

Liquidus Phase Relations and Liquid Properties in the System $\text{H}_2\text{O}-\text{NH}_3-\text{CO}_2-\text{H}_2\text{CO}$;
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Much attention has focussed this decade on minimum melting temperatures and liquid compositions relevant to icy satellites, particularly in the system $\text{H}_2\text{O}-\text{NH}_3$, where a cosmochemically important peritectic occurs at 176 K and 32.6% (by weight) NH_3 . This work examines the liquidus phase relationships for more complex assemblages of volatiles that may more closely resemble the low-temperature assemblages expected to occur in comets and many icy satellites. Parent volatiles observed or inferred to be present in percent-level or greater abundances in Comet Halley, for example, include H_2O , CO_2 , CO , CH_4 , NH_3 , and H_2CO (1, 2, 3, 4, 5). These volatiles are expected to be important in the evolution of comets and in the igneous differentiation of many icy satellites.

H_2O , NH_3 , H_2CO , and CO_2 are all highly thermochemically inter-active molecules and may be expected to be significantly partitioned in one chemical form or another into low-temperature partial melts. CO and CH_4 readily react with H_2O to form cage-like clathrate structures stable even near the melting point of pure ice. Since CH_4 and CO have extremely small electric dipole moments these molecules should not enter significantly into aqueous solutions formed by the partial melting of Comet Halley-like ices (J. Lunine, priv. com.).

CO_2 and polymeric H_2CO are present in Comet Halley with estimated molar abundance ratios relative to H_2O of ≈ 0.03 and 0.01 , respectively (3, 4). H_2CO reacts to form hexamethylenetetramine (HMT) according to the reaction: $6\text{H}_2\text{CO} + 4\text{NH}_3 \rightarrow (\text{CH}_2)_6\text{N}_4 + 6\text{H}_2\text{O} + 81 \text{ kcal}$ (6); calorimetric experiments show that this reaction occurs on laboratory time-scales at least down to 220 K. CO_2 can react with NH_3 and H_2O to form ammonium carbonate, ammonium carbonate hydrate, ammonium bicarbonate, or ammonia carbamate, depending on the stoichiometry of the reactants; the reaction of dry ice with ammonium hydroxide liquid occurs on laboratory time-scales; and, ammonium carbonates may have precipitated directly from the Solar Nebula under certain conditions (7). Given these rapid reaction rates the relevant solid-liquid equilibria in Comet Halley-like assemblages of ices will involve ammonium carbonates and HMT.

Liquidus phase relations have been explored experimentally in the ternary systems $\text{H}_2\text{O}-\text{NH}_3-\text{HMT}$, $\text{H}_2\text{O}-\text{NH}_3-(\text{NH}_4)_2\text{CO}_3$, and $\text{H}_2\text{O}-\text{HMT}-(\text{NH}_4)_2\text{CO}_3$; 100-500 ml of binary and ternary liquid mixtures of known composition were cyclically cooled and warmed above and below the temperatures where crystalline precipitates were first observed. Temperature measurements were made with chromel-alumel thermocouples. The identifications of the precipitating phases were assisted by observing crystal form with a hand lens and by noting whether the crystals floated or sank in the liquid. Supercooling was a general phenomenon observed in nearly all of the experiments. The true liquidus temperatures were bracketed from above and below, with uncertainties of about $0.3-3^\circ$. The experimental mixtures were prepared by mixing known quantities of analytical reagent-grade HMT, ammonium bicarbonate, ammonium hydroxide liquid (29.3% NH_3), and liquid ammonia, and distilled water.

The liquidus surface in the system $\text{H}_2\text{O}-\text{NH}_3-\text{HMT}$ is presented graphically in Figure 1. The results for the $\text{H}_2\text{O}-\text{NH}_3$ and the $\text{H}_2\text{O}-\text{HMT}$ binary systems agree closely with the results for these systems obtained by previous investigators (8, 9, 10, 11). The planetologically significant features of this ternary system include a ternary peritectic close in composition and temperature to the $\text{H}_2\text{O}-\text{NH}_3$ binary peritectic and a cotectic leading up in temperature away from the peritectic on a trend of HMT-enrichment and NH_3 -depletion. The peritectic is an invariant point where ammonia dihydrate, water ice, and HMT clathrate ($\text{HMT} \cdot 6\text{H}_2\text{O}$) coexist with an ammonia-water-rich liquid containing 2-4% HMT in solution; the application of heat after first melting results eventually in the complete melting of one or another of the solid phases, depending on the initial relative abundances of the three solid phases (this will most likely be the ammonia dihydrate); after this occurs, the further application of heat causes the liquid composition to migrate up a univariant cotectic (the ice-HMT clathrate cotectic if ammonia dihydrate is the first solid to be used up). The presence of as little as 2-4% HMT in the peritectic liquid may be an important factor governing the albedos of volcanically resurfaced icy satellites, since the UV or charged particle irradiations of HMT should produce black organic substances. The presence of HMT in ammonia-water liquids also appears to inhibit nucleation and to allow greater degrees of super-cooling to occur; this could have important consequences, since highly supercooled ammonia-water liquids can have viscosities orders of magnitude greater than the peritectic liquid viscosity reported below, thus possibly helping to explain the origin of the extremely thick volcanic flows observed on Ariel (12) and Miranda. Small amounts of HMT also directly increases the liquid phase viscosity.

First melting in the system $\text{H}_2\text{O}-\text{NH}_3-(\text{NH}_4)_2\text{CO}_3$ occurs at a ternary peritectic extremely close to the $\text{H}_2\text{O}-\text{NH}_3$ binary peritectic; a cotectic rises up in temperature away from the peritectic; ice, ammonium

carbonate hydrate ((NH₄)₂CO₃ · H₂O), and a cotectic liquid are the stable phases along this cotectic. In this system the peritectic liquid contains probably less than 0.1% ammonium carbonate in solution; a strong ammonium carbonate enrichment trend does not occur until the temperature has exceeded 250 K. Therefore, CO₂ may generally be ignored as a component in low-temperature ammonia-water liquids.

In each of the two systems above the first significant event to occur upon heating after melting begins is the exhaustion of one of the solid phases, which most likely will be the ammonia hydrate. In the combined quaternary system this also will probably be the case. If the ammonia-bearing liquid is extracted from the quaternary system prior to the exhaustion of yet another solid phase, then any additional melting of the solid residue can be described in the ammonia-free ternary system H₂O-HMT-(NH₄)₂CO₃ · H₂O. This system exhibits a eutectic near 257 K and 20% HMT + 16% ammonium carbonate hydrate + 65% water; stable solid phases at this eutectic include ice, HMT clathrate, and ammonium carbonate hydrate.

Liquid densities and viscosities were determined using the method described by Kargel (13). Liquid viscosities in the binary system H₂O-NH₃ are shown plotted against temperature in Figure 2. Experimental data and equations giving the ammonia-water liquid densities are in press (14). The density, viscosity, and composition of cotectic liquids in the system H₂O-NH₃-HMT are plotted as functions of the cotectic temperature in Figure 3.

References 1) Allen, M., et al., 1987, *Astronomy and Astrophysics* (in press); 2) Eberhardt, P., et al., 1987, *Astron. Astrophys.* (in press); 3) Feldman, P.D., et al., 1986, *Nature* **324**, 433-436; 4) Mitchell, D.L., et al., 1987, *Science* **237**, 626-628; 5) Huebner, W.F., 1987, *Science* **237**, 628-630; 6) Walker, J.F., 1964, *Formaldehyde*, 3rd ed, American Chemical Soc. Monograph Series, Reinhold Publ. Co., New York; 7) Lewis, J.S., and R.G. Prinn, 1980, *Astrophys. Jour.*, **238**, 357-364; 8) Postma, S., 1920, *Rec Trav. Chim.*, **39**, 515; 9) Mironov, K.E., 1955, *Zhur. Obsche. Khim.*, **25**, 1081-6; 10) Rollet, A.P., and G. Vuillard, 1956, *C. R. Acad. Sci. Paris*, **243**, 383-386; 11) Evrard, V., 1929, *Naturw. Tijdschr.*, **11**, 99-107; 12) Ruzicka, A., 1988, abstract in *LPS XIX*; 13) Kargel, J.S., 1987, abstract in *LPS XVIII*, 475-6; 14) Croft, S.K., et al., 1988, in press in *Icarus*; 15) Pinevich, G., 1948, *Kholodil. Tekh.*, **20**, 30-37.

Figure 1. Liquidus surface in the system H₂O-NH₃-HMT. Isotherms in degrees Centigrade: concentrations in weight percent. Below.

Figure 2. Viscosity of liquids in the system H₂O-NH₃. Contours give the log₁₀ of the viscosity in poises. Right

Figure 3. Cotectic liquid composition and physical properties in the system H₂O-NH₃-HMT.

Lower right.

