

## NOTES AND CORRESPONDENCE

Ammonia in the Atmosphere of Venus<sup>1</sup>

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18 September 1973 and 26 November 1973

## ABSTRACT

Several aspects of the chemistry of NH<sub>3</sub> in the Venus atmosphere are examined. Production of NH<sub>3</sub> and precipitation of NH<sub>3</sub> compounds are considered quantitatively. It is concluded that the high NH<sub>3</sub> mixing ratios reported by the Soviet Venera 8 landing probe appear to be inconsistent with the observed abundances of other gases in the Venus atmosphere.

The Soviet Venera 8 Venus landing probe has reported the presence of ammonia with a mixing ratio of 10<sup>-4</sup> to 10<sup>-3</sup> at 46 and 33 km above the surface (Surkov *et al.*, 1973). Bromophenol blue, a non-specific pH indicator, was used for the ammonia determination.

Previous discussions of the atmosphere of Venus have given little consideration to NH<sub>3</sub>; the present note examines several aspects of the chemistry of NH<sub>3</sub> on Venus, including production of NH<sub>3</sub> and precipitation of NH<sub>3</sub> compounds at various levels in the atmosphere. We shall consider the important questions of whether the Venera NH<sub>3</sub> data are consistent with the spectroscopically observed abundances of other gases, and why the NH<sub>3</sub> mixing ratio in the upper atmosphere of Venus is below the current detection limit of earth-based spectroscopy.

Data on the composition of the Venus atmosphere

are given in Table 1; calculations in the present paper were made assuming constant mixing ratios for these gases. In lieu of spectroscopic data for HBr and HI, equal mixing ratios for HCl, HBr and HI were assumed. In terms of solar or chondritic abundances, Cl > Br > I; however, because of ionic radius effects, a considerable fraction of the Cl on Venus, less Br, and even less I are likely to be bound in surface rocks. Therefore, the assumption of equal mixing ratios appears to be a reasonable approximation. HF is ignored because of the great instability of NH<sub>4</sub>F.

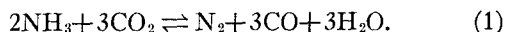
The temperature-pressure profile used in the present paper is given in Table 2. This profile is very similar to the profile (Model VII) given in NASA (1972). None of the calculations in the present note would be appreciably affected by using a somewhat different temperature-pressure profile.

TABLE 1. Atmospheric composition.

Species	Mixing ratio adopted in present paper	Observational data
CO <sub>2</sub>	0.97	0.93 to 0.97 (Avduevsky <i>et al.</i> , 1970)
N <sub>2</sub>	1 × 10 <sup>-2</sup>	< 2 × 10 <sup>-2</sup> (Surkov <i>et al.</i> , 1973)
CO	1 × 10 <sup>-4</sup>	(1-3) × 10 <sup>-4</sup> (Belton, 1968)
H <sub>2</sub> O	2 × 10 <sup>-3</sup> (upper limit)	5 × 10 <sup>-5</sup> (Young, 1972)
	1 × 10 <sup>-4</sup>	< 2 × 10 <sup>-3</sup> (Jones <i>et al.</i> , 1972)
	1 × 10 <sup>-6</sup> (lower limit)	(1-7) × 10 <sup>-3</sup> (Vinogradov <i>et al.</i> , 1968)
HCl	1 × 10 <sup>-6</sup>	1 × 10 <sup>-4</sup> (Belton, 1968)
	1 × 10 <sup>-6</sup>	1 × 10 <sup>-6</sup> (Fink <i>et al.</i> , 1972)
HBr	1 × 10 <sup>-6</sup>	1 × 10 <sup>-6</sup> (Belton, 1968)
HI	1 × 10 <sup>-6</sup>	6 × 10 <sup>-7</sup> (Young, 1972)
NH <sub>3</sub>		not detected
		not detected
		≤ 5 × 10 <sup>-8</sup> (Benedict, 1968)

<sup>1</sup> Contribution No. 83 of the Planetary Astronomy Laboratory, Massachusetts Institute of Technology.

Production of  $\text{NH}_3$  is governed by the reaction



Uncertainties in the mixing ratios are negligible for  $\text{CO}_2$  and probably about a factor of 2 or 3 for CO. However, the  $\text{H}_2\text{O}$  mixing ratio is subject to considerable uncertainty and disagreement. For this reason, equilibrium  $\text{NH}_3$  mixing ratios have been calculated for three  $\text{H}_2\text{O}$  mixing ratios. The  $\text{N}_2$  mixing ratio was assumed to be  $1.0 \times 10^{-2}$ ; this is probably an upper limit. The calculated equilibrium  $\text{NH}_3$  mixing ratios are shown in Fig. 1; thermochemical data were taken from Robie and Waldbaum (1968). At low temperatures, the equilibrium  $\text{NH}_3$ -producing reaction is kinetically limited. The temperature at which kinetics limits  $\text{NH}_3$  production in the Venus atmosphere is unknown. Furthermore, at temperatures of 310–340K the  $\text{NH}_3$  mixing ratio is subjected to a second absolute limit imposed by the total amount of  $\text{H}_2\text{O}$  or CO available in the atmosphere. For this reason, even if there were no kinetic inhibition,  $X_{\text{NH}_3}$  would reach a maximum near 325 ( $\pm 15$ )K. Above this altitude,  $\text{H}_2\text{O}$  or CO would be severely depleted by reaction (1).

Precipitation of the following  $\text{NH}_3$  compounds is considered:  $\text{NH}_4\text{Cl}$ ,  $\text{NH}_4\text{Br}$ ,  $\text{NH}_4\text{I}$ ,  $\text{NH}_4\text{HCO}_3$  and  $\text{NH}_4\text{NH}_2\text{CO}_2$ ; vapor pressure data were obtained from Kelly and Anderson (1935) and the *Handbook of Chemistry and Physics* (1962).  $\text{NH}_3$  mixing ratios in equilibrium with the above five  $\text{NH}_3$  compounds are shown in Fig. 1. For gases other than  $\text{NH}_3$ , the mixing ratios shown in Table 1 were used for the vapor pressure calculations.

The data plotted in Fig. 1 indicate that  $\text{NH}_4\text{NH}_2\text{CO}_2$  and  $\text{NH}_4\text{HCO}_3$  will not precipitate at any level in the atmosphere; these compounds require too high  $\text{NH}_3$  mixing ratios. At temperatures dependent on the  $\text{NH}_3$  mixing ratio, the  $\text{NH}_3$  halides will precipitate. For  $X_{\text{NH}_3}$  corresponding to  $X_{\text{H}_2\text{O}} = 1 \times 10^{-4}$ , the halides will precipitate at about the 400 to 350K level. If the production of  $\text{NH}_3$  is kinetically limited at temperatures above 400K,  $X_{\text{NH}_3}$  will be lower and the halides will precipitate higher in the atmosphere at lower temperatures.

Ammonium chloride precipitation has been suggested by Lewis (1968a) and by Kuiper (1969), but the

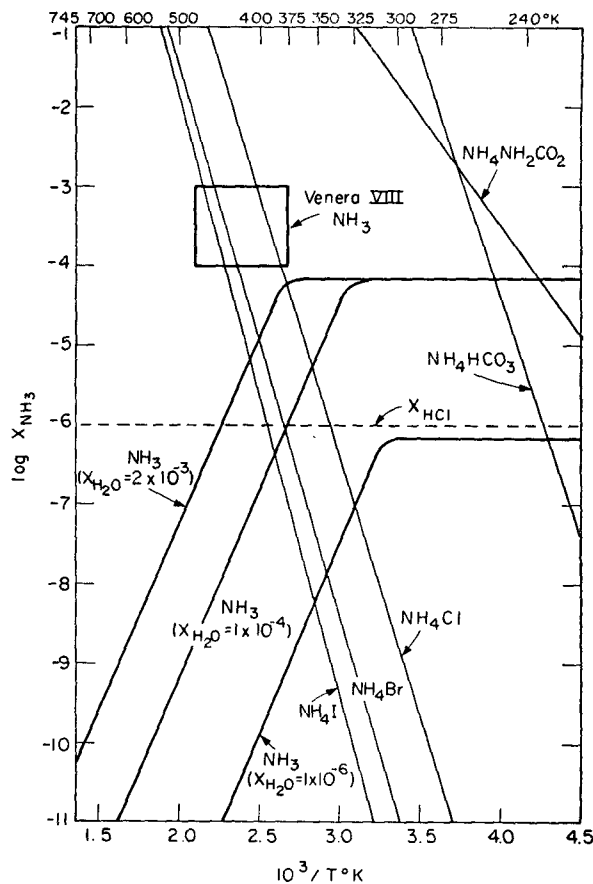


FIG. 1. Chemical equilibrium  $\text{NH}_3$  mixing ratios [reaction (1)] for  $X_{\text{H}_2\text{O}} = 10^{-6}$ ,  $10^{-4}$  and  $2 \times 10^{-3}$ ; in each case,  $X_{\text{NH}_3}$  becomes constant when the total amount of  $\text{H}_2\text{O}$  or CO is exhausted.  $\text{NH}_3$  mixing ratios in equilibrium with  $\text{NH}_4\text{Cl}$ ,  $\text{NH}_4\text{Br}$ ,  $\text{NH}_4\text{I}$ ,  $\text{NH}_4\text{HCO}_3$  and  $\text{NH}_4\text{NH}_2\text{CO}_2$  and the Venera 8  $\text{NH}_3$  results are also shown.

presence of HCl and absence of  $\text{NH}_3$  above the cloud tops strongly suggests  $X_{\text{NH}_3} < X_{\text{HCl}}$  at all levels in the atmosphere.  $X_{\text{HCl}}$  is observed to be  $10^{-6}$  near the cloud tops, which is in accord with the idea that  $\text{H}_2\text{O}$  and HCl are in chemical equilibrium with the 750K surface (Lewis, 1968b, 1970) if  $X_{\text{H}_2\text{O}} \approx 3 \times 10^{-4}$  in the lower atmosphere. Ten times more water require three times more HCl, which is comparable to the observational uncertainty in the HCl abundance. However, the maximum value of  $X_{\text{NH}_3}$  for such a wet model is  $2 \times 10^{-3}$ , some 700 times the expected HCl abundance for that model.  $\text{NH}_4\text{Cl}$  precipitation would leave an enormous excess of  $\text{NH}_3$ , dense  $\text{NH}_4\text{HCO}_3$  clouds, no observable HCl, and  $X_{\text{NH}_3} = 2 \times 10^{-6}$  at the 240K level.

If, following Kuiper, we consider the driest possible model ( $X_{\text{H}_2\text{O}} = 10^{-6}$ ), then we would expect  $X_{\text{HCl}} = 5 \times 10^{-8}$ , and  $X_{\text{NH}_3}$  could be only as high as  $7 \times 10^{-7}$  at best. Thus, small amounts of  $\text{NH}_3$  would still suffice to remove all HCl from the regions of the cloud tops. Certainly so dry a model cannot produce appreciable masses of ammonium-salt clouds.

TABLE 2. Temperature-pressure profile.

Temperature (°K)	Pressure (atm)
700	63
600	28
500	10.5
400	3.5
375	2.4
350	1.5
325	1.0
300	0.70
275	0.45
240	0.15

We conclude that the Venera 8  $\text{NH}_3$  mixing ratio of  $10^{-4}$  to  $10^{-3}$  at 46 and 33 km above the surface (about the 375–475K level) appears to be inconsistent with the abundances of other gases in the Venus atmosphere. If  $X_{\text{H}_2\text{O}}$  were as high as  $10^{-2}$ , then  $X_{\text{NH}_3}$  could exceed  $10^{-4}$  near the 400K level. However, recent radar data (Jones *et al.*, 1972) have provided a secure upper limit of  $X_{\text{H}_2\text{O}} = 2 \times 10^{-3}$ . With more reasonable  $\text{H}_2\text{O}$  mixing ratios of  $10^{-4}$  to  $10^{-6}$ , the  $\text{NH}_3$  mixing ratios near the 375–475K level should be several orders of magnitude lower than reported by Venera 8, even if the possible kinetic inhibition of  $\text{NH}_3$  formation is ignored.

Although there must be serious doubts about the validity of the Venera 8  $\text{NH}_3$  results, full understanding awaits publication of details of the analytic techniques used. A more sophisticated landing probe equipped to determine accurately a temperature-pressure-composition profile in the Venus atmosphere would permit an unambiguous resolution of the problems.

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