

VOLUMETRIC AND OPTICAL STUDIES OF 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 have measured the eutectic temperature and freezing point depressions for a 15.5 wt% sample of Na₂SO₄ in H₂O for pressures from 0.5-375 MPa. In the Ice-III regime, we identified two distinct phases, which we tentatively identify with mirabilite (Na₂SO₄·10H₂O) and heptahydrate (Na₂SO₄·7H₂O).

Background: Salts are found in many meteorites, are known to be abundant on the surface of 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 highly 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. In particular, sodium sulfates, especially thenardite (anhydrous) and mirabilite (the decahydrate) are expected to be among the more 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 on-going research program to characterize the physical and chemical properties of salts under conditions of low temperature and high pressure [8,9].

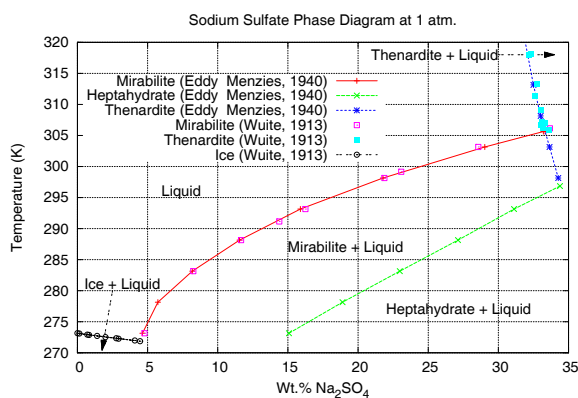


Figure 1: Phase diagram for Na₂SO₄ in H₂O at atmospheric pressure from [10,11]. The experiments are performed at a concentration of 15.5 wt.% sodium sulfate. The two solid phases relevant for this work are the decahydrate (mirabilite) and the heptahydrate.

Experiment: Approximately 1 mL of sample was loaded into a pressure cell (Fig. 2). This cell is made from a 316 stainless steel block with four ports (High Pressure Equipment Company #60-HF6). Two opposing ports contain replaceable plugs that have sapphire

windows sealed with epoxy. The third port contains a plug in which a silicon diode thermometer is installed, and the fourth connects the cell to the pressure system.

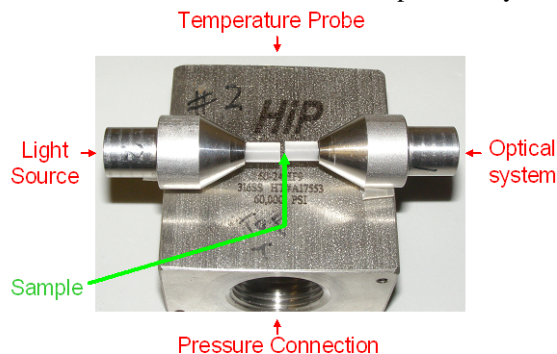


Figure 2: Pressure cell (exploded view) allows simultaneous pressure, temperature, and volume measurements.

A fiber optic light source is used to illuminate the sample, and an inverted periscope system is used to obtain images. The pressure system includes a transducer that responds to volume changes of the sample. The pressure cell is placed in an insulated container whose temperature can be controlled over the range from 210 to 300 K.

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 flash-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.

Results and Discussion: A typical image near the eutectic point is shown in Fig. 3. The image is approximately 2 mm across. The large crystals in the image are mirabilite. The smaller round crystals are rapidly melting, but a slight decrease in temperature or increase in pressure will cause them to regrow.

Results below 209 MPa. The results for pressures below 209 MPa are shown in Fig. 4. For comparison, the melting point for pure Ice Ih is also shown [12]. The addition of the salt results in a small depression of the freezing point that ranges from ~0.85 K at low pressure to ~1.5 K near 200 MPa.

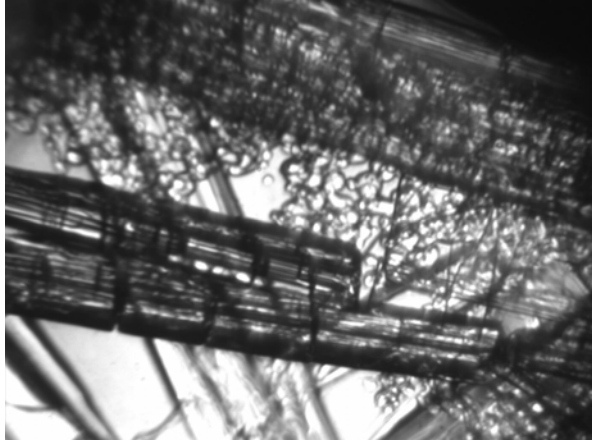


Figure 3: Coexistence of crystals near the eutectic point, $T = 253.1\text{K}$, $p = 314\text{ MPa}$ (on curve III-a in Fig. 5). The clear areas in the image are liquid.

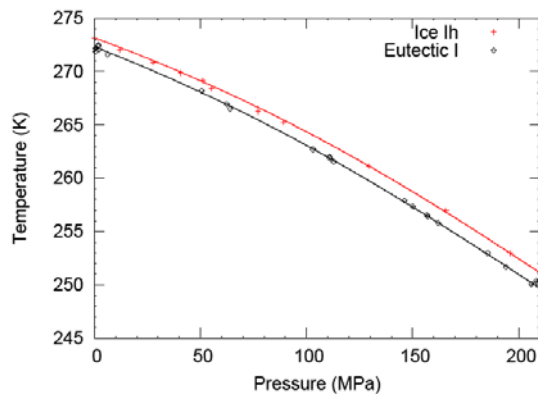


Figure 4: Eutectic temperature vs. pressure in the Ice Ih regime. The sodium sulfate causes a modest decrease in the freezing temperature.

Results above 209 MPa. At higher pressures, the results are more complex. We observed three distinct phases, illustrated in Fig. 5. In most trials, 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 (labeled ‘Eutectic IIIa’ in Fig. 5).

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 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 start below 209 MPa with existing Ice Ih crystals and gradually increase the pressure while decreasing the temperature, we obtain the points labeled ‘Eutectic I’ in Fig. 5. The volume expands upon freezing, and the eu-

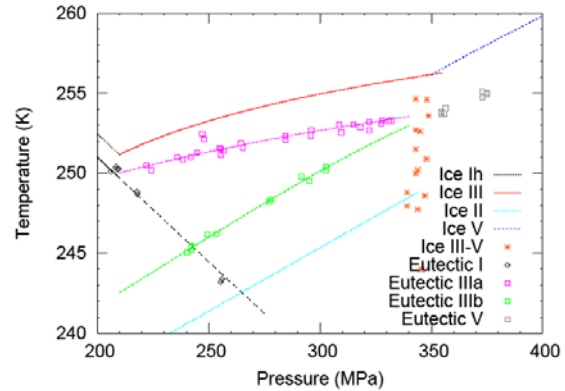


Figure 5: Eutectic temperature vs. Pressure and ice transitions [12] in the Ice III and V regimes. Three distinct phases were observed in the Ice III regime.

eutectic temperatures follow the extrapolation of the eutectic line from Fig. 4.

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 cryo-lava 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., Hogenboom, D.L., and Kargel, J.S. (2009) *LPS XL*, Abstract #2033. [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.