

**THE PHASE DIAGRAM OF AMMONIA MONOHYDRATE: A NEW HIGH-PRESSURE POLYMORPH;** D.L. Hogenboom,<sup>1</sup> J.S. Kargel,<sup>2</sup> T.C. Holden,<sup>1</sup> and M. Buyyounouski,<sup>1</sup>  
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**Overview.** In a continuation of previous investigations of the system H<sub>2</sub>O-NH<sub>3</sub> [1], we have modified our high-pressure apparatus with the addition of a new thin-walled flexible teflon sample capsule. The capsule allows us to observe melting and subsolidus transitions between phases and to make precise measurements of relative densities. Results are presented for a sample of 50.25 mass-% NH<sub>3</sub> (near the ammonia monohydrate composition of 48.6% NH<sub>3</sub>) at pressures from 10 MPa to 400 MPa and temperatures from 140 K to 205 K. We have found persuasive evidence of a high-pressure polymorph of ammonia monohydrate. A preliminary phase diagram of ammonia monohydrate includes two branches of the melting transition, corresponding to ammonia monohydrates I and II, and the subsolidus transition between these solids. These data seem to be inconsistent with those reported by Boone and Nicol [2], who did not observe a high-pressure polymorph. In an accompanying abstract by Kargel and Hogenboom (this volume), we re-examine our and Boone and Nicol's data in an attempt to reconcile the two.

**Experimental.** The details of the experiment have been described previously [1]. Briefly, our data consist of measurements of temperature, pressure, and transducer voltage. The voltages correspond almost linearly to sample volume. Thus, for example, in Fig. 1 melting of a solid phase to a lower density liquid produces a sharp rise in voltage. We have not yet made calibration runs to determine the volume-voltage relationship in the new experiment design that uses the teflon sample capsules, though a rough calibration of relative density changes can be done with volume data given by Croft et al. [3], who found that the congruent melting of ammonia monohydrate at 0.1 MPa produces about a 4% volume expansion. The volume change at 8 MPa (the lowest pressure we investigated) would not be much different. At the start of a data run the sample is pressurized at a temperature well above the melting point and then cooled slowly. The liquid supercools and eventually crystallizes to a more dense or less dense phase depending upon the conditions. Before the development of the flexible sample capsules, sample filled the pressure vessel and narrow connecting tubing. The rigidity of the frozen sample often prevented further density changes from being detected until the sample began to melt. The use of flexible sample capsules now permits the investigation of the subsolidus region. The capsules are fabricated from two end pieces machined from TFE rod and a piece of heat-shrinkable FEP tubing. These pieces are "welded" together with a small torch. The capsules are loaded with liquid sample under vacuum and closure is made with a TFE set screw in one of the end pieces.

**Results and interpretation.** Figures 1 and 2 show raw data from four runs typical of the behavior of the sample containing 50.25% NH<sub>3</sub> at pressures below and above 300 MPa, respectively. The runs at pressures <300 MPa encountered a single solid phase, as shown by the simple melting behavior (Fig. 1). This solid apparently is the familiar low-pressure polymorph of ammonia monohydrate (mono I). Runs at pressures above 300 MPa (Fig. 2) consistently indicate the existence of a second solid phase that is stable in a separate temperature-pressure region from that of mono I. These phases, mono I and ammonia monohydrate II (mono II) are, respectively, less dense and more dense than the supercooled liquid at pressures greater than ~300 MPa. Mono I underwent a subsolidus transition to mono II in every run above 300 MPa.

At the melting point and 0.1 MPa, mono I has a density ~0.037 g cm<sup>-3</sup> greater than that of the liquid of the same composition [3]. This density difference decreases with pressure until at ~300 MPa there is no measurable difference in the density of the solid and the 50.25%-NH<sub>3</sub> liquid at the melting point, although they have different thermal expansivities. When encountered above ~300 MPa, mono I has a density less than the liquid's.

The pressure-temperature melting curve has two branches, corresponding to the two solids (Fig. 3). Fits to the three 2-phase coexistence curves intersect at a triple point near 198 K, 330 MPa. The slope dP/dT of the coexistence curve between mono I and mono II is very shallow and opposite in sign compared to the slopes of the melting curves. Since the volume change is negative, we know that the reaction from mono I to mono II is endothermic, but the small magnitude of the slope indicates that the ratio of L/ΔV (latent heat divided by volume change) is much smaller than in the case of melting of mono I and mono II. The slope of the mono I melting curve at the limit of zero pressure is consistent with the Clapeyron slope as calculated from the data of [3].

In the near future we expect to make the necessary calibration runs to measure the compression of teflon and the fluid surrounding the capsule so as to enable calculations of absolute sample densities.

**References.** [1] Hogenboom, D.L. *et al.* 1994, The ammonia-water phase diagram and phase volumes to 4 kbars (abstract), *Lun. Planet. Sci. Conf. XXV*, 555-556. [2] Boone, S. and Nicol, M.F., 1991, Ammonia-water mixtures at high pressures: Melting curves of ammonia dihydrate and ammonia monohydrate and a revised high-pressure phase diagram for the water-rich region, *Proc. Lunar Planetary Sci.*, **21**, 603-612. [3] Croft, S.K., Lunine, J.I., and Kargel, J.S., 1988, Equations of state of ammonia-water liquid: Derivation and planetological applications, *Icarus*, **73**, 279-293.

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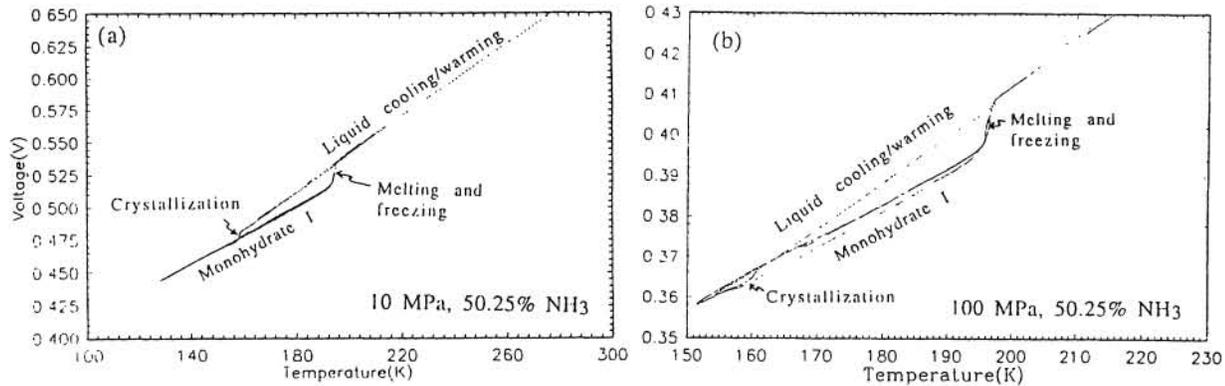


Figure 1. Experimental runs for the composition  $\text{NH}_3 = 50.25\%$  by mass and typical of pressures  $<300$  MPa. Voltage is almost linearly related to sample volume. (a) Run at 10 MPa. The initial warming and melting was reversed just before melting would have been completed. Recooling and then renewed warming retraced the initial warming curve (not readily visible here). (b) Run at 100 MPa. Initial melting was reversed and the sample refroze. The solid then melted on the same melting curve observed previously.

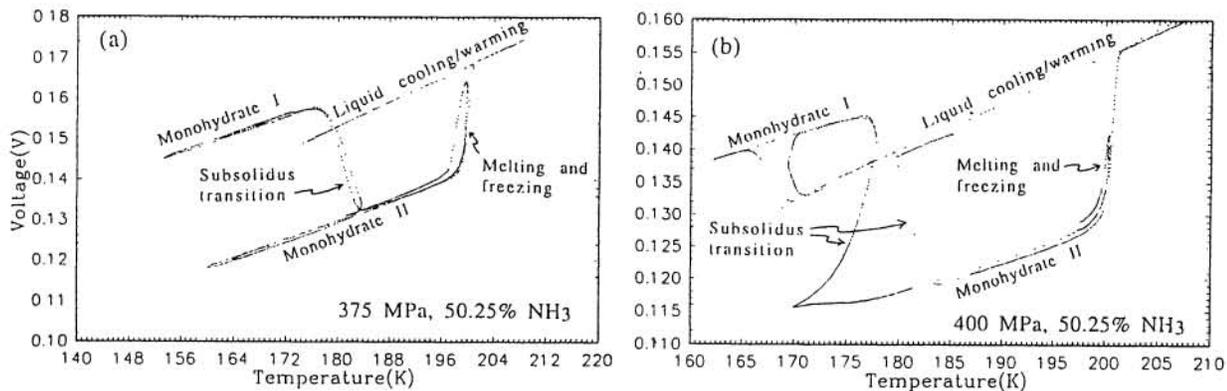


Figure 2. Raw data from runs for a composition  $\text{NH}_3 = 50.25\%$  by mass and typical of pressures between 300 and 400 MPa. (a) Run at 375 MPa with reversals. Transition from ammonia monohydrate I to ammonia monohydrate II is repeatable but not readily reversible. Melting/freezing transition is repeatable and reversible. (b) Run at 400 MPa with reversals, again showing a repetition of similar behavior during multiple coolings and warmings. This run, like all runs above 300 MPa, exhibits behavior similar to that seen in Figure 2a.

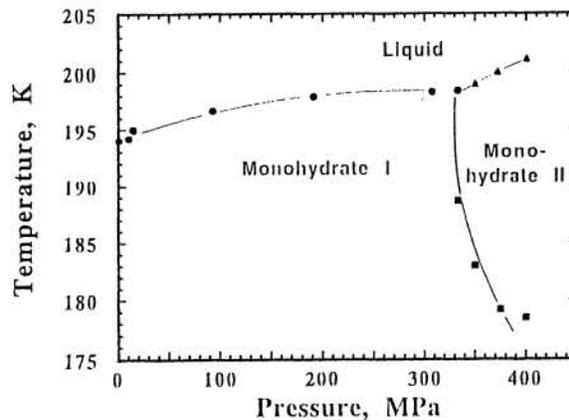


Figure 3. Phase diagram of the composition  $\text{NH}_3 = 50.25\%$  showing the subsolidus transition between ammonia monohydrates I and II and the melting curves.