Geophysical Research Abstracts
Vol. 13, EGU2011-1838, 2011
EGU General Assembly 2011

Freezing curves of salt - water systems and implications for possible cryo-brines on Mars

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New findings of expeditions reveal large quantities of salt deposits on Mars. Furthermore there exists strong evidence for the at least temporarily existence of liquids at Martian temperature conditions, that down to 200 K. Some salt - water systems are known forming cryo-brines with such low freezing temperatures. However, a systematic collection of low-temperature salt - water phase equilibria is missing and physico-chemical data of cryo-brines are nearly absent, particularly for temperatures below 250 K.

In this contribution a review is given for available freezing curve data of more than 120 binary and ternary salt - water systems. Particular emphasis was led on perchlorates and chlorides. In many cases the reported eutectic points can be meta-stable, because the stability of the solid cryo-hydrates was not proofed thoroughly. Often the stoichiometry of the cryo-hydrate is not known.

The data are analyzed for regularities of the effect of various cation - anion combinations on the decrease of freezing temperatures. Calculations of the activity coefficient of water along the freezing curves more clearly point out the opposing effects of ion hydration and ion association or metal ion complexation. The stronger the hydration of cations or anions (F-) the lower the water activity and thus the freezing temperature. This is true for cations like Li+, Mg2+, Ca2+, Zn2+, Al3+ or the lanthanide ions Ln3+. For salts of these ions the freezing curves fall steepest, if complex formation or ion association with anions is not important. Thus the lowest eutectic temperatures could be reached, if not a solid cryo-hydrate is crossing the freezing curve at a relatively "high" temperature.

For some salt solutions the temperature - concentration dependence of the water activity coefficient is compared for low and enhanced temperatures to elucidate the effect of very low temperatures.

Ternary salt - water systems can give considerable lower eutectic temperatures. However, investigations of ternary systems are very scarce and nearly not existent for systematic determinations of the eutectic points.

As a conclusion from this work it has to be stated that from the existing database for phase equilibria with cryo-brines a number of salts can be found with eutectic temperatures below 200 K, also for salts consisting of elements expected in larger amounts on Mars. Nevertheless this list is very incomplete and predictions for low-lying aqueous eutectics with salt mixtures can not be made presently. New experimental work has to be done to determine phase equilibria with and thermodynamic data of cryo-brines. The latter represents also an inevitable presumption for the development of geochemical models for very low temperatures.