

THERMODYNAMIC MODELING OF THE DELIQUESCENCE OF PERCHLORATE/CHLORIDE SALT MIXTURES USING GEOCHEMIST'S WORKBENCH (GWB): APPLICATION TO THE PHOENIX SURFACE CHEMISTRY A. Elsenousy¹, V.F. Chevrier¹. ¹ Arkansas Center for Space and Planetary Sciences, 202 Old Museum Building, University of Arkansas, Fayetteville, AR, USA, 72701. amira@uark.edu.

Introduction: Perchlorate (ClO_4^-) salts were recently discovered in Martian arctic region by the Phoenix lander [1]. Perchlorates are deliquescent salts that can absorb water vapor from the atmosphere and it could be the reason for the formation of brines across the Martian surface [2].

Deliquescence of individual perchlorate salts has been studied through experiments [3]. Nevertheless, the effect of other species that found in the Martian regolith such as chlorides (Cl^-), sulfates (SO_4^{2-}), chlorate (ClO_3^-) on deliquescence of perchlorates is not well studied yet. Therefore, studying binary salt mixtures of perchlorates and other salts is more relevant to the Martian regolith type. Indeed, like for eutectic temperatures, the deliquescence of binary mixtures of salts should be lower than for individual salts.

Chlorides were also found at the Phoenix landing site [1] and studying its effect on the deliquescence of perchlorates will help to understand the conditions of aqueous brines formation and their stability on Mars. Here we aim to determine the RH_{eut} (at which partially formation of aqueous phase) and the DRH (at which complete deliquescence will occur) for the relevant salt mixtures. Salts mixtures that incorporated in our study are $\text{NaClO}_4/\text{NaCl}$, $\text{Mg}(\text{ClO}_4)_2/\text{MgCl}_2$ and finally KClO_4/KCl .

Methodology: We are modelling the deliquescence and efflorescence of the following 3-salt mixtures: KClO_4/KCl at 298 K and 273 K, $\text{NaClO}_4/\text{NaCl}$ at 273, 253 and 243 K, and $\text{Mg}(\text{ClO}_4)_2/\text{MgCl}_2$ at 273, 253 and 243 K. We used the Geochemist's Work Bench (GWB) software package to model the effect of the perchlorate mole ratio $m\text{ClO}_4^-/(m\text{ClO}_4^- + m\text{Cl}^-)$ and chloride mole ratio $m\text{Cl}^-/(m\text{Cl}^- + m\text{ClO}_4^-)$ on the deliquescence relative humidity (DRH) of these mixtures, where $m\text{ClO}_4^-$ is the moles of perchlorate ion and $m\text{Cl}^-$ is the moles of chloride ion.

Since GWB is not able to do direct calculation of salt equilibria by varying humidity, we used the inverse approach. Rather than starting from a pure salt and increasing humidity, we started from a liquid solution, we decreased the amount of water through evaporation. Although previous experiments showed there is an hysteresis between deliquescence (RH increases) and efflorescence (RH decreases) [3], from a thermodynamic point of view both processes are identical. This allows us to use the codes to determine deliquescence points for various binary salt mixtures. Thus, for a fixed temperature, we calculate the

evaporation of binary mixture at an initial molar ratio and record the dominant salt and the water activity (= DRH at equilibrium). Then, we repeat the simulation for various mol ratios. This basically corresponds to a slice. Although time consuming, this method can be used with various numerical codes (FREZCHEM in particular for deliquescence below 0°C).

Results and Discussion: The humidity phase transitions of several binary salt mixtures have been studied experimentally by [4, 5 and 6] and theoretically by [7]. The deliquescence behavior of salt mixtures of KClO_4/KCl and $\text{Mg}(\text{ClO}_4)_2/\text{MgCl}_2$ is shown in Fig. 1 and 2, respectively, as a plot of relative humidity (RH%) vs. mole fraction of each salt. where $m\text{KClO}_4$, $m\text{KCl}$, $m\text{Mg}(\text{ClO}_4)_2$ and $m\text{MgCl}_2$ are the moles of KClO_4 , KCl , $\text{Mg}(\text{ClO}_4)_2$ and MgCl_2 mixtures, respectively. The DRH values of the two pure components are represented by the solid triangles at $x = 1$ and $x = 0.97$ (almost identical to $x = 0$) for KClO_4/KCl mixture and at $x = 1$ and $x = 0.90$ for $\text{Mg}(\text{ClO}_4)_2/\text{MgCl}_2$. Complete deliquescence of the salt mixture appears above the Deliquescence Relative Humidity (DRH) lines of the two salts. The DRH values decrease following the lines to a minimum at a concentration of ~ 0.995 (KClO_4/KCl) and ~ 0.99 ($\text{Mg}(\text{ClO}_4)_2/\text{MgCl}_2$) known as the eutonic concentration.

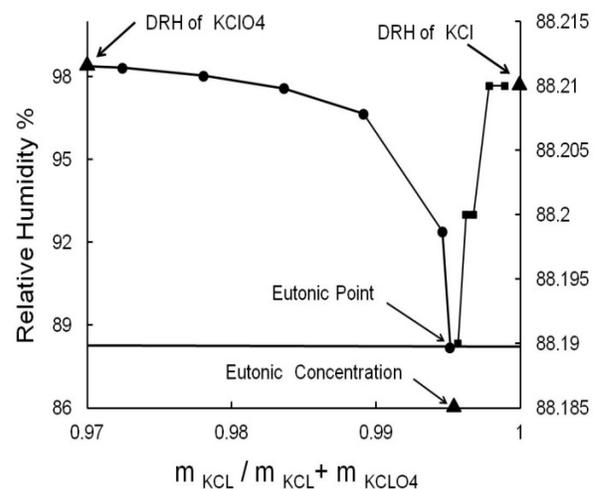


Figure 1. Deliquescence phase diagram of KClO_4/KCl binary salt mixture at 273 K using GWB model. Scales on vertical axes are for each salt.

At low RH values both mixtures of KClO_4/KCl and $\text{Mg}(\text{ClO}_4)_2/\text{MgCl}_2$ consists entirely of a solid phase. When the RH is increased to reach the eutonic

relative humidity value, R_{Heut} , 88% and 35% of both $KClO_4/KCl$ and $Mg(ClO_4)_2/MgCl_2$ mixtures respectively, an aqueous phase is formed. The solid phases exist in equilibrium with the aqueous phases when the RH is above R_{Heut} but below the DRH line.

The composition of these solids is a mixture of each original salt. Through increasing the RH around the 2-phase mixture of both $KClO_4/KCl$ and $Mg(ClO_4)_2/MgCl_2$ the ratio of aqueous to solid salt will increase regularly. The final humidity at which complete deliquescence occurs depends on the initial composition of the solid mixture. Above the DRH curve, only an aqueous phase is present which contains the same salt mole ratio of the original solid.

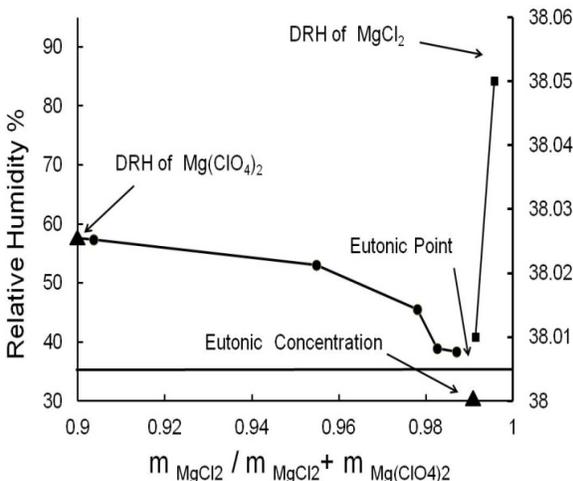


Figure 2. Deliquescence phase diagram of $Mg(ClO_4)_2/MgCl_2$ binary mixture at 273 K using GWB model. Scales on vertical axes are for each salt.

We also ran some preliminary tests at higher temperature, 298 K in this case for $(KCl/KClO_4)$. As expected we observe a decrease in the eutonic relative humidity from 88% to about 84% (Fig. 3).

Conclusions: Salt Mixtures at the eutonic concentration appears to have low DRH values. Furthermore, the R_{Heut} for the binary salt mixture is systematically lower than the DRH of each individual salt at a fixed temperature. Accordingly, we observe that presence of a little amount of a more deliquescent salt such as KCl cause aqueous solution to form at a RH value far below the DRH of the less deliquescent salt as $KClO_4$. This aspect of salt mixtures is more relevant to the Martian soil where mixtures of salts coexist.

The previous explanation of the salt mixtures diagram is based on the thermodynamic theory and is only valid to phase transitions that arise when the RH is increased around a salt mixture. Future work will focus on other relevant salts, and comparing our

modeling results to experiments focusing on binary mixtures.

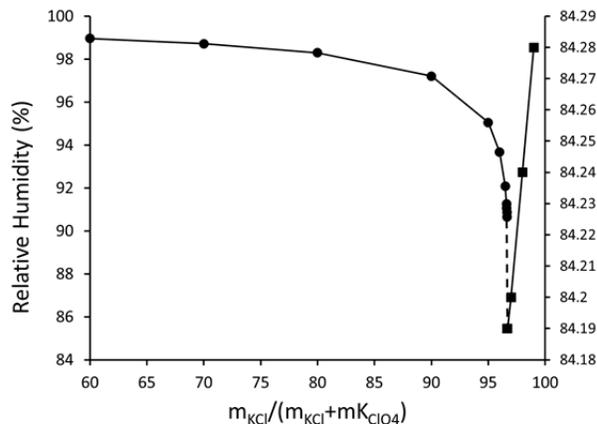


Figure 3. Deliquescence phase diagram of $KClO_4/KCl$ binary salt mixture at 298 K using GWB model. Scales on vertical axes are for each salt.

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] McEwen A. S., et al. (2011) *Science*, 333(6043), 740-743. [3] Gough, R. V. et al. (2010) *Earth and Planetary Science Letters*, 312 (3-4), 371-377. [4] Carroll, S. et al. (2005) *Geochemical Transactions*, 6(2), 19-1930. [5] Tang, I., and H. Munkelwitz (1993) *Atmos. Environ.*, 27A(4), 467-473. [6] Yang, L. T. et al. (2006) *J. Solut. Chem.*, 35(4), 583-604. [7] Potukuchi, S., and A. S. Wexler (1995) *Atmos. Environ.*, 29(14), 1663-1676.