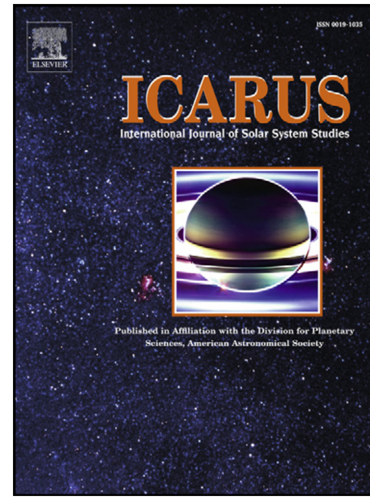
Accepted Manuscript



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PII: S0019-1035(10)00444-6
DOI: 10.1016/j.icarus.2010.11.025
Reference: YICAR 9638

To appear in: *Icarus*

Received Date: 31 May 2010
Revised Date: 12 November 2010
Accepted Date: 17 November 2010

Please cite this article as: Möhlmann, D., Thomsen, K., Properties of cryobrines on Mars, *Icarus* (2010), doi: 10.1016/j.icarus.2010.11.025

Properties of cryobrines on Mars

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Running head: Properties of Cryobrines on Mars

Abstract
Brines, i.e. aqueous salty solutions, increasingly play a role in a better understanding of physics and chemistry (and eventually also putative biology) of the upper surface of Mars. Results of physico-chemical modelling and experimentally determined data to characterize properties of cryobrines of potential interest with respect to Mars are described. Eutectic diagrams, the related numerical eutectic values of composition and temperature, the water activity of Mars-relevant brines of sulfates, chlorides, perchlorides and carbonates, including related deliquescence relative humidity, are parameters and properties, which are described here in some detail. The results characterize conditions for liquid low-temperature brines ("cryobrines") to evolve and to exist, at least temporarily, on present Mars.

Key words: Mars; Mars, surface; Mars, chemistry, Aqueous solutions

1. Introduction

The discussion of a possible presence of brines on Mars dates back more than 30 years (Brass, 1980; Clark and Van Hart, 1981), and it has recently culminated with in-situ discoveries in course of NASA´s Phoenix mission (Hecht et al., 2009, Renno et al., 2009) and related stability investigations (Chevrier et al., 2009). The solidification of brines depends on temperature and concentration. The Phoenix results have shown that, at least temporarily, liquid brines can be possible on Mars. Liquid cryobrines, i.e. brines with a eutectic temperature below 0° C, are the only type of liquid which could stably exist on present Mars. Liquid brines on Mars are relevant in view of possibly related rheological processes, which are enabled to proceed or to be triggered by brines, and also when studying conditions for biological processes. These possible but yet to (in depth) be studied consequences are the reason for the increase in the interest in brines on Mars.

Preconditions for brines to evolve are the presence of water and salts. According to the current knowledge, the evolutionary history of Mars can be characterized for the first about half of billion years (the so called "Noachian") by pH-neutral liquid water and a related formation of clays. Then (in the so called "Hesperian"), and in parallel with a rapid cooling, active volcanism has with the formation of sulfates and chlorides (and probably other salts too) supported an evolution towards acidic conditions. The last about 2.5 billion years (the so called "Amazonian") are to be characterized by the formation of a surface of anhydrous ferric oxides (Bibring et al., 2009; Catling, 2009). Liquid water has after the Noachian increasingly been disappeared from the surface of Mars. Surface imaging and geomorphology have revealed indications for increasingly sporadic but nevertheless massive (catastrophic) temporary surface water floods and flows (Carr and Head, 2009; Hauber et al., 2009). These episodes may have via drying of salt lakes (by evaporation or freeze drying) led to the formation of salt deposits. At present, water is on Mars mainly in form of ice in the polar caps with an amount of the order of 2 10^{18} kg, what is comparable to that of present terrestrial Greenland ice, and in form of globally circulating atmospheric water vapour, which is fed by the polar ices. Liquid water may temporarily exist in the sub-surface of present Mars in comparatively small portions of interfacial water (by premelting (Dash et al., 2006) and by adsorption of atmospheric vapour at grain-ice interfaces) or of sub-surface melt water (by greenhouse melting, cf. Möhlmann, 2010 a, b). Thus, conditions for brines to form also on present Mars are given, either directly via salts and liquid water, which can (at least temporarily) exist in the in the sub-surface, or via deliquescence by capturing atmospheric water at (and also in) the porous, shallow, and salty sub-surface. Therefore, deliquescence is to be seen as a key mechanism to, at least temporarily, evolve on the surface of present Mars.

Table I

Investigations by remote spectroscopy from Mars-orbiting satellites, by in-situ measurements and by analyzing SNC meteorites have already shown that there are salts on Mars, like sulfates, chlorides and perchlorates (cf. next section).

As described by Table I, the physico-chemical properties of brines depend on salt concentration(s) and temperature, and they are to be described in terms of the number of solvents (participating soluble salts) in binary, ternary etc. mixtures, and their eutectic point (in temperature and composition). The stability of brines on Mars depends strongly on their water activity, i.e. their capability to evaporate and to dry out. Furthermore, and as mentioned above, deliquescence, i.e. the liquefaction of salts by sorption of atmospheric water vapour, is a brine-forming process, which can be of relevance for the present Mars. Parameters to characterize thermodynamic stability and deliquescence are described in the following for brines, which probably are of relevance for Mars. The basis to model these properties is the "Extended (universal quasi-chemical) UNIQUAC-model" (Thomsen, 2005). The results of that modelling are, where possible, compared with experimentally determined values.

The low eutectic temperatures of Lithium brines may well be of interest also for Mars. Lithium has indirectly shown to exist on Mars via measurements of the presence of Lithium isotopes in the SNC-meteorites Shergotty, Nakhla, and Zagami (Magna, 2006).

Instead of liquid water, what in macroscopic amounts cannot be stable at the present surface of Mars, liquid brines can be expected to (at least temporarily) evolve there via deliquescence, also at present. This might also be of biological relevance since life processes need a liquid agent to transport nutrients and waste and to export entropy, and this not necessarily by pure water (what can not be easily found in real nature). Liquid cryobrines can support that transports too. The content of liquid (deliquescence generated) cryobrines on Mars depends on location, season and daytime. The duration of the liquid state due to deliquescence can (over appropriate months) be of hours per day (then the liquid dries out again, day for day), the temperatures have temporarily to be above the eutectic point of the solution to permit the formation of the temporary liquid state. Local maximum appearance of such temporary liquids (also inside protecting porous media) is where the atmospheric water content is highest. To have deliquescence, the time-dependent atmospheric humidity rh(t) has to be larger than the water activity a_W of the solution (exactly rh[%] > 100 a_W). Then, the amount of the liquid stuff depends on that amount of water vapour what can be taken from the atmosphere (typically in the range of a few (10 - 100) micrometers; note that about 10 precipitable micrometers of the atmospheric column are a characteristic measure). Larger amounts could evolve over longer periods with $T > T_e$ and rh[%] > 100 a_W, only.

2. Salts on Mars

Salts are an important component of the soil in the surface of present Mars, which contains minerals of sulfates, chlorides, perchlorates, and carbonates, and mixtures of them, and other solid grains.

2.1 Sulfates

Sulfates have already soon after the Viking missions been proposed to occur on Mars (Settle, 1979; Burns, 1987; Burns and Fisher, 1990; Clark and Baird, 1979; Clark and Van Hart, 1981). Related estimates of the bulk chemistry have indicated the presence of 17.9 % FeO (as Fe^{2+} and/or Fe^{3+}) and 14.2% S (Dreibus and Wänke, 1987), and sulfate contents of (6 – 8) % have been found in the fine-grained surface material at the Viking and pathfinder sites (Clark et al., 1982; Foley et al., 2003).

Sulfates have also been found in martian dust on a global scale (Bandfield, 2002) and in cemented soil (Cooper and Mustard, 2001).

Sulfates of about 30 wt% are reported to have been detected by the MERs within saline sediments on Mars (Brückner, 2004; Rieder et al., 2004; Moore, 2004; Clark, 2004). Geochemical modelling (Rieder et al., 2004, Clark, 2004) and spectroscopic investigations (Lane et al., 2004) indicate that other sulfate minerals are expected to be present. Vaniman et al. (2004) have studied properties and presence of salt hydrates like $MgSO_4$ n H_2O. Measurements by the MarsExpress OMEGA-spectrometer (Bibring et al. 2007; Gendrin et al., 2004; Michalski et al., 2010) have shown the existence of the sulfate minerals gypsum and Kieserite, and the presence also of other sulfates at numerous different sites, and Mini-TES data indicate the presence of hydrous and anhydrous sulfates (Christensen, 2004).

The following sulfate-related minerals are in discussion in view of their presence on Mars (cf. Bishop et al., 2004; Bishop et al., 2007): Gypsum ($CaSO_4$ 2 H_2O), Kieserit ($MgSO_4$ H_2O), Starkeyite ($MgSO_4$ 4 H_2O), Szomolnokit ($Fe^{2+}SO4$ H_2O), Kornelite ($Fe_2^{3+}(SO_4)_3$ 7 H_2O), Rozenite ($FeSO_4$ 4 H_2O), Cocumbite ($Fe_2(SO_4)_4$ 9 H_2O), Jarosite ($K_2Fe_6(SO_4)_4$ $(OH)_{12}$), Ferricopiapite ($(Fe,Al,K)Fe_5(SO_4)_6(OH)_2$ 20 H_2O), and Schwertmannite ($Fe_{16}O_{16}$ $(OH)_{12}(SO_4)_2$ n H_2O), and this list is not complete.

The presence of sulfate-deposits at different sites on Mars has in great detail been verified by MRO-CRISM-observations (Bishop et al., 2007; Bishop et al., 2009; Wendt et al., 2010).

Direct terrestrial laboratory analyses of martian (SNC) meteorites have shown the presence of sulfates (Treiman et al., 1993; Gooding et al., 1991) in these meteorites, and thus on Mars too.

2.2 Chlorides and perchlorates

Osterloo et al. (2008) have reported indications for chloride bearing materials on the basis of THEMIS data (Mars Odyssey Thermal Emission Imaging System, cf. Christensen et al., 2004) and using supporting imaging data by MGS and MRO.

The found deposits are reported to be comparatively small (< 25 km^2) but globally widespread in middle and late Noachian and early Hesperian terrains (Osterloo et al., 2008). The following chlorides are in discussion in view of their presence on Mars: Halite (NaCl), Sylvite (KCl), Sinjarite ($CaCl_2$) 2 H_2O), and Bischofite ($MgCl_2$ 6 H_2O).

Chlorides have also been identified in direct terrestrial analyses of martian meteorites (Treiman and Gooding, 1992).

The detection of the perchlorate ion ClO_4^- was a surprising first indication of the existence of perchlorates on present Mars (Hecht et al., 2009; Kounaves, 2009). Mg^{2+} and Na^+ were observed to be the dominating cations, and also K^+, Ca^{2+}, NH_4^+. The Wet Chemistry Laboratory of the Phoenix Lander (Hecht et al., 2009) has also indicated the existence of halide ions Cl^-, Br^-, and I^- at the Phoenix landing site, which has a pH value (H^+ ion) 7.7 ± 0.5. These observations indicate that the soil at that site is in the form of $Mg(ClO_4)_2$ and/or $Ca(ClO_4)_2$. These alkaline perchlorate salts have a strong freezing point depression (cf. Chevrier et al., 2009), and they are deliquescent.

2.3 Carbonates

The first successful identification of a strong infrared spectral signature from surficial carbonate minerals was made by MRO-CRISM (Ehlmann, 2008) and Morris et al. (2010) have identified magnesium-iron carbonates in the outcrop, which has been investigated by Spirit. The spectral modeling has identified a key deposit dominated by a single mineral phase that is spatially associated with olivine outcrops. The dominant mineral appears to be magnesite, while morphology inferred with HiRISE and thermal properties suggest that the deposit is lithic.

It is to be noted that Shergotty-Nakhla-Chassigny type meteorites from Mars contain evidence for Fe-Mg-Ca-carbonates (in ALH84001 “rosettes”), albeit at volume fractions less than 1% (Bridges et al., 2001).

The possible absence of more extensive carbonate deposits on Mars may be due to a possible low pH aqueous environment on early Mars.

2.4 Ternary and higher mixtures

Ternary (and higher) mixtures will exhibit a further reduction of the eutectic temperature, but only very little is gained by mixing the salts. In most cases it gives only a lowering of the eutectic temperature by one or two degrees. Therefore, this aspect of multiple mixtures will not be discussed in this paper.

3. The Extended UNIQUAC model

The Extended UNIQUAC model (Thomsen, 2005) is an activity coefficient model for electrolytes. It is constructed by combining a term for the long range, electrostatic interactions with a term for short-range interactions. The term for long-range interactions is the so-called extended Debye-Hückel term (Debye and

Hückel, 1923). The term for short-range interactions is the UNIQUAC local composition model (Abrams and Prausnitz, 1975). This thermodynamic model requires very few model parameters and has a built-in temperature dependency. The parameters in the model are fitted to experimental data.

4. Eutectic diagrams

The eutectic point is the point, where the liquid (solution) and the solid phase (salt) of the brine are in equilibrium. Thus, to have liquid brines at a site on Mars, the soil temperatures have at that site to be above the eutectic temperature of the possibly liquid brine of the appropriate salt. The following Figures give examples of eutectic diagrams of chlorides, carbonates, perchlorates, sulfates and hydroxides. Fig. 1 illustrates that behaviour for NaCl $2H_2O$ (hydrohalite). Experimental data are shown as circles. The experimental data come from a long range of sources from the open literature. These and similar data can be found in the CERE electrolyte data bank at DTU chemical Engineering (CERE Data bank for electrolytes, 2010).

Fig. 1

Fig. 2

Fig.3

Fig.4

The phase diagram in Fig. 4 is a theoretical phase diagram calculated with the Extended UNIQUAC model. The parameters in the model are based on a large number of data on the water activity and the solubility of ferric sulphate in sulphuric acid solutions. The data include the comprehensive works of Rumyantsev et al. (2004) and Velázquez-Rivera et al. 2006. In the binary $Fe_2(SO_4)_3$ – H_2O system, ferric sulphate precipitates as solid solutions which are various mixtures of Fe_2O_3, SO_3, and H_2O. The phase diagram in Fig. 4 is theoretical in the sense that it shows how the phase diagram would look like if no solid solutions were formed. Experimental data for the binary system without sulphuric acid are scarce because of the complex phase behavior. A single experimental point from Wirth and Bakke (1914) is marked in Fig. 4. The real phase diagram of this binary system is probably very similar to Fig. 4, but the identities of the solid phases are not well defined.
Note that Chevrier and Altheide (2008) have derived a lower eutectic temperature of about 205 K with an eutectic composition of about 48% $Fe_2(SO_4)_3$. This issue requires further investigation. The result is important in view of the identification of brine-candidates to understand the composition of putative temporarily liquid droplets, as imaged by Phoenix (Renno et al., 2009).

Fig. 5

5. Relative humidity and water activity

The deliquescence relative humidity (DRH) of a salt is a measure (by %) of the water activity of saturated solutions of the salt. It is the specific relative humidity, characteristic for each of the salts, when they get liquid by sorption of atmospheric water vapour. DRH and water activity are related via DRH[%] = 100 a_w = 100 p_w/p_w^{sat}. In this equation, a_w is the water activity, p_w is the partial pressure of water and p_w^{sat} is the vapour pressure of pure water at the relevant temperature. By knowing the DRH of a salt, it is therefore possible to calculate the minimum amount of moisture in the atmosphere required for the salt to evolve as brine.

Table II

It is interesting to note that among other salts (cf. Table II), $CaCl_2$ is among the salts, which on Mars could form brines by deliquescence at rather low temperatures. There is on Earth a lake with a high $CaCl_2$-content, the (currently shrinking) Don Juan Pond at Antarctica. It is a small and very shallow hypersaline lake in the west end of Wright Valley (South Fork), Victoria Land, Antarctic. The Don Juan Pond is the saltiest body of water on Earth with a salinity level of over 40%. It is the only one of the Antarctic hypersaline lakes that almost never freezes. The calculated composition for its water is $CaCl_2$ (3.72 mol/kg) and NaCl (0.50 mol/kg), at the temperature of -51.8°C (Marion, 1997). That would be equivalent to 413 g of $CaCl_2$ and 29 g of NaCl per kg of water.
Another interesting aspect is that phosphoric acid H_3PO_4 can remain liquid down to about -70° C, and therefore be one of the liquid agents in the surface of Mars (cf. Table II). Greenwood and Blake (2006) recently have discussed presence and distribution of phosphorous on Mars, and that the phosphorus concentration is there correlated with sulfur and chlorine. The positive correlation of these three elements with each other in soils at both sites of the Mars Exploration Rover (MER) is seen as pointing towards a globally homogeneous soil component. By the way, Greenwood and Blake (2006) show that the similar concentration of phosphorus in soils at the two MER sites, coupled with positive correlations to chlorine and sulfur, can be explained as resulting from mixing and homogenization of phosphate, sulfate, and chloride in a large acidic aqueous reservoir, such as an early acidic ocean, since acidic thin-film or acid-fog weathering cannot explain the high phosphorus content of ancient (ca. 3–4 Ga) sulfate-rich rocks in outcrop at Meridiani.

6. Stability and deliquescence of brines on Mars

Brines will loose water by evaporation and sublimation. Taylor et al. (2006) have determined the effective sublimation rate of water ice on Mars by taking into account the constraints for the propagation of the water vapour through the near-surface atmosphere of heavier CO_2-molecules. The numerical values, derived by them, describe sublimation on Mars between temperatures of 0° C and -50° C. These results will analytically be approached here by

$$Z_{sub} = \frac{9.217\ 10^{14}}{\sqrt{2\pi m_{H_2O} k\ T(t)}} e^{-\frac{9754.92}{T(t)}} \quad , \qquad (1)$$

where $Z_{sub}[m^{-2}\ s^{-1}]$ is the "sublimation rate", m_{H2O} is the mass of a water molecule, T(t) is the temperature in K, and k is Boltzmann´s constant (cf. Möhlmann, 2010). The corresponding loss rate Z_{br} of water in brines is then given by $Z_{br}(T) = a_W(T)\ Z_{sub}(T)$, where $a_W(T)$ is the water activity of the brine. Related loss or gain in height h of a brine are given with the water mass density $_W$

$$dh/dt = Z_{br}\ (m_{H_2O}/\rho_W) \qquad (2)$$

The order of magnitude of Z_{br} is with $a_W = 1$ for T = 220 K given by $2\ 10^{18}$ molecules per square meter and second (or $4\ 10^{20}\ m^{-2}\ s^{-1}$ for 250 K). This is equivalent to a height loss (over one sol) of about 6 micrometer (or 10^{-3} m for 250 K). Average temperatures in the range between about 220 K and 250 K are typical for the winter at low- and mid-latitudes. This indicates that brines at and near the surface, which may have evolved on early Mars, must, after millions of years of evaporation and sublimation, have been dried out in favour of later (and present) salt deposits. Thus, liquid brines, like liquid bulk water, can under present conditions not permanently be stable on the surface of Mars. There they may appear temporarily only. Of course, better stability could be given in closed volumes like sub-surface cavities.
On the other side, deliquescence due to sorption of atmospheric water vapour could cause an at least temporary liquefaction of originally dry salts under the presently given thermo-physical conditions on Mars. The minimum relative atmospheric humidity for deliquescence to evolve is the "DRH" (deliquescence relative humidity). The atmosphere of Mars contains water vapour with an average mixing ratio of about $3\ 10^{-4}$. Figs 6 and 7 exemplarily describe surface temperature and related relative humidity for an arbitrarily chosen northern mid-latitude location (30° N, 0° E) at northern summer and winter. Obviously, and under "normal" conditions at this latitude, high relative humidity is reached only at late night and early morning hours at temperatures, which are below the eutectic temperatures of possibly relevant salts (cf. Table II).
High relative humidity and saturation (with following frost formation) will only occasionally and locally be reached in cold seasons at low- and mid-latitudes in late night and morning hours (cf. Schörghofer and Everett, 2007). Better humidity conditions for deliquescence to evolve (incl. oversaturation) can be given at high

latitudes and near to the sublimating permanent ice cap, while normally the rh-values at mid- and low latitudes do not reach the saturation level. But to have deliquescence of appropriate salts, i.e. liquefaction of these salts, the environmental temperature must be above the eutectic temperature T_e of that salt. It seems to be difficult to simultaneously met on Mars these two conditions of a humidity rh > DRH and temperature $T > T_e$. Thus, to find locations and appropriate time (season) where the conditions in favour of deliquescence (of some appropriate salts) are simultaneously given sufficiently long, is a current challenge. Probably, high latitudes are more appropriate sites for deliquescence to evolve, at least temporarily, as shown by imaging of brine droplets (cf. Renno et al., 2009). But, as has been shown by Schörghofer and Edgett (2006), e.g., water ice based frost can temporarily evolve on Mars also at mid and low latitudes. Then also conditions for a locally restricted temporary formation of brines via deliquescence may be given there if appropriate salts are present.

Fig. 6

Furthermore, improved conditions for saturation of the atmospheric water content and related condensation and freezing on the mid-latitude surface have been shown to also happen, at least sporadically, by imaging of temporary frost on the surface (cf. Fig. 8). There are numerous other images of these frost phenomena on the surface of Mars, including equatorial sites (cf. Landis et al., 2007).

Fig. 7

The atmospheric humidity can more or less stably reach the saturation level over the polar caps during the cool seasons. These sites are therefore appropriate for the appearance of brines, preferably in spring, when the temperatures start to reach the eutectic temperatures of salts, which are present there. Sunward pointing slopes are the most appropriate sites where locally the surface temperatures can sufficiently increase. During summer, the atmospheric humidity may decrease there and be less than the DRH. Liquid brines will dry out then. In spring, the temporarily evolving liquid brines may cause rheological phenomena (cf. Möhlmann and Kereszturi, 2010) also on present Mars.

The diurnal accumulation ("growth", integrated over one sol) of a cryobrine by sorption of atmospheric water vapour, as described by Eq. (2), can be estimated to be for the location at 0°E, 60° N at L_S = 0° - 30° in the range around 2 m (per sol) at temperatures between 150 K and 154 K at that site and season, and by using the data of the Mars Climate Database (Lewis et al., 1999) for temperature and atmospheric water content. Thus, longer accumulation periods of the order of months are required in this case to get macroscopic dimensions.

Fig. 8

7. Conclusions

The presence of salts on and in the surface of Mars and of water vapour (up to saturation) in the near-surface martian atmosphere indicate the possible existence of at least temporarily present liquid brines at temperatures far below 0° C.

Evaporation (in warm early time) and (later) sublimation must have dried out salt lakes on the surface of Mars, which might have existed in the Noachian and early Hesperian. Salt lakes without sub-surface supply of water might be possible on present Mars in closed sub-surface cavities only.

Deliquescence is the only origin of liquid cryobrines, which can exist, at least temporarily, on the surface of present Mars. Renno et al. (2009) have discussed that droplets, which have been observed on a strut of the Phoenix-Lander, are the first direct observations of temporarily liquid brines on Mars.

Key conditions for liquid low-temperature brines to exist on and in the upper surface of Mars are surface temperatures above the eutectic temperature ($T > T_e$) and simultaneously an atmospheric humidity rh > DRH (deliquescence relative humidity) at these temperatures.

Possible candidate-chemicals are described in detail, which can fulfil the necessary conditions to form liquid cryobrines on Mars. Properties of these salts and brines can be calculated by using the Extended UNIQUAC model (Thomsen, 2005).

Sunward pointing slopes seem to be appropriate locations to first reach the required temperatures above the eutectic temperature also at high latitudes. There, these liquid brines may cause rheologic processes there, also at present (cf. Möhlmann and Kereszturi, 2010).

The possibly only sporadically given necessary amount of atmospheric humidity at sufficiently high temperature limits the appearance of liquid cryobrines at mid- and low latitudes, but the at least episodic presence of water-ice-frost at these latitudes (cf. Schörghofer and Edgett, 2006) indicates that these deliquescence formed brines may, at least temporarily, be present also there.

It is a challenging task for future missions to Mars to identify regions and local sites on Mars where liquid cryobrines can evolve, at least temporarily.

Acknowledgments

The authors wish to thank Wolfgang Voigt, TU Freiberg/Germany, for helpful comments to improve the manuscript. This research (by D.M.) has been supported by the Helmholtz Association through the research alliance "Planetary Evolution and Life".

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Tables

Brine	Eutectic temperature T_e[K]	Eutectic composition [%]
[a]Ice + Na_2SO_4 10 H_2O	271	3.8 Na_2SO_4
[a]Ice + K_2SO H_2O	271	7.1 K_2SO_4
[a]Ice + $MgSO_4$ 11 H_2O	269	17 $MgSO_4$
[a]Ice + K_2SO_4 H_2O + KCl	261	0.9 K_2SO_4, 19.5 KCl
[a]Ice + NaCl 2H_2O	251	23.3 NaCl
[a]Ice + Na_2SO_4 10 H_2O + NaCl 2H_2O	251	0.12 Na_2SO_4, 22.8 NaCl
[a]Ice + NaCl 2 H_2O + KCl	250	20.2 NaCl, 5.8 KCl
[e]Ice + $Fe_2(SO_4)_3$	247***	39 $Fe_2(SO_4)_3$
[a]Ice + $MgCl_2$ 12 H_2O	239.5	21.0 $MgCl_2$
[d]Ice + $MgCl_2$ 12 H_2O + KCl	239	21.0 $MgCl_2$, 1.2 KCl
[a]Ice + $MgCl_2$ 12 H_2O + NaCl 2 H_2O	238	22.7 $MgCl_2$, 1.6 NaCl
[a]Ice + $MgCl_2$ 12 H_2O + KCl	238	22.? $MgCl_2$, 2.? KCl
[a]Ice + $MgCl_2$ 12 H_2O + $MgSO_4$ 7 H_2O	238	20.8 $MgCl_2$, 1.6 $MgSO_4$
[c]Ice + $NaClO_4$ 2H_2O	236 (±1)	52 $NaClO_4$
[a]Ice + $CaCl_2$ 6H_2O	223	30.2 $CaCl_2$
[a]Ice + $CaCl_2$ 6H_2O + KCl	221	29.3 $CaCl_2$, 1 KCl
[a]Ice + $CaCl_2$ 6H_2O + NaCl 2 H_2O	221	29.0 $CaCl_2$, 1.5 NaCl
[a]Ice + $CaCl_2$ 6H_2O + $MgCl_2$ 12 H_2O	218	26.0 $CaCl_2$, 5 $MgCl_2$
[c]Ice + $Mg(ClO_4)_2$	212 (±1) **	44 $MgClO_4$
[f]Ice + LiCl	207	24.4 LiCl
[b]Ice + $Fe_2(SO_4)_3$*	205 (±1)	48 (±2) $Fe_2(SO_4)_3$
[g]Ice +LiI	204	48.2 LiI
[h]Ice + LiBr	201	39.1 LiBr

Table I. Possibly Mars-relevant binary and ternary non-organic cryobrines ([a] Brass(1980),[b] Chevrier and Altheide (2008), [c] Chevrier et al., 2009), [d] Usdowski and Dietzel (1998),[e] This work, [f] Voskresenskaya and Yanat'eva, 1936, [g] Linke and Seidell, 1965). * taken from Chevrier and Altheide, (2008), ** based on the UNIQUAC-model, Chevrier et al. (2009) use 206 K for the eutectic temperature. *** cf. *.

Salt	Eutectic temperature [K]	Water activity	Wt % salt
H_3PO_4	203	0.41	60
LiCl	206	0.48	24
KOH	210	0.50	32
$Mg(ClO_4)_2$	212	0.53	44
$AlCl_3$	214	0.53	25
$ZnCl_2$	221	0.58	52
$CaCl_2$	226	0.60	30
$NiCl_2$	230	0.64	30

Table II. Properties of eutectic points of salts exhibiting the lowest water activity at temperatures at and below 230K. The properties were calculated with the Extended UNIQUAC model. Note that the water activity of LiBr and LiI at the eutectic point will not be very different from that of LiCl.

Figure captions

Fig. 1 Phase diagram of the chloride-brine: NaCl-H_2O. The eutectic point is at T_e = 251 K at a concentration c_e = 23.3 % (b.w.) . The brine is solid at $T < T_e$, it is liquid left and above the given equilibrium curve, while it is a liquid mixture of ice in a liquid solution at $T > T_e$ and $c < c_e$. An also liquid mixture of solid salt crystals in a liquid solution will be found for $T > T_e$ and $c > c_e$.

Fig. 2 Phase diagram of the carbonate brine system: K_2CO_3 – H_2O. The phase diagram consists of three branches, one for ice, one for $K_2CO_3{\cdot}6H_2O$, and one for $K_2CO_3{\cdot}1½H_2O$. The calculated eutectic temperature is 239 K.

Fig. 3 Phase diagram of the perchlorate brine $Mg(ClO_4)_2$. The eutectic point is at T_e = 206 K at a concentration c_e = 44 % (b.w.). The brine is solid at $T < T_e$, it is liquid left and above the given equilibrium curve, while it is a liquid mixture of ice in a liquid solution at $T > T_e$ and $c < c_e$. An also liquid mixture of solid salt crystals in a liquid solution will be found for $T > T_e$ and $c > c_e$. The equilibrium curve has only two branches in the temperature range considered, one for Ice and one for $Mg(ClO_4)_2{\cdot}6H_2O$.

Fig. 4 Theoretical phasediagram of a sulfate brine. Ferric sulfate forms a heptahydrate and a hexa hydrate in this temperature range. Ferric sulphate forms various solid solutions in aqueous solutions. The solids formed in a real solution will therefore not be pure. The single experimental point marked in this diagram is from Wirth and Bakke (1914).

Fig. 5 Phase diagram for the NaOH – H_2O system. The diagram consists of four branches and the solubility of both $NaOH{\cdot}3½H_2O$ and $NaOH{\cdot}H_2O$ show retrograde behaviour.

Fig. 6 Diurnal temperature profile (over 1 sol) at 30° N and 0° E for northern winter (L_S = 270° – 300°) – lower curve – and northern summer (L_S = 90° – 120°) – upper curve. Data are taken from the Mars Climate Database (Lewis et al., 1999; http://www-mars.lmd.jussieu.fr/mars/html).

Fig. 7 Diurnal profile (over 1 sol) of the atmospheric relative humidity at the martian surface at 30° N and 0° E at northern winter (L_S = 270° – 300°) – upper curve – and northern summer (L_S = 90° – 120°) – lower curve. Data are taken from the Mars Climate Database (Lewis et al., 1999; http://www-mars.lmd.jussieu.fr/mars.html .

Fig. 8 Frost deposits (observed occasionally only) at the Viking-2 Lander site (48° N, 226° W, Photo: NASA, PIA00571).

Figures

Fig. 1 – 5 will be sent separately.

Fig.6

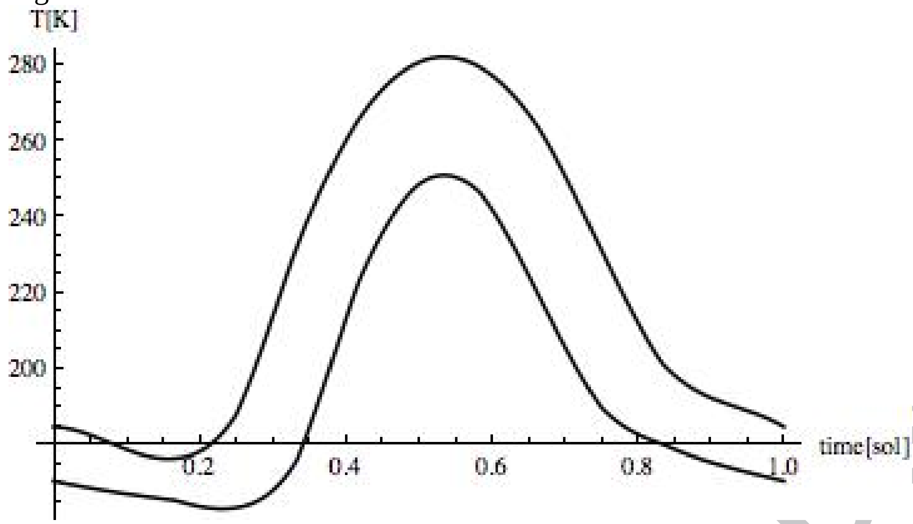


Fig. 7

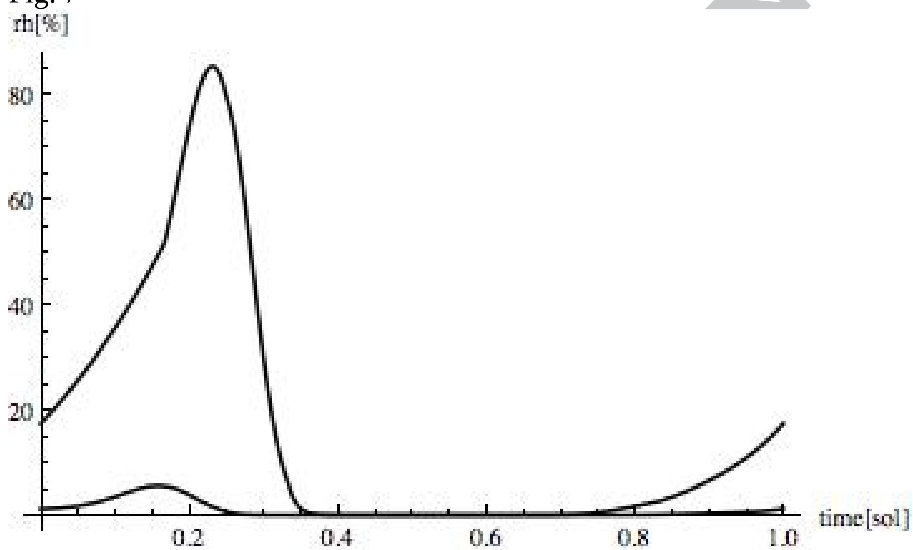
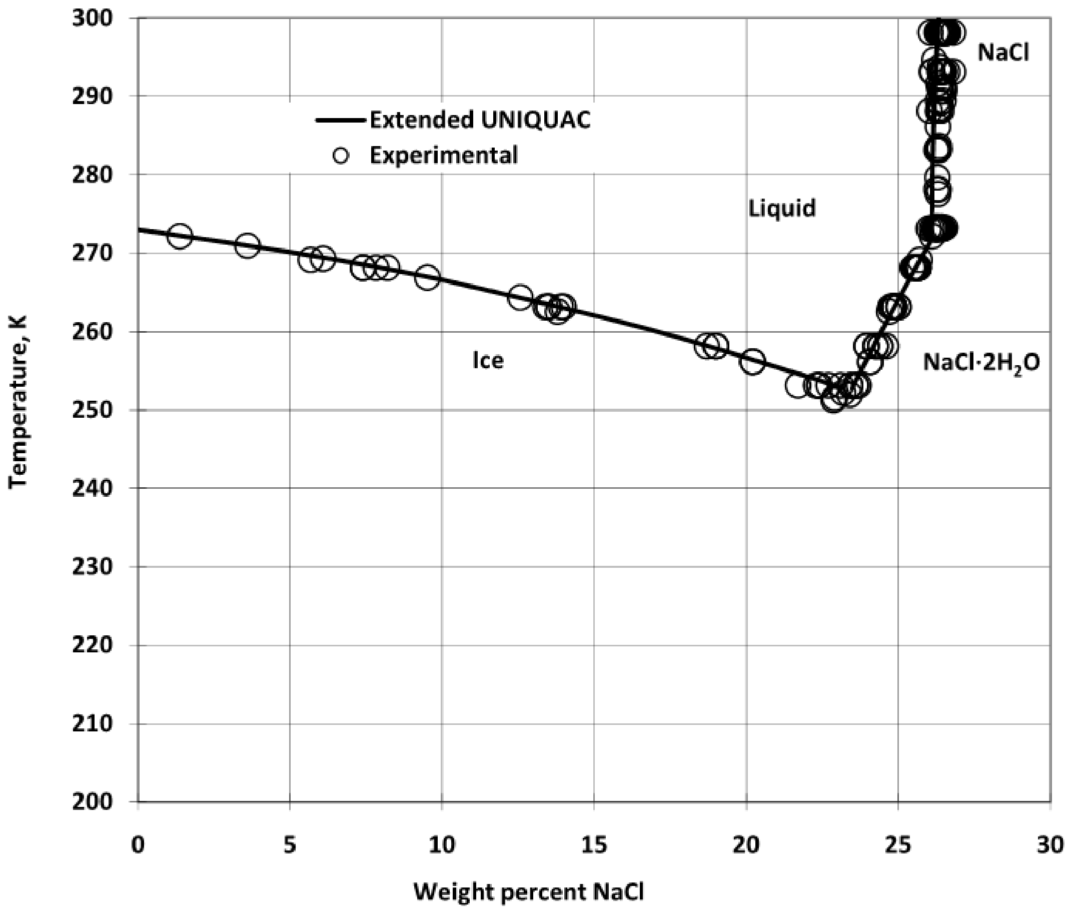
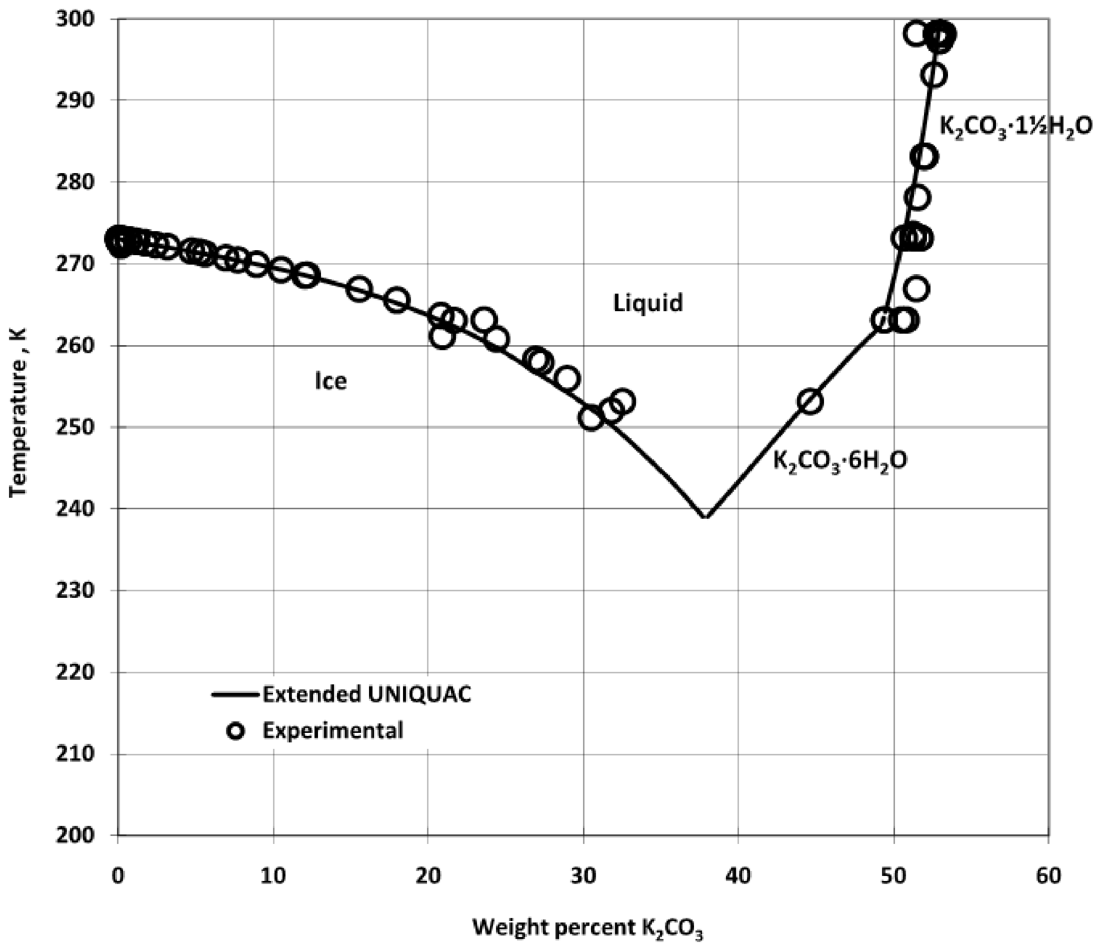


Fig.8



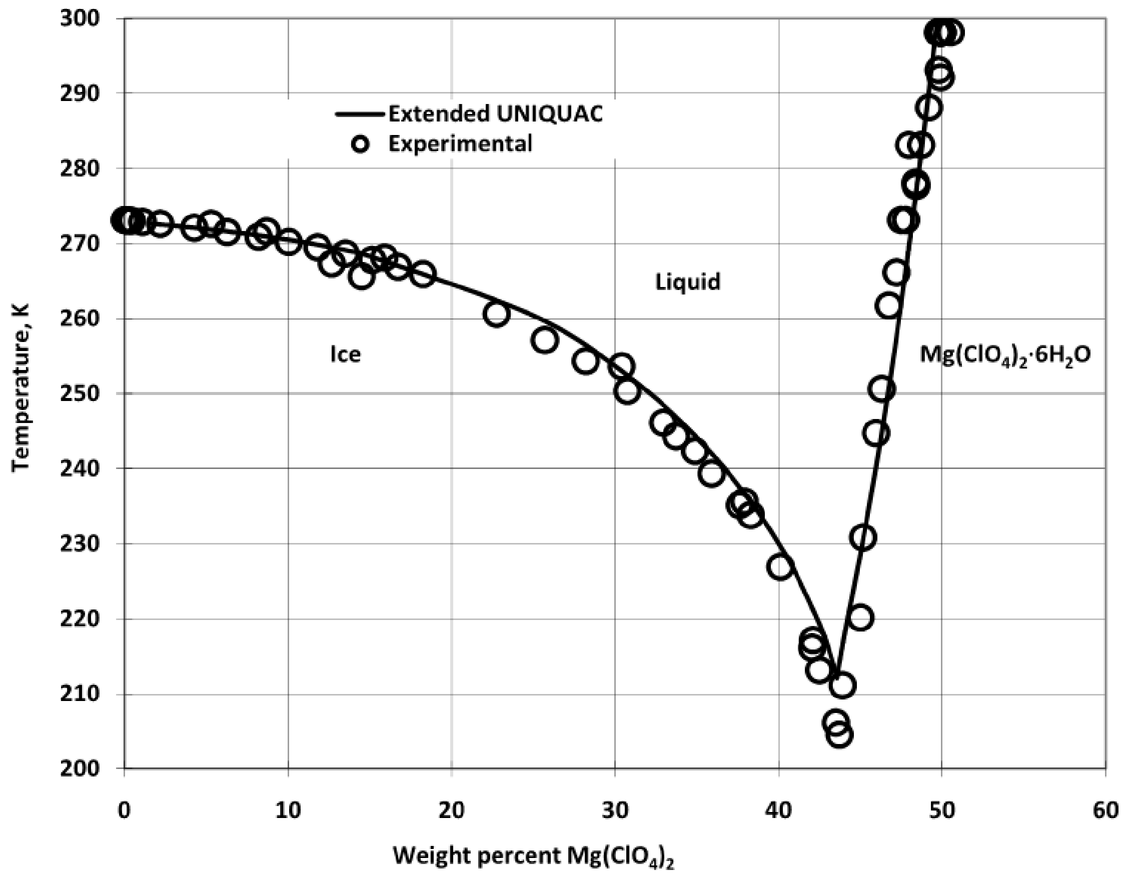
300
290
280
270
260
250
240
230
220
210
200
Temperature, K
Extended UNIQUAC
Experimental
Liquid
NaCl
Ice
NaCl·2H2O
0
5
10
15
20
25
30
Weight percent NaCl

757



300
290
280
270
260
250
240
230
220
210
200
Temperature , K
0
10
20
30
40
50
60
Weight percent K2CO3
Liquid
Ice
K2CO3·1½H2O
K2CO3·6H2O
Extended UNIQUAC
Experimental

758



300
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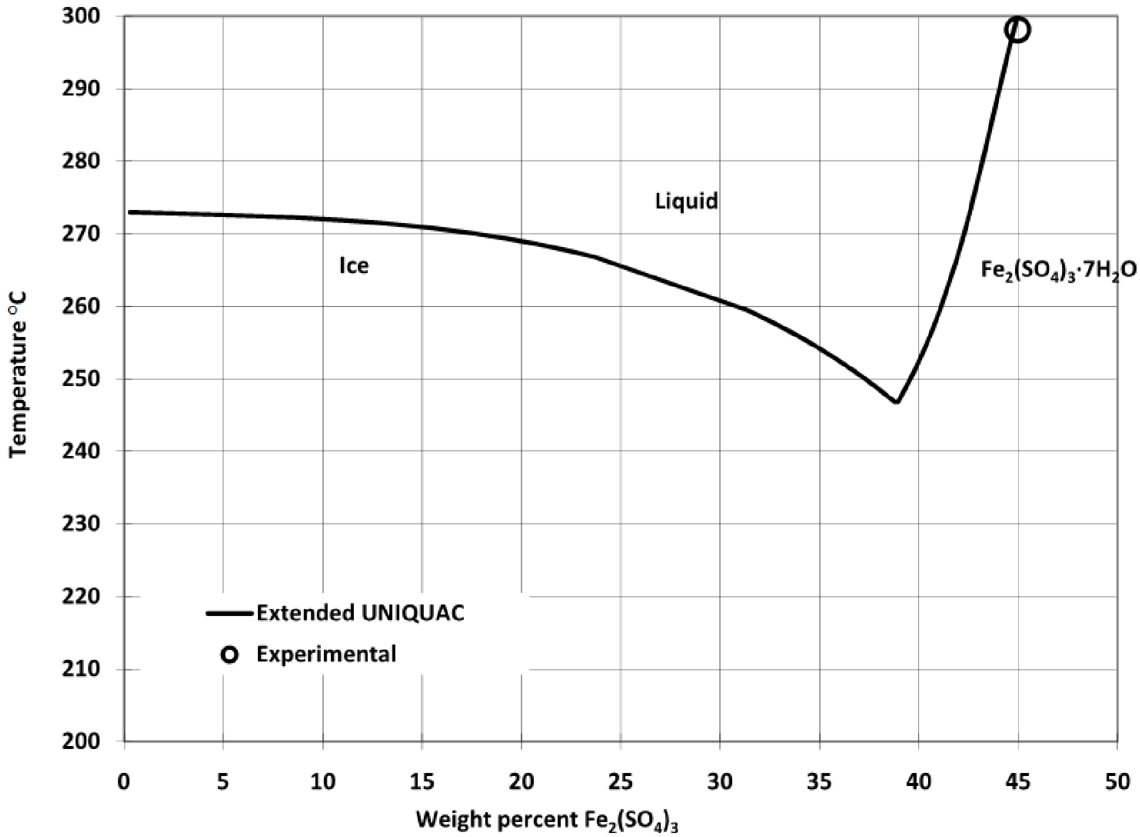
240
230
220
210
200
Temperature, K
Extended UNIQUAC
Experimental
Liquid
Ice
Mg(ClO4)2·6H2O
0
10
20
30
40
50
60
Weight percent Mg(ClO4)2

759



300
290
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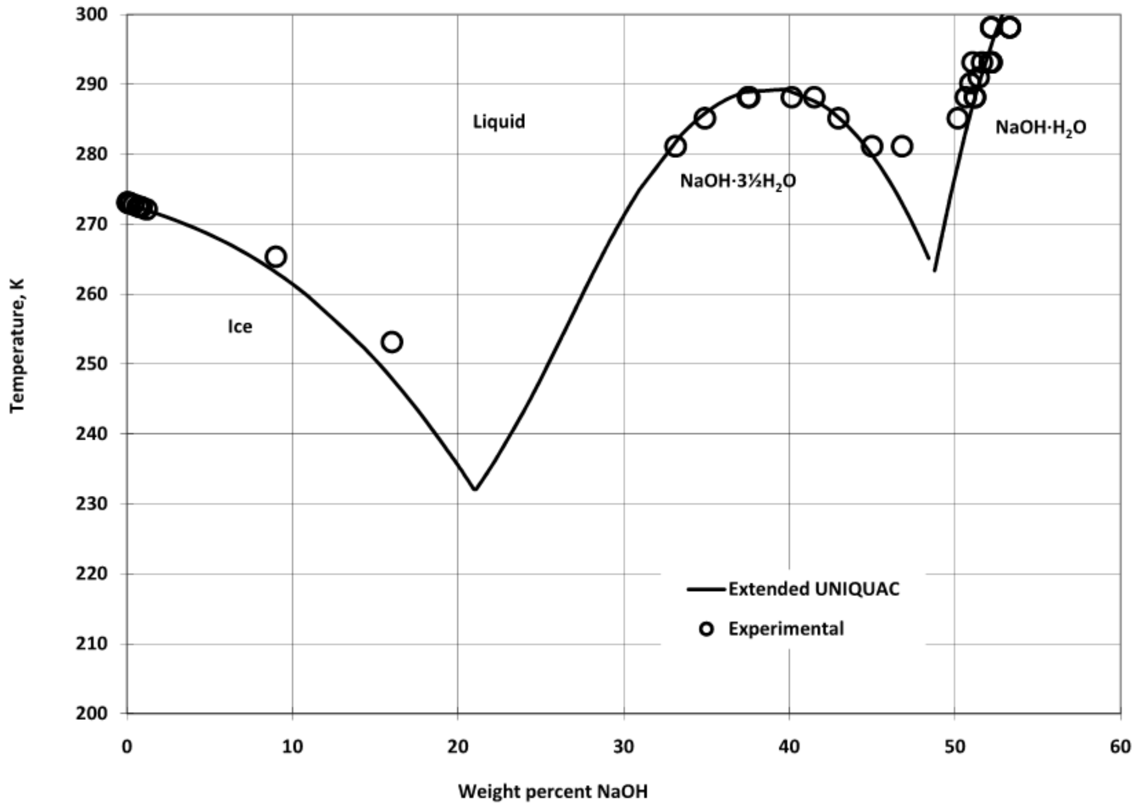
270
260
250
240
230
220
210
200
Temperature °C
Liquid
Ice
Fe2(SO4)3·7H2O
Extended UNIQUAC
Experimental
0
5
10
15
20
25
30
35
40
45
50
Weight percent Fe2(SO4)3

760



300
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280
270
260
250
240
230
220
210
200
0
10
20
30
40
50
60
Temperature, K
Weight percent NaOH
Liquid
Ice
NaOH·3½H₂O
NaOH·H₂O
Extended UNIQUAC
Experimental

761

Cryobrine-salts exist on Mars

Physico-chemical properties of cryobrines (Eutectic temperature, phase diagrams, DRH) are presented

Cryobrines can temporarily evilve on preswent Mars

Liquid cryobrines can cause rheological processes on Mars possibly liquid brine of the appropriate salt. The following Figures give examples of eutectic diagrams of chlorides, carbonates, perchlorates, sulfates and hydroxides. Figs. 1, 2, 3 and 5 illustrate that behaviour for NaCl - $2H_2O$, the K_2CO_3 – H_2O system, magnesium-perchlorate, and the NaOH-H_2O system (hydrohalite). Experimental data are shown as circles. The experimental data come from a long range of sources from the open literature. These and similar data can be found in the CERE electrolyte data bank at DTU chemical Engineering (CERE Data bank for electrolytes, 2010).