

VOLUMETRIC AND OPTICAL STUDIES OF HIGH PRESSURE PHASES OF $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ WITH APPLICATIONS TO EUROPA. A. J. Dougherty¹, D. L. Hogenboom¹, and J. S. Kargel², ¹Dept. of Physics, Lafayette College, Easton, PA 18042, e-mail: doughera@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 report eutectic temperature and freezing-point depression as a function of pressure for a 15.5 wt.% sample of Na_2SO_4 in H_2O using a volumetric cell with sapphire windows. Data runs were made at pressures ranging from 0.4 MPa to 325 MPa, and temperatures from 240 K to 300 K. Eutectic melting points for $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ (mirabilite) were measured, and visual movies of crystallization and melting were obtained over this pressure range.

Relation to previous work: This work is a continuation of our on-going research program to characterize the physical and chemical properties of salts under conditions of low temperature and high pressure. Salts are found in many meteorites, are known to be abundant on the surface of Mars [1], and are possibly major surface constituents on Europa [2,3]. 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.

This work complements earlier studies of phase equilibria in the $\text{Na}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ system at Lafayette College in which a sample of the same composition was used and eutectic melting points were determined [4,5]. The earliest studies [4] did not allow optical identification of the relevant phases, while Ref. [5] primarily addressed pressures less than 200 MPa, in the Ice- I_h regime.

Experiment: Approximately 1 mL of sample was loaded into a pressure cell that was placed in an insulated, temperature-controlled bath. The pressure cell was designed to allow optical access to the sample, to aid in identifying the crystal phases. This cell is made from a 316 stainless steel block with four ports, known as a cross (High Pressure Equipment Company #60-HF6). Two opposing ports contain replaceable plugs that have sapphire windows sealed in them with epoxy. The third port contains a plug in which a silicon diode thermometer was installed. The fourth port connects the cell to the pressure system. The system allows simultaneous measurements of temperature, pres-

sure, and volume, as well as providing optical images of any growing or dissolving crystals.

The experiments were done at 15.5 wt.% Na_2SO_4 . At that concentration, and at atmospheric pressure, mirabilite ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$) is the stable form of the solid, though a second form has been observed at lower temperatures in Refs. [6], [7], and [8], as well as in our own lab. This phase has been identified as the heptahydrate, $\text{Na}_2\text{SO}_4 \cdot 7\text{H}_2\text{O}$ [6].

Results and Discussion: The results for a run at 250 MPa are shown in Fig. 1. The vertical scale is a voltage that varies approximately linearly with volume, and the horizontal scale is temperature.

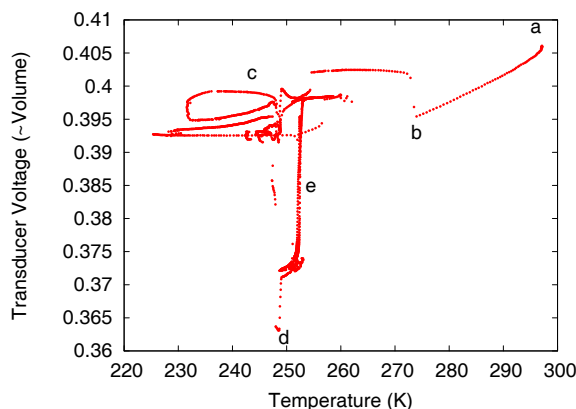


Figure 1. Experimental data run at 250 MPa.

After pressurizing to 250 MPa at a temperature high enough for the sample to be a homogeneous liquid (point a in Fig. 1) we began cooling. After supercooling to 273 K (point b) a sharp increase in volume (voltage) indicated rapid crystallization, presumably of mirabilite. (Although mirabilite is denser than the original solution, the remaining water-rich solution is less dense, leading to a slight overall increase in volume.) Fig. 2 shows the form of those first crystals near point (b).

Upon further cooling, the sample solidified at point (c) to an opaque solid, presumably consisting of mirabilite and Ice-III. At this point, the system was frozen solid and we were not able to detect pressure and volume variations reliably. After warming to about 250 K (point d), the system became soft enough for the transducer to respond, and we were once again able to measure pressure and volume variations. Since

Ice-III is denser than the liquid, the overall volume of the sample decreased significantly.

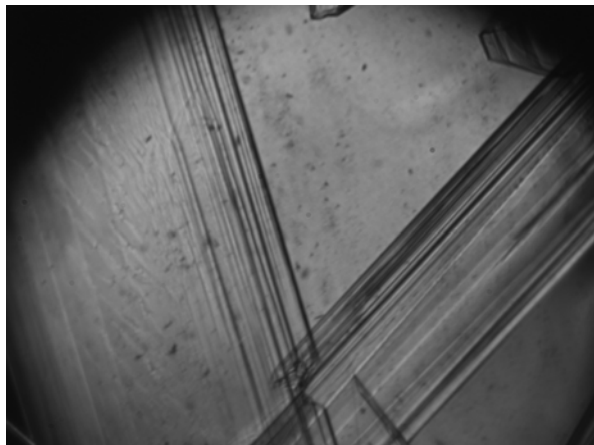


Figure 2: Mirabilite crystals observed corresponding to point (b) in Fig. 1, at a temperature of 273.5 K and a pressure of 248.8 MPa. The bright area at the center of the image is liquid.

Further slow warming towards point (e) brought about rapid eutectic melting. This was a reversible transition—the data near (e) actually contains three separate freezing/melting transitions. As the temperature and volume rose, the pressure also increased slightly. A typical image during eutectic melting is shown in Fig. 3.

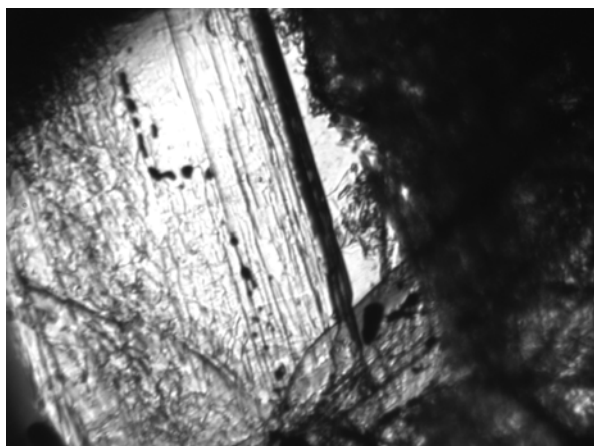


Figure 3: Eutectic melting at $T = 252.8$ K and $p = 248.2$ MPa. The crystals from Fig. 2 are visible in the background. The dark mass at the upper right is a collection of many small crystals, all rapidly dissolving.

For each run, we extracted the range of temperatures and pressures corresponding to eutectic melting. The resulting eutectic temperatures and pressures are shown in Fig. 4.

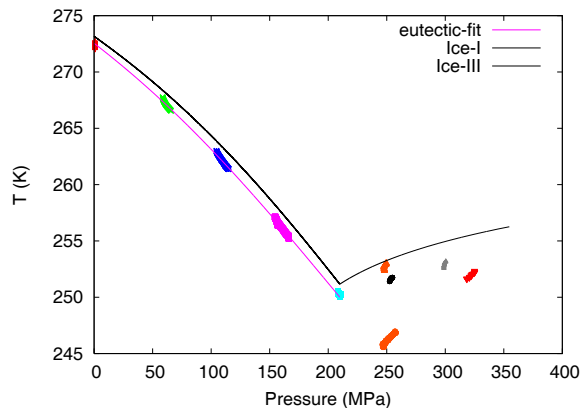


Figure 4. Eutectic temperature as a function of pressure. Shown for comparison are the Ice-I_n and Ice-III melting lines.[9]

Discussion: The freezing point depression for this system is small but there is a clear increase in the freezing point depression from about 0.85 K at low pressure to about 1.5 K near 200 MPa. In the Ice-III regime, the freezing point depression is also rather small, but the trend is less clear. In one run at 250 MPa, we observed a significantly lower eutectic temperature, but we have not been able to reproduce that result. We speculate that perhaps that run involved the metastable heptahydrate instead of mirabilite. The value at 325 MPa is also lower than the value at 300 MPa, and needs confirmation as well. We are currently constructing an enhanced version of the apparatus suitable for runs at higher pressures (up to 400 MPa) to obtain more reliable data in that regime.

References: [1] Squyres, S.W. *et al.* (2004) *Science*, 306. [2] McCord, T.B. *et al.* (1998) *Science*, 280, 1242. [3] Kargel, J.S. *et al.* (2000) *Icarus* 148, 226-265. [4] Hogenboom, D.L. *et al.* *LPS XXX*, Abstract #1793. [5] Dougherty *et al.* (2006) *LPS XXXVII*, Abstract #1732. [6] Hamilton, A. (2008) *Journal of Physics D-Applied Physics*. 41, 212002. [7] Hall, C. and Hamilton, A. (2007) *Icarus*, 198 (1): 277-279. [8] Eddy R.D. and Menzies A.W. (1940) *J. Phys. Chem*, 44, 207-235. [9] Bridgman, P.W. (1911) *Proc. Amer. Acad. Arts Sci.* 47, 441.