

**THERMODYNAMIC PROPERTIES OF AQUEOUS CHLORATE SOLUTIONS AND THEIR APPLICATIONS TO MARS.** J. Hanley<sup>1</sup>, V. F. Chevrier<sup>1</sup>, D. Berget<sup>2</sup>, and R. D. Adams<sup>1</sup>, <sup>1</sup>Arkansas Center for Space and Planetary Sciences, MUSE 202, University of Arkansas, Fayetteville, AR 72701, jhanley@uark.edu; <sup>2</sup>Drake University, 2507 University Ave, Des Moines, IA 50311.

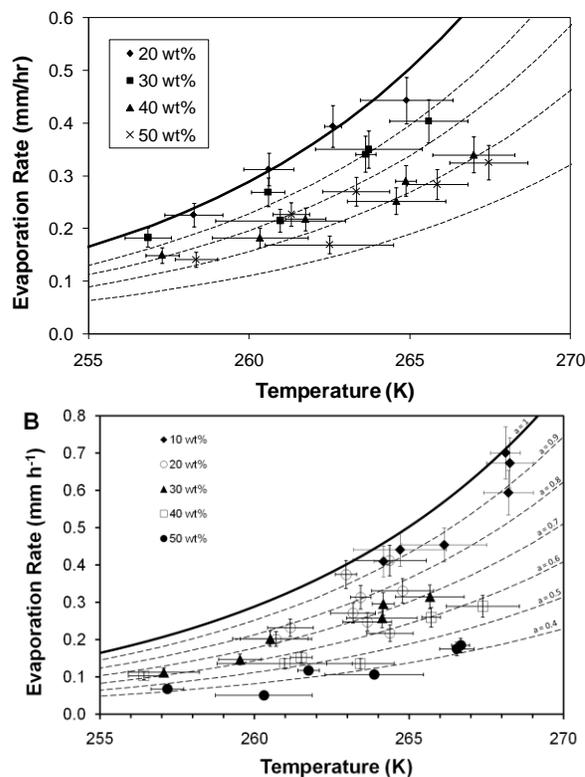
**Introduction:** The discovery of perchlorate ( $\text{ClO}_4^-$ ) by Phoenix [1] has triggered a high interest in this ion, which is rare on the surface of Earth. Perchlorate solutions have very low eutectics that favor the potential formation of liquid water on the surface of Mars [2]. The mechanisms by which such a highly oxidized ion may form, especially on Mars, remain largely unknown. Two major pathways are possible: atmospheric oxidation of aerosols, potentially through UV [3], or reaction of strong oxidants like  $\text{H}_2\text{O}_2$  with chlorides in liquid or solid form. A major problem for these models is the lack of thermodynamic data. Between chloride (Cl oxidation state -1) and perchlorate (ox. state +7), three other ions exist: hypochlorite  $\text{ClO}^-$  (ox. state +1), chlorite  $\text{ClO}_2^-$  (ox. state +3) and chlorate  $\text{ClO}_3^-$  (ox. state +5). These ions may be present (and undetected) at the Phoenix landing site as intermediate species of the processes leading to perchlorates.

To further understand these ions, we have started a detailed investigation of the thermodynamic properties of the intermediate oxidation states of chlorine oxyanions [4]. Of these intermediate species, chlorate is the most stable [5] and therefore most expected to be present with perchlorate in the Phoenix soils. In a first step, we focused on sodium and magnesium chlorates as the most relevant to the Phoenix chemistry [2,6].

**Methods: Evaporation Rates.** Experiments were performed in a Mars simulation chamber using the same methods as in Chevrier *et al.*, 2009 [2]. A sample of chlorate solution was placed into a chilled  $\text{CO}_2$  environment, which was then pumped down to  $7.00 \pm 0.01$  mbar, while still maintaining less than 1% relative humidity (RH). The mass loss (in grams) was measured and the evaporation rate  $E$  (in  $\text{mm h}^{-1}$ ) was determined.

**Activity of Water and Pitzer Parameters.** The Pitzer method for determining the activity of water takes into account various thermodynamic parameters and ion interactions, such as charge, stoichiometric ratios and concentration. However, the Pitzer parameters used in thermodynamic models do not exist for many of these chlorine oxyanions. Since the evaporation rate is a function of the water activity, we can use our experimental results to solve the evaporation equation for the activity of water at a given concentration. From the activity of water versus concentration, we can solve the Pitzer equations and determine the parameters for each cation – anion pair [2,7].

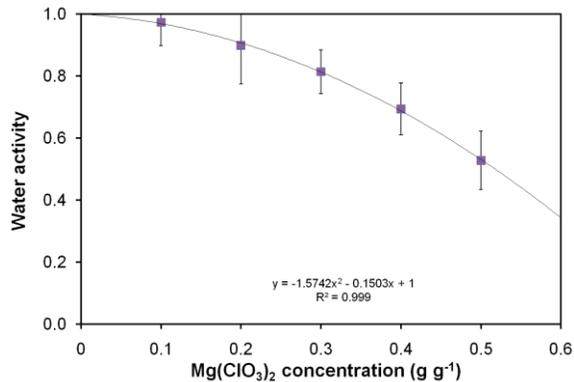
**Results: Evaporation Experiments.** At temperatures between 256 and 267 K, evaporation rates of sodium chlorate (Fig. 1A) range from  $0.141 \text{ mm h}^{-1}$  (50 wt% at 258 K) to  $0.443 \text{ mm h}^{-1}$  (20 wt% at 264 K). As



**Figure 1.** Evaporation rate of A)  $\text{NaClO}_3$  and B)  $\text{Mg}(\text{ClO}_3)_2$  as a function of sample temperature and concentration. Dashed lines are theoretical evaporation rates for each concentration or for various activities of water, calculated from a modified Ingersoll [8] equation and/or Pitzer model [9]. The solid line is for pure supercooled water.

seen in previous studies, evaporation rate is dependent both directly on the temperature and inversely on the concentration of the solution [2]. For instance, the evaporation rate of a 50 wt% solution ranges from  $0.141$  to  $0.325 \text{ mm h}^{-1}$  over 9 K. The evaporation rate is also dependent on salt concentration: at 265 K, the 20 wt%  $\text{NaClO}_3$  evaporates at  $0.443 \text{ mm h}^{-1}$  while the 50 wt% evaporates at  $0.284 \text{ mm h}^{-1}$ . These trends are also seen for  $\text{Mg}(\text{ClO}_3)_2$  solutions (Fig. 1B).

**Activity of Water.** We used our modified Ingersoll equation [2,7] to solve for the activity of water for  $\text{Mg}(\text{ClO}_3)_2$  at various concentrations (Fig 2). From this we are able to solve for the Pitzer parameters. Also, lowering the activity of water will lower its freezing temperature in a very consistent way. We can thus extrapolate from activity of water vs concentration to temperature vs concentration in order to obtain the ice line for the stability diagrams (Fig. 3).



**Figure 2.** Activity of water for various  $\text{Mg}(\text{ClO}_3)_2$  solution concentrations, calculated by solving our modified Ingersoll equation for brine evaporation rate [2,7].

**Discussion:** The results of our experiments have shown that evaporation rates have a direct relationship with the temperature of the solution and an inverse relationship with the concentration. This is consistent with all other salt solutions that have been measured in our laboratory. Increasing concentrations of salt will lower the activity of water, which has the effect of lowering both the evaporation rate and the freezing point. By solving for activity of water from our experimental evaporation rate, we will be able to empirically solve for the Pitzer parameters.

There is a clear lack of thermodynamic data for the various species of oxidized chlorine, especially those associated with magnesium. From the literature and our own data as described above, we have constructed stability diagrams for  $\text{NaClO}_3$  and  $\text{Mg}(\text{ClO}_3)_2$ , as shown in Fig. 3. While Fig. 3A uses theoretical calculations from the Pitzer parameters [8], there is an absence of Pitzer parameters for  $\text{Mg}^{2+}$  and  $\text{ClO}_3^-$ . In Fig. 3B the lines are polynomial regressions used to fit our data.  $\text{NaClO}_3$  (Fig. 3A) does not form any hydrates, which is in accordance with its high eutectic of 250 K. On the other hand,  $\text{Mg}(\text{ClO}_3)_2$  (Fig. 3B) forms three hydrates (2, 4 and 6), which, interestingly, correspond exactly to the hydrates of Mg-perchlorate.

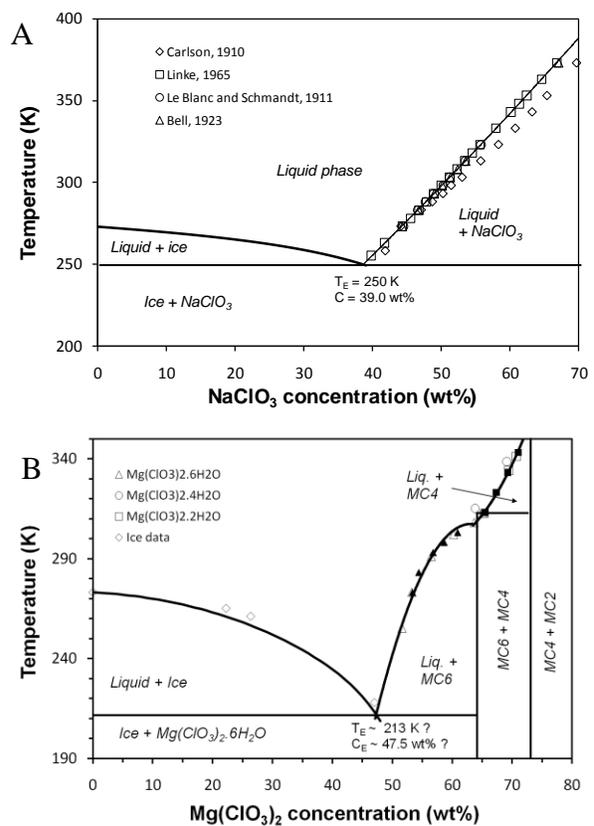
Future work will include extracting the activity of water and the salt's Pitzer parameters for each chlorine oxyanion, in turn enabling us to model evaporation and freezing processes under martian conditions [10].

Once thermodynamic properties are calculated, we will simulate Phoenix surface conditions with all oxidized chlorine species present. Our model in Geochemical Workbench uses a new database, based on the Pitzer model but for low temperatures. This allows for simultaneous freezing and evaporation, giving us the best possible scenarios to determine exactly which species will precipitate.  $\text{ClO}^-$  (hypochlorite) and  $\text{ClO}_2^-$  (chlorite) are both quite unstable [5] and thus unlikely to be present. However,  $\text{ClO}_3^-$  is almost as stable as perchlorate, and may be present (yet undetected) at the

Phoenix landing site. If this is the case, it would be interesting to know what the molar ratios between  $\text{ClO}_4^-$  and  $\text{ClO}_3^-$  would be. Additionally, we would be able to pin down the associated cations, whether they are  $\text{Na}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{K}^+$  or  $\text{Ca}^{2+}$ .

**Conclusions:** The evaporation rates of  $\text{NaClO}_3$  are similar to those of  $\text{NaClO}_4$ .  $\text{Mg}(\text{ClO}_3)_2$  shows a larger range in evaporation rates, and while its eutectic might be very low (213K),  $\text{Mg}(\text{ClO}_4)_2$  has the lowest eutectic temperature relevant to the Phoenix landing site, which, along with its low evaporation rates, suggests that it should be the dominant liquid phase there [2]. The other oxidized chlorine compounds require further study as they have intermediate eutectic temperatures that could potentially affect surface geochemistry.

**References:** [1] Hecht M.H. et al. (2009) *Science*, 325, 64-67. [2] Chevrier V.F. et al. (2009) *GRL*, 36, L10202. [3] Catling D. C. et al. (2010) *JGR*, E00E11. [4] Chevrier V. et al (2009) *New Mars Chem. Workshop* [5] Kang et al (2006) *Anal. Chim. Acta*, 567, 48-56. [6] Marion G. M. et al. (2009) *LPS XL*. [7] Chevrier V.F. and Altheide, T.S (2008) *GRL*, L22101. [8] Ingersoll, A. P. (1970), *Science*, 168, 972-973. [9] Pitzer, K. S. (1991), Ch. 3. *Activity coefficients in Electrolyte Solutions. 2nd Edition*, pp. 75-154, CRC Press. [10] Rivera-Valentin, E.G. et al. (2011) *LPS XLII* #1074



**Figure 3.** Stability diagrams of (A)  $\text{NaClO}_3$  and (B)  $\text{Mg}(\text{ClO}_3)_2$ . In Fig. A lines are theoretical calculations [8]. In Fig. B the lines are polynomial fits due to the absence of Pitzer parameters for  $\text{Mg}^{2+}$  and  $\text{ClO}_3^-$ .