

**THERMODYNAMIC PROPERTIES OF HYPOCHLORITES AND CHLORITES: APPLICATIONS TO THE PHOENIX SURFACE CHEMISTRY.** A. Elsenousy<sup>1</sup>, V. Chevrier<sup>1</sup>. <sup>1</sup> Arkansas Center for Space and Planetary Sciences, 202 Old Museum Building, University of Arkansas, Fayetteville, AR, USA, 72701. [amira@uark.edu](mailto:amira@uark.edu).

**Introduction:** Perchlorates ( $\text{ClO}_4^-$ ) were discovered by Phoenix lander 2008 with a concentration of  $\sim 2.4$  wt% [1]. This discovery brought a high attention for this rare ion on the surface of the Earth [2]. Chlorides ( $\text{Cl}^-$ ) also was found at the Phoenix landing site with a concentration of 0.54 wt%. Between chloride and perchlorate ions three other oxidized ions are exist: hypochlorite  $\text{ClO}^-$  (ox. state +1), chlorite  $\text{ClO}_2^-$  (ox. state +3) and chlorate  $\text{ClO}_3^-$  (ox. state +5). These oxidized ions might be exist as intermediate species on the surface of Mars but remained undetected. Moreover, some of these ions (hypochlorite “bleach” and chlorite) being extremely unstable and strong oxidants, they could explain the lack of organic material as observed by MSL on Mars [6]. Two main pathways are possible for the formation of perchlorates through this intermediate ions: first, oxidation of aerosols by the UV radiations, second, reaction of some strong oxidants such as hydrogen peroxide and ozone [3,4,5]. Therefore, it is important to have detailed study on the thermodynamic properties and stability of these intermediate ions.

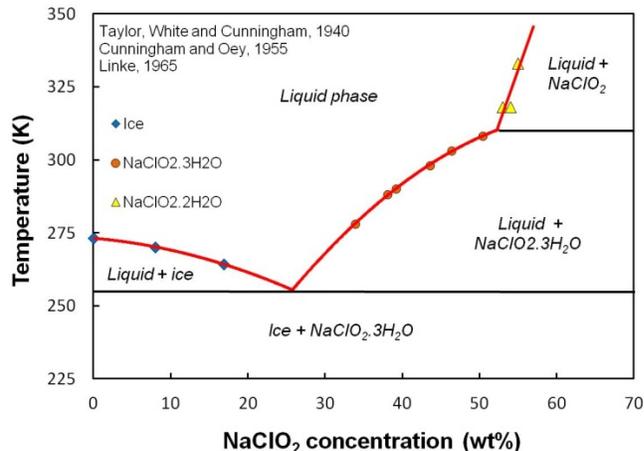
We started a detailed study of the thermodynamic properties of hypochlorites ( $\text{ClO}^-$ ) and chlorites ( $\text{ClO}_2^-$ ) salts. Salts incorporated in this study are Na-hypochlorites, Na-chlorites and Ca-hypochlorite (other compounds of  $\text{K}^+$  or  $\text{Mg}^{2+}$  do not exist or are too unstable). Using a combination of literature data and experiments on evaporation [7] we determine the thermodynamic (Pitzer) parameters that control their stability. These parameters can then be included in numerical models of evaporation or freezing (Geochemist’s Workbench or FREZCHEM).

**Experimental Methods:** From literature data, we have constructed stability diagrams of hypochlorite and chlorite salts for  $\text{NaClO}$  and  $\text{NaClO}_2$  as shown in Figure 1 and 2. Solubility data come from [8,9,10,11]. Unfortunately, there is only very limited existing data on the stability diagram of  $\text{Ca}(\text{ClO})_2$  [12] and none for  $(\text{CaClO}_2)_2$ .

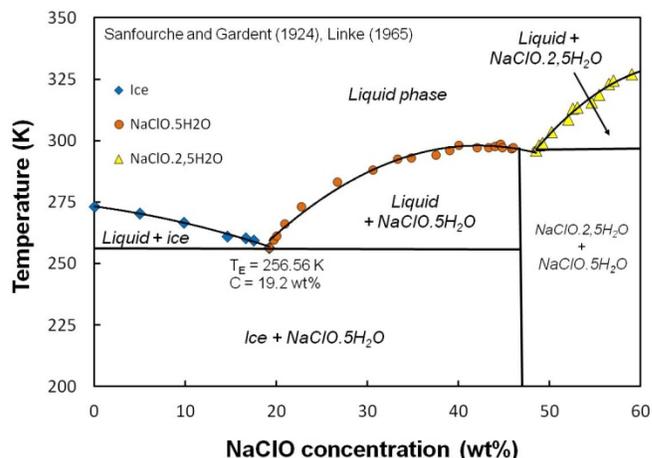
Evaporation rate data of  $\text{Ca}(\text{ClO})_2$  were made using D.I water and Ca-hypochlorite at concentrations of 5, 10 and 15 wt%. Evaporation rates were measured in our Martian simulation chamber at pressure of 7.00 mbar of pure  $\text{CO}_2$  and at temperatures ranging from 260 to 274 K (Fig. 3). The relative humidity was systematically maintained below 1%. The mass and temperature were recorded for the sample at each concentration.

**Results and Discussion:**

**Stability diagrams:** Figure 1 shows the stability diagram of sodium chlorite ( $\text{NaClO}_2$ ). The diagram shows that it forms only one hydrate ( $\text{NaClO}_2 \cdot 3\text{H}_2\text{O}$ ). The eutectic temperature of sodium chlorite is 255 K at a concentration of 26 wt%. Figure 2 shows the stability diagram of sodium hypochlorite  $\text{NaClO}$ , which forms two hydrated forms;  $\text{NaClO} \cdot 5\text{H}_2\text{O}$  and  $\text{NaClO} \cdot 2.5\text{H}_2\text{O}$ . It has eutectic temperature of 256.5K at concentration of 19.2 wt%.



**Figure 1.** Stability diagram of sodium chlorite. The lines are polynomial fits of the data.

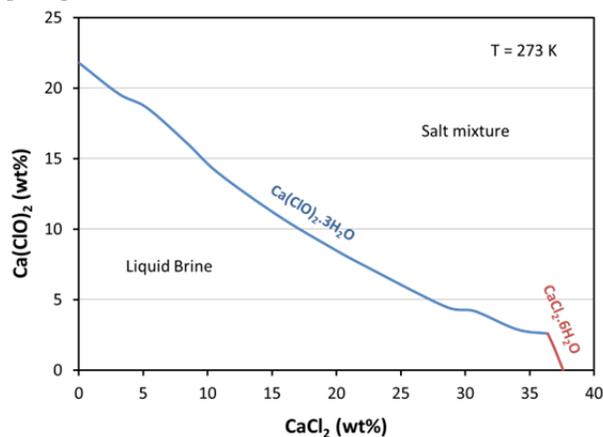


**Figure 2.** Stability diagram of sodium hypochlorite. The lines are polynomial fits of the data.

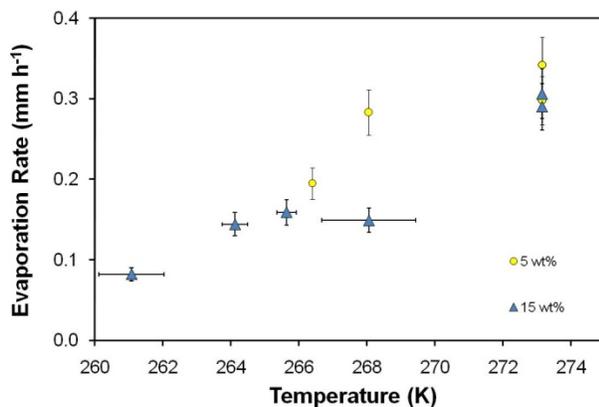
Concerning calcium hypochlorite, we could only find data at 273 K and mixed with calcium chloride (Fig. 3). These data suggest that calcium hypochlorite

forms hydrates (a trihydrate in this case). However we do not have any information on the eutectic temperature of this salt. Therefore, this requires new experimental data to determine more accurate thermodynamic properties of  $\text{Ca}(\text{ClO})_2$ . Nevertheless, these data can inform on deliquescence properties or binary mixtures.

**Evaporation rate results:** At temperatures between 260 and 273 K, evaporation rates of calcium hypochlorite (Fig. 4) range from  $0.08 \text{ mm h}^{-1}$  to  $0.32 \text{ mm h}^{-1}$  at 15 wt%. At temperatures between 266 and 273 K, evaporation rates of calcium hypochlorite range from  $0.2 \text{ mm h}^{-1}$  to  $0.35 \text{ mm h}^{-1}$  at 5 wt%. Similar to results with other salts, the evaporation rate is dependent on temperature and on the concentration of the solution [7,13].



**Figure 3.** Stability diagram of calcium hypochlorite (blue) and calcium chloride (red) mixtures for concentrations at 273.15 K.



**Figure 4.** Results of evaporation rate data of calcium hypochlorite for concentrations of 5 and 15 wt% at temperature ranges of 260 - 274 K.

**Conclusions:** From these diagrams, and especially evaporation rates and freezing temperature (or ice – liquid equilibrium lines), we can extract the Pitzer parameters for each anion – cation couple [14], which we can include in thermodynamic model databases.

We are currently calculating the Pitzer parameters for Calcium hypochlorite from evaporation data, and sodium hypochlorite / chlorite from freezing temperatures.

**Acknowledgements:** This work is funded by NASA Mars Data Analysis Program grant #NNX10AE10G.

**References:** [1] Hecht M. H. et al. (2009) *Science*, 325, 64-67. [2] Chevrier V. et al. (2009) *Geophys. Res. Lett.* 36.[3] Catling, D. C. et al. (2010) *J. Geophys. Res.*, 115, E00E11. [4] Jackson W. A. et al. (2010) *Environ. Sci. Technol.*, 44(13), 4869–4876. [5] Rao, B. et al. (2010) *Environ. Sci. Technol.*, 44(8), 2961–2967. [6] Ming et al. (2013), *Science*, DOI:10.1126/science.1245267. [7] Chevrier V.F. et al. (2009), *Geophys. Res. Lett.*, 36(L10202), DOI: 10.1029/2009GL037497. [8] Sanfourche A. and L. Gardent, *Bulletin de la Société Chimique de France*, 35 (serie 4), 1088-1093. [9] Taylor M.C. et al. (1940), *Industrial and Engineering Chemistry*, 32(7), 899-903. [10] Cunningham G.L. and T.S. Oey (1955), *J. Am. Chem. Soc.*, 77, 799-801. [11] Linke W. F. (1965), *Solubilities of inorganic and metal organic compounds : a compilation of solubility data from the periodical literature*, 4th Edition ed., American Chemical Soc. [12] O'Connor E.A. (1927), *Journal of the Chemical Society (Resumed)*, 2700-2710. [13] Chevrier V.F. and T.S. Altheide (2008), *Geophys. Res. Lett.*, 35(L22101), DOI: 10.1029/2008GL035489. [14] Hanley J. et al. (2012) *Geophys. Res. Lett.*, 39(L08201), DOI: 10.1029/2012GL051239.