

EUTECTIC TEMPERATURES FOR LOW AND HIGH PRESSURE PHASES OF SODIUM SULFATE HYDRATES WITH APPLICATIONS TO EUROPA. A. J. Dougherty¹, J. A. Avidon¹, D. L. Hogenboom¹, and J. S. Kargel², ¹Dept. of Physics, Lafayette College, Easton, PA 18042, e-mail: doughera@lafayette.edu, avidonj@lafayette.edu, hogenbod@lafayette.edu, ²Department of Hydrology and Water Resources, The University of Arizona, Harshbarger Building, PO Box 210011, Tucson, AZ 85721-0011, e-mail: kargel@hwr.arizona.edu

Introduction: We measured the eutectic temperature and freezing point depression for a 15.5 wt.% sample of Na_2SO_4 in H_2O for pressures from 0.5 to 375 MPa. Below 209 MPa, only a single phase was typically observed. Above 209 MPa, however, several different phases were observed. In the Ice-III regime, we tentatively identified two distinct phases as mirabilite ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$) and heptahydrate ($\text{Na}_2\text{SO}_4 \cdot 7\text{H}_2\text{O}$), and explored their stability.

Background: Salts are found in many meteorites, are abundant on Mars [1-3], and are possibly major surface constituents on Europa [4,5]. In the Solar System's cold and humid regions, many salts are hydrated. The sulfate hydrates are especially important on hydrous worlds where the sulfur has not been thoroughly reduced and sequestered as sulfide minerals or in the planetary core. Potassium jarosite and magnesium sulfate hydrates have been found on Mars; solid solutions or stoichiometric sulfate compounds with sodium are inherently likely. The pure sodium sulfates, especially thenardite (anhydrous) and mirabilite (the decahydrate) are expected to be important extraterrestrial salts on many aqueously altered planets, satellites, and asteroids. More recently, the possible role of the heptahydrate has received attention [6,7].

This work is part of our continuing program to characterize the physical and chemical properties of salts under low temperature and high pressure [8,9].

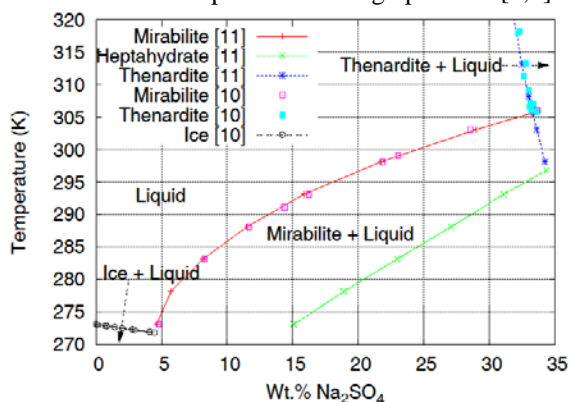


Figure 1: Phase diagram for Na_2SO_4 in H_2O at atmospheric pressure from [10,11]. The two solid phases relevant for this work are the decahydrate (mirabilite) and the heptahydrate.

Experiment: Approximately 1 mL of sample was loaded into a pressure cell. This cell is made from a

316 stainless steel block with four ports. Two opposing ports contain plugs that have sapphire windows sealed with epoxy. The third port contains a plug with a silicon diode thermometer, and the fourth connects the cell to the pressure system. A fiber optic light is used to illuminate the sample, and an inverted periscope is used to obtain images. The pressure system includes a transducer that responds to volume changes of the sample. The pressure cell is insulated, and temperature can be controlled between 210 and 300 K. We generally use very slow cooling and warming so that equilibrium can be closely approached.

In a typical experiment, the system starts as a homogeneous fluid at about 300 K, and is cooled steadily. As the system becomes supersaturated, mirabilite crystals precipitate from solution. Upon supercooling below the eutectic temperature, the system freezes and becomes an opaque solid. We then slowly warm up until eutectic melting commences. At the eutectic transition, the sample volume changes rapidly, and the crystals can be seen dissolving in the images. We verify that the transition is reversible, and record the temperature and pressure at the transition. By slowly changing the pressure and temperature, we can trace out the eutectic temperature as a function of pressure.

Results and Discussion: A typical image near the eutectic point in the Ice-III regime is shown in Fig. 2. The large underlying crystals in the image are mirabilite. The smaller round crystals overlying them

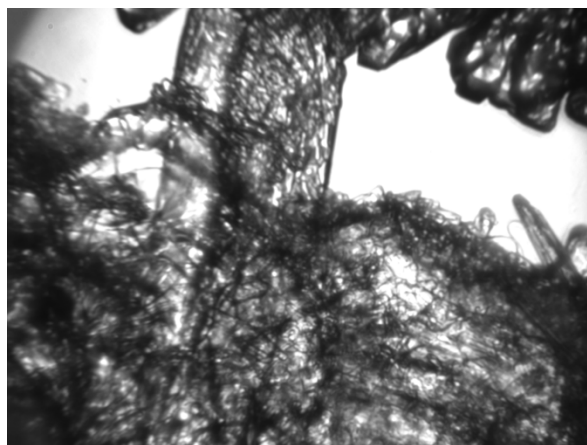


Figure 2: Coexistence of crystals near the eutectic point, $T = 249.5\text{K}$, $p = 295\text{ MPa}$ (on curve III-b in Fig. 4). The clear areas in the image are liquid. The image is approximately 2 mm across.

are rapidly melting, but a slight decrease in temperature or increase in pressure will cause them to regrow.

The results for pressures from 0.1 to 375 MPa are shown in Fig. 3. For comparison, the melting curves for pure Ice Ih and Ice III, as well as the Ice III-V boundary, are included [12].

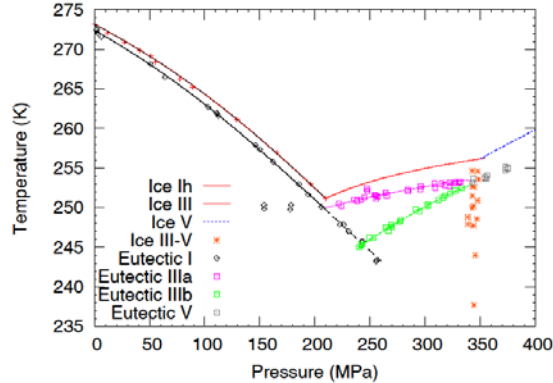


Figure 3: Eutectic temperature vs. pressure. The sodium sulfate causes a modest decrease in the freezing temperature in the Ice Ih regime. At higher pressures, the behavior is more complex.

Results below 209 MPa. At low pressures, the system usually froze to a mixture of mirabilite and Ice Ih. The eutectic temperature was slightly below the freezing point of pure ice, ranging from $\sim 0.85\text{K}$ below at low pressure to $\sim 1.5\text{K}$ at 200 MPa. In a few trials (150 and 175 MPa in Fig. 3) the system initially solidified to a denser solid with a lower melting temperature, but that state was unstable and not easily reproduced.

Results above 209 MPa. At higher pressures, we observed three distinct phases, illustrated in Fig. 4. In most trials (labeled ‘Eutectic IIIa’ in Fig. 4), the freezing point depression was relatively small, but increased gradually with pressure. The density of the sample increased upon freezing, consistent with an Ice-III based eutectic.

In some cases, labeled as ‘Eutectic IIIb’, the eutectic temperature was considerably lower (but well above the Ice II transition). As was observed for IIIa, the density of the sample increased upon freezing. We speculate that this may be the heptahydrate. The state labeled IIIb had a higher density than IIIa, but we were not able to measure absolute densities with this apparatus.

The IIIa and IIIb lines appear to converge near 350MPa, near the Ice III-V boundary. Above 350 MPa, we only observed one phase. Finally, if we started below 209 MPa with existing Ice Ih crystals and gradually increased the pressure while decreasing the temperature, we obtained the points labeled ‘Eutectic I’ in Fig. 4. The volume expanded upon freezing, and

the eutectic temperatures followed the extrapolation of the low pressure eutectic line from Fig. 3.

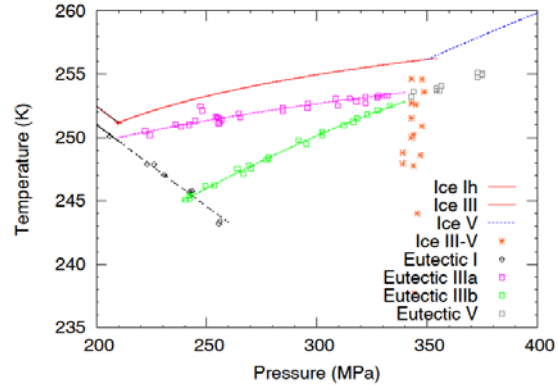


Figure 4: Eutectic temperature vs. Pressure and ice transitions [12] in the Ice III and V regimes.

Planetary implications: Several ice phases, two hydrate phases, the anhydrous salt, and a liquid phase exist in this system. Supercooling and nucleation from metastable states, as well as annealing into stable states, or geothermal heating, can cause phase and volume changes. Rapid temperature shifts, such as cryolava cooling, chilling of intruded brine dikes deep inside cold icy crusts, or diurnal temperature cycling in terrestrial or Martian soils or playa surfaces, may cause metastable phase assemblages to form, including both solid assemblages (often including metastable eutectic intergrowths) and liquids, whereas slow heating or cooling may cause stable assemblages to form at the outset or to form upon slow annealing. Attendant volume changes may drive compressional or tensional tectonics (extensional fracturing, polygonal crack formation, swelling, folding, thrusting, and so on).

References: [1] Squyres, S.W. *et al.* (2004) *Science*, 306. [2] Mangold N, Gendrin A, Gondet B, *et al.* (2008) *ICARUS* 194, 519-543. [3] Kargel, J.S., Furfaro, R., Prieto-Ballesteros, O., Rodriguez, J.A.P., Montgomery, D.R., Gillespie, A.R., Marion, G.M., Wood, S.E. (2007) *GEOLOGY*, 35,: 975-978. [4] McCord, T.B. *et al.* (1998) *Science*, 280, 1242. [5] Kargel, J.S. *et al.* (2000) *Icarus* 148, 226-265. [6] Hamilton, A. (2008) *Journal of Physics D-Applied Physics*. 41, 212002. [7] Hall, C. and Hamilton, A. (2008) *Icarus*, 198 (1): 277-279. [8] Hogenboom, D.L., Kargel, J.S., Ganasan, J.P., and Lee, L (1995) *Icarus* 115, 258-277. [9] Dougherty, A.J., Avidon, J.A., Hogenboom, D.L., and Kargel, J.S. (2011) *LPS XLII*, Abstract #1242. [10] Wuite, J.P. (1913) *Z. Physik. Chem.* 86, 349-382. [11] Eddy R.D. and Menzies A.W. (1940) *J. Phys. Chem*, 44, 207-235. [12] Bridgman, P.W. (1911) *Proc. Amer. Acad. Arts Sci.* 47, 441.