AMMONIA-WATER MIXTURES AT HIGH PRESSURES REVISITED. S. Boone and M. F. Nicol, Dept. of Chem. and Biochem., UCLA, Los Angeles, CA 90024-1569.

We have continued with our examination of the phase relations of mixtures of ammonia and water, $(NH_3)_X(H_2O)_{1-X}$. (1) High pressures were generated by compressing the samples in a diamond-anvil cell. Sample pressures were determined by the ruby luminescence technique and phase determinations were made by microscopic examination of the samples under normal and polarized light. Samples were loaded by immersing the diamond-anvil cell in a solution with composition, $X_i$, then closing the cell thus trapping some of the solution in the sample chamber.

Five samples with $0.33 < X_i < 0.38$ were prepared using stainless steel 316 gaskets. These samples were intended for growing single crystals for x-ray diffraction studies. Although we were successful in growing single crystals of this material, we were unable to collect diffraction patterns from them. All of these samples were chilled to temperatures below 150 K within three hours of loading and were maintained at pressures below 1.8 GPa and below 250 K throughout the experiments. This was done in an effort to control the reaction between the sample and the gasket which was discussed in (1). (This is also the reason for the gold-plating used on the gaskets confining the samples described below.) From the phase data collected from these samples, the melting curve of ammonia dihydrate, $NH_3{\cdot}2H_2O$, was determined to conform to the equation $T = 176 + 60P - 8.5P^2$, where T is temperature in K and P is pressure in GPa. It extends from about 0.06 GPa and 179 K, where the Ice I liquidus joins the low-pressure $NH_3{\cdot}2H_2O$ peritectic, to about 1.4 GPa and 243 K, where the Ice VI liquidus meets the high-pressure $NH_3{\cdot}2H_2O$ peritectic. We found that under these experimental conditions X was lowered by about 0.02 or 0.03 by the reaction between the gasket and the sample. We also found that $NH_3{\cdot}2H_2O$ nucleates much more readily on stainless steel 316 than on gold.

The melting behavior of a sample at the composition of ammonia monohydrate, $NH_3{\cdot}H_2O$, ($X_i = 0.501$) was examined from pressures of 0.5 GPa to 4.3 GPa. The sample was confined in a gold-electroplated gasket and was observed to melt seven times. From these data the melting curve was determined to conform to $T = 194 + 37P - 0.98P^2$. This represents a minor correction to the findings in (2) which were collected using samples which were loaded by a different technique and which were compressed in unplated Inconel gaskets. No other transitions were observed. This is consistent with the spectral data of Koumvakalis. (3)

The phase transitions for a sample with the composition $X_i = 0.414$ were observed at pressures from 0 to 6.5 GPa and at temperatures from 125 to 400 K also in a gold electroplated gasket. Besides the transitions in the liquidus region, three solid-solid transitions were observed at low temperature which are consistent with the high pressure stability limit of $NH_3{\cdot}2H_2O$. This transition boundary is linear to within our experimental error and extends from the intersection of

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the $NH_3{\cdot}2H_2O$-$NH_3{\cdot}H_2O$ eutectic and the eutectic of Ice VIII and $NH_3{\cdot}H_2O$ at about 2.3 GPa and at 245 K to higher pressure and lower temperature with a slope of about - 0.072 GPa $K^{-1}$.

The findings of this work and (1) are summarized in Fig. 1.

References

1. Cynn, H.-C., et al. (1988) *Proc. 19th Lun. Pla. Sci. Conf.*, pp. 433 - 441.
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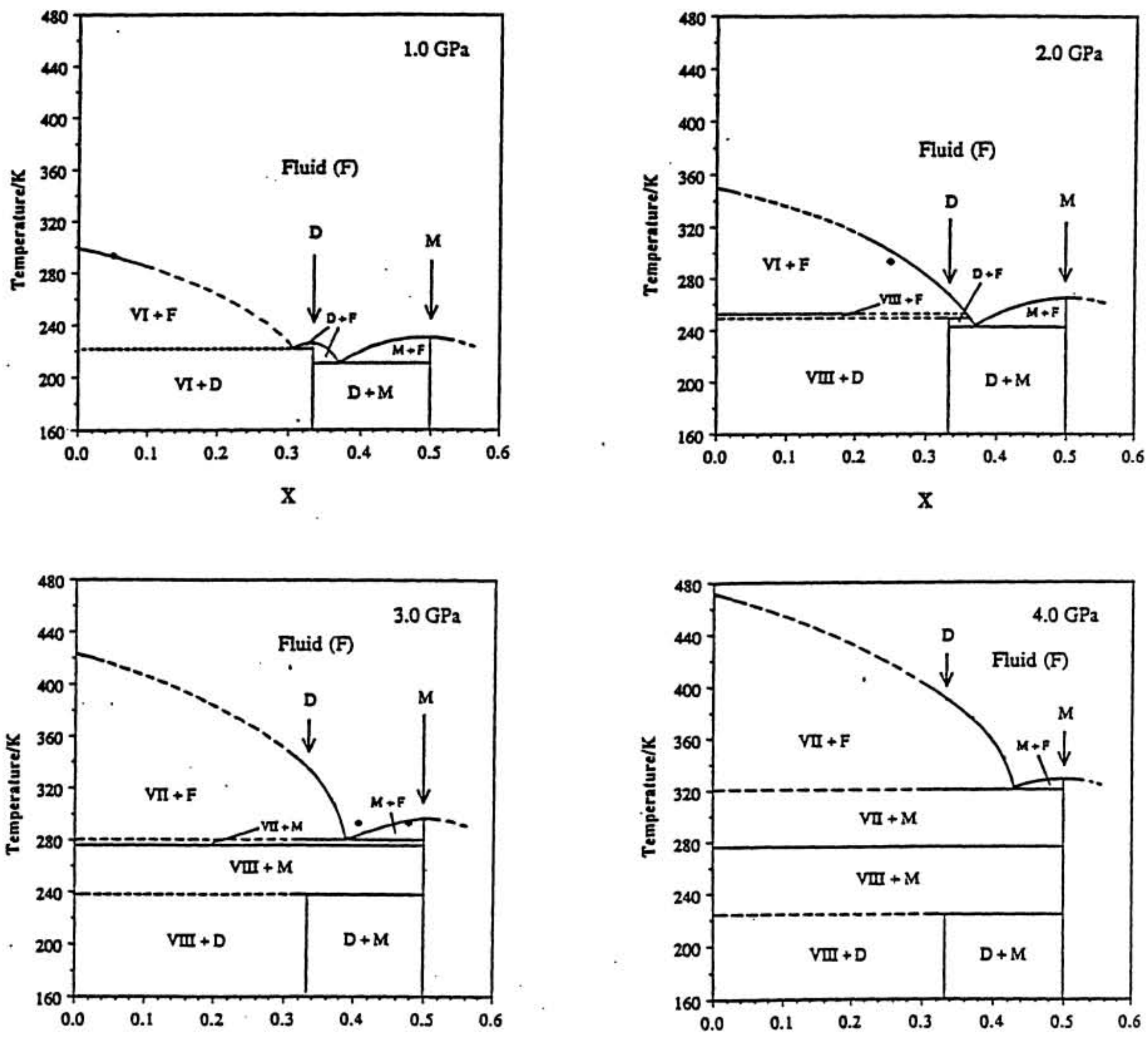


Figure 1 - Isobaric phase diagrams for ammonia-water mixtures, $(NH_3)_X(H_2O)_{1-X}$, for $0 \leq X \leq 0.6$ and P = 1.0 to 4.0 GPa. Letters correspond to stable phases: D = $NH_3{\cdot}2H_2O$, M = $NH_3{\cdot}H_2O$, Roman numerals = ice polymorphs with the same designations. Diamonds correspond to the liquidus boundaries proposed in Ref. 1 for a room temperature study performed by Cynn. Dotted boundaries correspond to unconfirmed transitions which were outside the experimental range or are, for some other reason, uncertain.