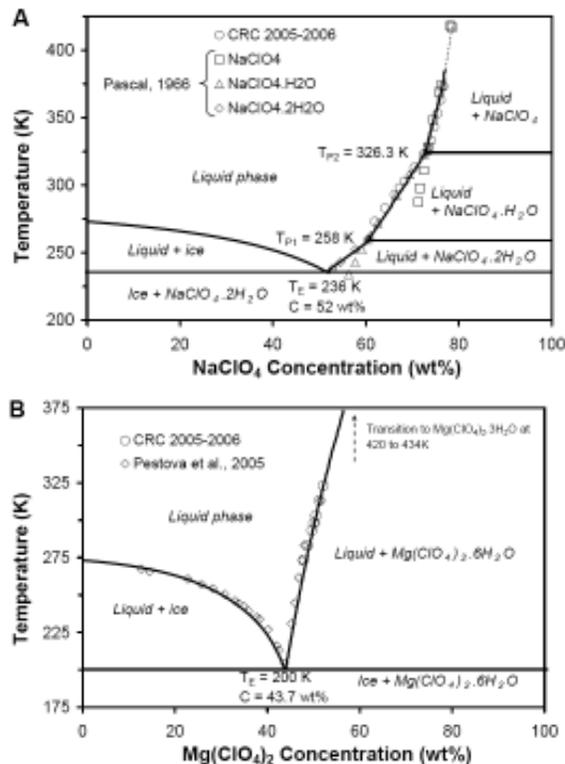


Figure 3. Phase diagram for sodium (A) and magnesium (B) perchlorate. Solid lines are theoretical based on data from CRC and Legendre (1962).

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