

AMMONIA-WATER DENSITIES AND PHASE RELATIONS TO FOUR KILOBARS D.L. Hogenboom¹ and J.S. Kargel²; ¹Physics Department, Lafayette College, Easton, PA 18042; ²Lunar and Planetary Laboratory, University of Arizona, Tucson, AZ 85721

Introduction. Ammonia-water cryovolcanism is widely suspected to have been important in the evolution of icy satellites in the outer solar system. We report experimental determinations of ammonia-water liquid densities and solid-liquid phase relations, following from previous work [1-3]. We have determined ice liquidus temperatures for liquids containing 10, 20, and 28.6 wt. % NH_3 at several pressures, and the melting behavior of ammonia hydrates at several pressures for mixtures containing 28.6 and 32.1% NH_3 . Our new data cover the entire range of interior pressures in small to intermediate sized icy satellites and in the outer 200 kilometers or so of the largest icy satellites.

The Experiment. Our apparatus and procedure have been modified slightly from those described previously [1]. The essential components of the system are shown in Figure 1. The change in volume of the sample is measured with a transducer which detects the position of an alnico magnet floating on a mercury column. The transducer generates a DC voltage which changes as the sample volume changes. After calibrating with water and correcting for compression of the mercury and sample in the expansion pipe we estimate the uncertainty in our reported densities is less than 0.15%. A comparison of our densities with direct volumetric measurements [3] indicates a similar uncertainty.

Since our last report, the temperature measurement and control system has been improved by placing the silicon diode thermometer in a copper sleeve in good thermal contact with the sample pressure vessel. A heating tape was also used to balance the heat lost to the liquid nitrogen bath, permitting good control of heating and cooling rates.

Liquid and solid volumes. The density, ρ , of 28.6 wt.% $\text{NH}_3\text{-H}_2\text{O}$ at roughly 20 bars is given as a function of temperature, T, by the equation $\rho = 0.997612 - 0.185481 \times 10^{-3}T - 0.498297 \times 10^{-6}T^2$. The density of the ammonia dihydrate-composition liquid (32.1 wt.% NH_3) at 303.15 K is given as a function of pressure by the equation $\rho = 0.8789 + 0.3645 \times 10^{-4}P - 0.2434 \times 10^{-8}P^2$, where P is in kilobars.

Since we can not directly observe the contents of the bomb we rely on the volumetric behavior of the system to infer the identity of solid phases. We observe two solid phases, apparently water ice-I and ammonia monohydrate, which are less dense than co-existing ammonia-water liquids. We also observe solids which are denser than the liquid, apparently including ammonia dihydrate and ices-II, -III, and -V.

Supercooling and crystallization behavior. Samples were quickly cooled (several K/minute) from room temperature to about 120 K, without crystallization, where the temperature then remained more or less constant for several hours, and then began to warm slowly (about 0.03 K/minute). Failure to cool below about 130 K at least for several hours typically failed to result in crystallization of ammonia hydrate. Given the necessary time and temperature conditions we typically observed a 3- to 4-fold increase in the warming rate of the bomb and the enclosed sample in the interval from about 130 to 140 K. This enhanced warming was often accompanied by a slight decrease in voltage. We interpret these effects to be due to the volumetric adjustment and latent heat release caused by the crystallization of ammonia dihydrate.

Solid-liquid phase relations. Figures 2 and 3 show representative temperature-voltage plots for crystallized mixtures containing 28.6 wt.% NH_3 (voltage is inversely related to density). For pressures of one kilobar and lower the melting behavior of mixtures of ice and ammonia dihydrate is simple. The iso-voltaic stretch on the warming curves in Figures 2 and 3 is due to the plugging of the bomb with crystals. Melting at 20 bars occurs cleanly at 176.2 \pm 0.2 K, in agreement with the peritectic melting point at 1 atm (20 bars pressure has a negligible effect on the melting point). Melting is indicated by a sharp rise in voltage as the bomb first unplugs and then as ammonia dihydrate yields a less dense peritectic liquid phase plus a small amount of water ice. The melting reaction is reversible (ammonia dihydrate re-crystallizes) if the sample is re-cooled very slowly (0.01 K/min) before all the ammonia dihydrate has melted.

Above one kilobar a more complex (but repeatable) melting behavior is usually observed (Figure 3). The sample apparently crystallizes to ammonia dihydrate but it melts differently. In the first stage of melting the voltage rises sharply. But instead of levelling off at a value near that of the ice melting curve, as it does below 1 kilobar, the voltage continues to rise. The voltage peaks and then, in the second stage of melting, descends toward the ice melting curve. Endothermic effects indicative of a melting reaction, observable as a depression in the warming rate, occur continuously during both these stages of melting. The first stage of melting is consistent with the melting of ammonia dihydrate and its partial re-crystallization to a low-density assemblage of water ice and ammonia monohydrate; this stage apparently is irreversible (ammonia dihydrate does not re-crystallize), since the voltage continues to rise if the sample is slowly re-cooled before the first stage of melting is complete. The second stage of the reaction is consistent with the eutectic melting of ammonia monohydrate and water ice. The second stage is reversible (ammonia monohydrate can be re-crystallized) if the sample is very slowly re-cooled prior to the final disappearance of ammonia monohydrate. Excess water ice melts gradually after the ammonia hydrates have completely melted; the liquidus is indicated in Figure 3 by the break in slope where the warming curve meets the liquid cooling curve.

The observations above seem to imply that ammonia dihydrate is the stable ammoniacal phase near the melting point below 1 kilobar, whereas ammonia monohydrate is stable above 1 kilobar (although ammonia dihydrate may exist metastably above a kilobar). Figure 4 is a phase diagram of the mixture containing 28.6% NH_3 . The solidus, including the metastable dihydrate melting curve, has been reproduced in several experiments. The liquidus is preliminary.

In accordance with prior expectations [2] we find that the ice-I liquidus drops to lower temperatures and the peritectic shifts to slightly water-richer compositions as pressure is applied. Apparently around 200 bars the peritectic

AMMONIA-WATER SYSTEM Hogenboom D.L. and Kargel J.S.

composition crosses that of ammonia dihydrate; ammonia dihydrate melting then becomes congruent, and the peritectic becomes a eutectic. This eutectic becomes more water rich as pressure is applied, finally attaining a minimum of about 29% NH_3 at 2 kilobars.

Implications. 1) Igneous distillation of solar system ices by partial melting and then re-melting can yield liquids as ammonia-rich as 35.4 wt.% NH_3 (the monohydrate-dihydrate eutectic) at pressures less than about 200 bars, but above this pressure the accessible liquid compositions are restricted to the water-rich side of the ice-dihydrate eutectic. 2) High-pressure, relatively water-rich eutectic liquids are forced to precipitate water ice as they ascend and de-pressurize, resulting in relatively viscous slurries. 3) A high pressure transition in one of the ammonia hydrates is required at some pressure between 4 and 10 kilobars to fit both these data and those of [2].

Acknowledgements. We thank Guy Consolmagno, Steven Croft, John Lewis, Jonathan Lunine, and Robert Strom for constructive comments and encouragement. This study has been partially supported by the NASA Planetary Atmospheres Program and the Uranus Data Analysis Program.

References. [1] Hogenboom, D.L., J. Winebrake, G.J. Consolmagno, and W. Dalrymple III, *LPS XX*, 420-421. [2] Cynn, H.C., S. Boone, A. Koumvakalis, M. Nicol, and D.J. Stevenson, 1989, *Proc. 19th Lunar Planet. Sci. Conf.*, G. Ryder and V.L. Sharpton (eds.), Cambridge Univ. Press and Lunar and Planetary Inst. (Publ.), Houston, p. 433-441. [3] Croft, S.K., J.I. Lunine, and J.S. Kargel, 1988, *Icarus*, 73, 279-293.

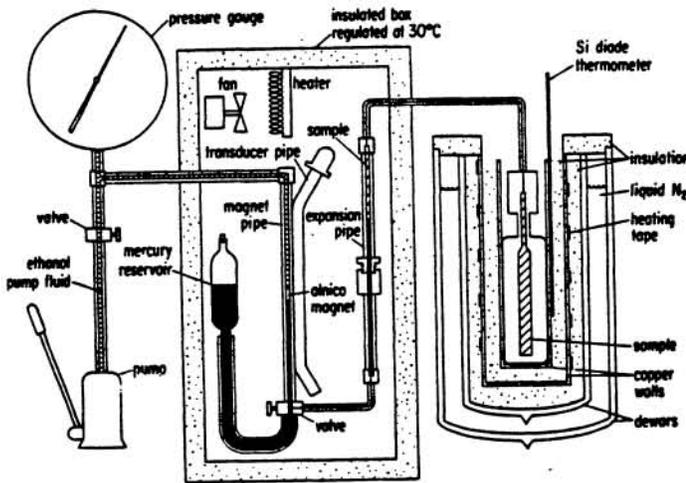


Figure 1. Schematic of high-pressure apparatus.

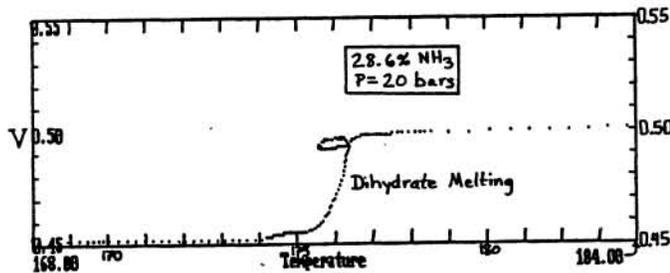


Figure 2. Ammonia dihydrate melting at 20 bars with reversal.

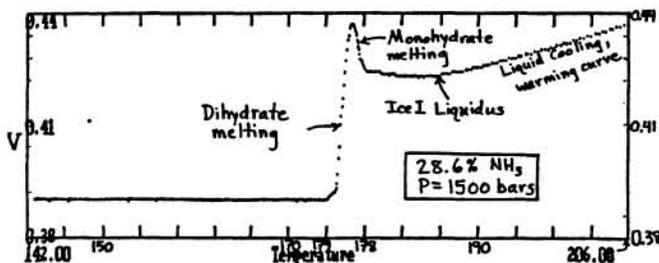


Figure 3. Melting at 1500 bars showing metastable dihydrate melting followed by stable monohydrate melting at their respective eutectics.

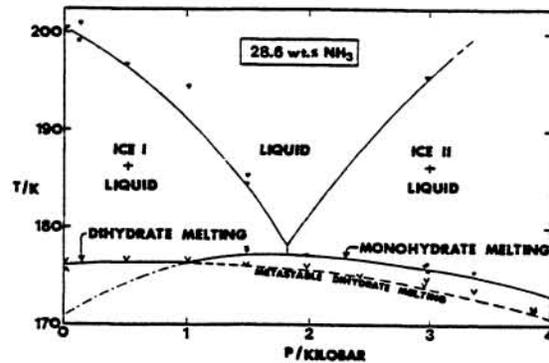


Figure 4. Phase diagram for 28.6% ammonia mixture.