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THE ROLE OF AQUEOUS CHEMISTRY IN DETERMINING THE COMPOSITION AND CLOUD STRUCTURE OF THE UPPER TROPOSPHERE ON URANUS

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ABSTRACT

Aqueous chemistry on Uranus affects the atmospheric abundances of NH_3 and H_2S below the methane cloud base. We present a complete thermochemical equilibrium model for the H_2O-NH_3-H_2S system. Inclusion of H_2S increases the aqueous removal of NH_3 to 20%–30%, but aqueous chemistry alone cannot account for the depletion of NH_3 in the 150–200 K region of the atmosphere required to fit microwave observations. Formation of NH_4SH clouds can account for the observed depletion provided the H_2S/NH_3 ratio is enhanced by a factor of 4 relative to solar. Perturbations to the chemical balance between N and S, for example by the general circulation on Uranus, would then produce regions with either NH_3 or H_2S aloft.

Subject headings: molecular processes — planets: atmospheres — planets: Uranus

I. INTRODUCTION

Observations of Uranus at radio wavelengths indicate that ammonia may be severely depleted in the 150–200 K region of the atmosphere (Gulkis, Janssen, and Olsen 1978; de Pater and Massie 1985). Gulkis, Janssen, and Olsen (1978) propose an enhancement of H_2S relative to NH_3, such that formation of an NH_4SH cloud removes 99% of the NH_3, as originally discussed by Trinn and Lewis (1973). Temporal variations in microwave brightness temperature have been observed as the aspect of Uranus changed from nearly equator-on in 1965 to nearly pole-on in 1986 (Klein and Turegano 1978; Gulkis, Olsen, and Klein 1983). Gulkis, Olsen, and Klein (1983) infer an equator-to-pole decrease in the NH_3 abundance, leaving H_2 and H_2O the dominant opacity sources in the polar regions. Alternatively, Atreya and Romani (1984) argue that aqueous chemical reactions are predominantly responsible for the NH_3 depletion.

We present a model for the chemical reactions controlling the composition of the upper troposphere on Uranus. We have critically reexamined the thermodynamic data for the potential condensates in the atmospheres of the giant planets (Carlson, Prather, and Rossow 1987). Rather than rely on empirical fits to laboratory data, we incorporate the detailed reactions of the aqueous chemistry. We use the "warm" temperature profile derived by Atreya and Romani (1984), which is consistent with results of the *Voyager* Radio Science Subsystem occultation experiment (Tyler *et al.* 1986).

The effects of aqueous chemistry, discussed in § II, are insufficient to account for the depletion of NH_3. When S is enhanced, latitudinal variations in the general circulation more readily provide a mechanism for producing an equator-to-pole gradient in NH_3. We discuss the chemical balance between NH_3 and H_2S in § III.

II. RESULTS

Chemical reaction rates in the cloud-forming region are assumed to be in thermodynamic equilibrium at fixed pressure and temperature (see Carlson, Prather, and Rossow 1987 for a detailed description of the model as applied to Jupiter). Table 1 summarizes the chemical reactions and the associated thermodynamic data used in this investigation.

We define a reference model with solar abundances of O, C, N, and S (Cameron 1982) and the "warm" profile (Atreya and Romani 1984). These elements are found as H_2O, CH_4, NH_3, and H_2S below the water cloud with respective mixing ratios of 1.38×10^{-3}, 8.35×10^{-4}, 1.74×10^{-4}, and 3.76×10^{-5}. The water cloud forms at 320 K (79 bar) and remains liquid to 264 K (41 bar), due to solution effects. The aqueous reactions deplete atmospheric NH_3 and H_2S by 12% and 17%, respectively (Fig. 1). The decreasing atmospheric partial pressures of NH_3(g) and H_2S(g) with altitude are offset by the increased solubilities of NH_3 and H_2S, about a factor of 10 as the temperature decreases from 310 K to 260 K. Ionic composition is controlled by the pH of the solution which, for this reference model, ranges from 9 at cloud base to 10 at the freezing point. The dominant sulfur species in solution is HS^-, while NH_3 is equally partitioned between NH_3(a) and NH_4^+. Charge balance in the solution is primarily between NH_4^+ and HS^-; the latter buffers the solution, keeping the pH relatively low.

Results for the NH_3-H_2O system are denoted by the dotted lines in Figure 1. Large differences are seen in the pH and NH_4^+ concentrations. In the absence of buffering by H_2S, charge balance is maintained between NH_4^+ and OH^-, and thus, OH^- concentrations increase by more than an order of magnitude. Ammonia is present in this solution predominantly as NH_3(a), and the amount of NH_3 removed by the

TABLE 1

THERMODYNAMIC DATA AT 298.15 K FOR THE REACTIONS USED IN THE MODEL

Reaction	ΔH (kJ mol^{-1})	ΔG (kJ mol^{-1})	ΔS (J [mol K]$^{-1}$)
$H_2O(g) \Rightarrow H_2O(l)$	−45.00	−8.57	−122.20
$H_2O(g) \Rightarrow H_2O(s)$	−51.25	−7.97	−145.17
$NH_3(g) \Rightarrow NH_3(s)$	−31.67	9.86	−139.29
$NH_3(g) + H_2S(g) \Rightarrow NH_4SH(s)$	−89.97	−0.38	−282.45
$H_2S(g) \Rightarrow H_2S(s)$	[a]	[a]	[a]
$CH_4(g) \Rightarrow CH_4(a)$	−14.24	16.36	−102.60
$H_2(g) \Rightarrow H_2(a)$	−4.18	17.57	−72.90
$NH_3(g) \Rightarrow NH_3(a)$	−34.61	−9.99	−82.39
$H_2S(g) \Rightarrow H_2S(a)$	−19.12	5.69	−83.10
$H_2O(l) \Rightarrow H^+ + OH^-$	56.80	79.84	−77.27
$NH_3(a) + H^+ \Rightarrow NH_4^+$	−51.74	−52.74	3.47
$H_2S(a) \Rightarrow H^+ + HS^-$	22.11	40.45	−61.57
$HS^- \Rightarrow H^+ + S^=$	50.27	73.64	−76.61
$2NH_4^+ + S^= \Rightarrow (NH_4)_2S$	0.35	−0.21	0.71
$(NH_4)_2S + H_2S(g) \Rightarrow (NH_4)_sS_2 + H_2(g)$	32.64	39.17	−11.85

[a] See Carlson *et al.* 1987.

SOURCES.—*Handbook of Chemistry and Physics* 1983; *International Critical Tables* 1928; Kelley and King 1961; Wagman *et al.* 1968; Stull and Prophet 1971.

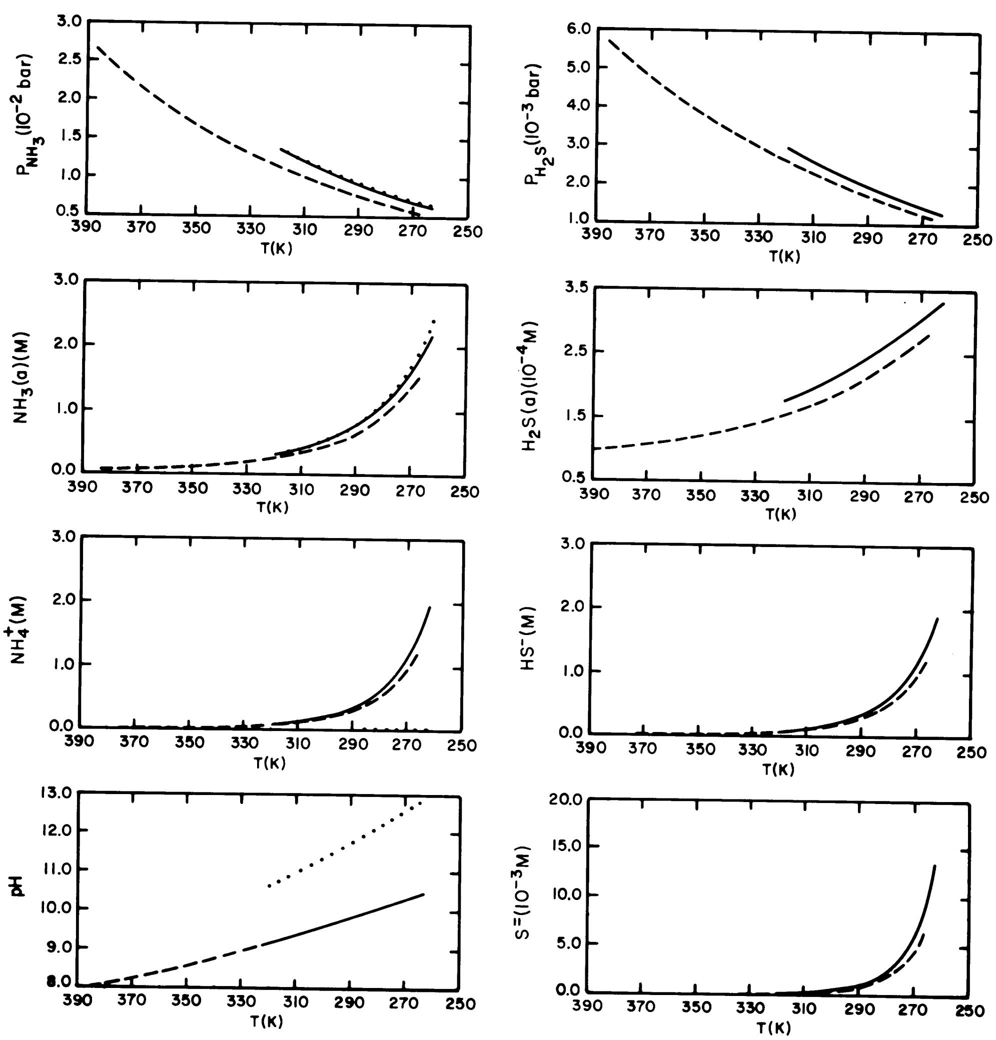

FIG. 1.—Properties of the water cloud chemistry on Uranus as a function of temperature. A comparison is made between the complete aqueous chemistry determined by the three component system, NH_3-H_2O-H_2S (*solid lines*), by the chemistry without H_2S (*dotted lines*), and by the chemistry with a 10 × solar enhancement of H_2O (*dashed lines*). The partial pressures of NH_3 and H_2S in the atmosphere are shown in the top panels; the molar concentrations of the dissolved (aqueous) gases in the cloud drops, in the panels immediately below. Ionic concentrations of NH_4^+, HS^-, and $S^=$, as well as pH are also included.

water cloud, NH_3(a) plus NH_4^+, is substantially reduced. The addition of H_2S reactions, therefore, increases the dissolved ammonia, and maximizes the removal of NH_3 by the water cloud.

Aqueous chemical reactions for the NH_3-H_2O system are included by empirical formulae in the models of Lewis (1969), Weidenschilling and Lewis (1973), and Atreya and Romani (1984). Depletion of atmospheric H_2S by aqueous chemistry is simulated in Weidenschilling and Lewis (1973) and Atreya and Romani (1984), again by empirical formula (Leyko 1964). They do not, however, solve the complete NH_3-H_2O-H_2S system: they neglect feedbacks on dissolved ammonia as discussed above and hence should underestimate the depletion of NH_3 and H_2S.

We investigate the influence of temperature on the thermochemistry using the "cold" profile derived by Atreya and Romani (1984) and solar abundances. With this profile, the base of the H_2O cloud occurs at much greater pressures, 270 bar (344 K). The pH increases from 8.7 at cloud base to 11.2 as the cloud remains liquid up to 242 K and intersects the NH_4SH cloud. At this level aqueous reactions have depleted the abundances of NH_3 and H_2S by 20% and 30%, respectively.

Enhancing the H_2O abundance by a factor of 10 (*dashed lines* in Fig. 1) shifts the cloud base to 386 K (150 bar, "warm" profile). The pH increases from 8 at cloud base to 9.2 at 320 K (79 bar, cloud base for solar abundance of H_2O). In this region, the warmer temperatures result in lower solubilities for NH_3, leading to lower values for the pH. Consequently, aqueous reactions are less efficient in their removal of the weak acid H_2S. By 320 K, 90% of the water has condensed, removing only 17% of the NH_3 and 13% of the H_2S, leaving a solar abundance of H_2O yet to condense. Above this point, results are parallel to those for the reference case; see Figure 1. From 320 K to 266 K the cloud remains liquid and aqueous chemistry further depletes NH_3 by 12% and H_2S by 16%. In total, abundances of NH_3 and H_2S are depleted by 27% and 26%, respectively.

Formation of NH_4SH depletes the remaining abundances of NH_3 and H_2S in a stoichiometric ratio of 1 : 1. In our reference model the base of the NH_4SH cloud is located at 232 K (26 bar). NH_3 is depleted by an additional 18%, yielding a mixing ratio of 1.2×10^{-4} at 186 K (13 bar). At this level, H_2S is effectively removed from the atmosphere, topping the NH_4SH cloud. An ammonia ice cloud forms at 160 K (8 bar). With the "cold" profile the base of the NH_4SH cloud occurs at a higher pressure, 82 bar (242 K). Formation of NH_4SH depletes NH_3 by an additional 20%, yielding an ammonia mixing ratio of 1.1×10^{-4} and an H_2S mixing ratio of 1×10^{-9} at cloud top (190 K, 37 bar). Above the NH_4SH cloud, an NH_3 cloud forms at 168 K (24 bar). When H_2O is enhanced by a factor of 10, more NH_3 is removed in the water cloud, but the location of the NH_4SH cloud base is unchanged. The NH_4SH cloud is chemically topped at 184 K (12 bar) by the removal of H_2S, and the NH_3 cloud is shifted to 158 K (7.5 bar). The combined effects of aqueous chemistry and formation of NH_4SH result in an NH_3 depletion of 30% (reference model); 36% (solar, "cold" profile); and 43% (10 × solar H_2O).

III. DISCUSSION

Depletion of NH_3 through the combined effects of aqueous reactions and formation of NH_4SH is insufficient to reduce the ammonia abundance to 10^{-6}, the upper limit suggested by Gulkis, Janssen, and Olsen (1978). Removal of NH_3 by aqueous reactions alone, 12%, is considerably less than the 70%–90% reported by Atreya and Romani (1984) and is consistent with the results of Weidenschilling and Lewis (1973). Alternatively, Fegley and Prinn (1986) have shown that, if water is enhanced by a factor of 500 × solar, then most of the gaseous NH_3 is removed in the transition from supercritical to subcritical when 54% of the water condenses (647 K, 2300 bar). Their results (see their Fig. 3) are also inconsistent with Atreya and Romani (1984).

With a solar N/S ratio, the formation of NH_4SH accounts for only an additional 18% depletion. Alternatively, a subsolar abundance of NH_3 leaves unexplained the source of higher microwave opacity at lower latitudes. Therefore, we agree with Gulkis, Janssen, and Olsen (1978) that the NH_3/H_2S ratio cannot be solar. Indeed the enhanced CH_4 abundance (Tyler *et al.* 1986) suggests that other elemental abundances are nonsolar; hence, we investigate enhanced abundances of S. The key to our explanation of the latitudinal gradient in NH_3 is that the NH_3/H_2S ratio must be close to one at the base of the NH_4SH cloud: slight deviations about unity can produce dramatic compositional changes, creating regions with either NH_3 or H_2S aloft.

Atreya and Romani's calculations (1984, Table 13) for solar abundances and the "warm" profile show a decrease of NH_3 mixing ratio from 1.74×10^{-4} (solar) to 2.2×10^{-5} at 225 K (25 bar) corresponding to a depletion of 87%. They attribute all of this depletion to aqueous chemistry, even though the 225 K level is above the base of their NH_4SH cloud (their Fig. 18). Removal of 1.5×10^{-4} (87%) NH_3 in 1.38×10^{-3} H_2O produces an average concentration of 5.5 M (10% mole fraction). Since solution strength increases monotonically with decreasing temperature (see Fig. 1) the concentration at the freezing point (263 K; *International Critical Tables* 1928) must be greater than the average value. Using the empirical formula for the NH_3-H_2O system referenced in their paper (Wilson 1925; *International Critical Tables* 1928), the equilibrium mixing ratio of NH_3 over a 5.5 M solution at 264 K is 5.74×10^{-4}, which is 3 times their initial abundance. Their NH_3 mixing ratio of 2.2×10^{-5} at 225 K corresponds to an equilibrium solution of 2.2 M which is insufficient to account for the 87% depletion. The results of Atreya and Romani (1984) appear to be inconsistent with chemical equilibrium.

Our investigations of the effects of varying the temperature profile (6% more NH_3 removed for the "cold" profile) or increasing the water abundance (13% more NH_3 removed for 10 × solar H_2O) show that neither of these changes can account for the large NH_3 depletion.

Using solar abundances of O and N and an enhanced mixing ratio of 1.56×10^{-4} for H_2S results in a slight excess of NH_3 aloft (see Fig. 2, *solid lines*). The base of the water cloud is still at 79 bar (320 K), but the cloud remains liquid through the base of the NH_4SH cloud at 240 K (30 bar). At 240 K, NH_3 and H_2S are depleted by 22% and 14%, respec-

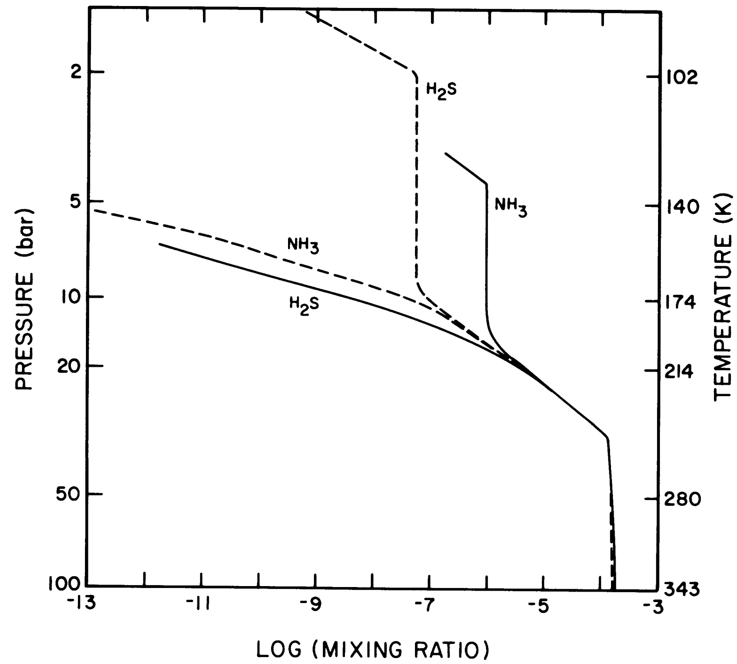

FIG. 2.—Vertical profiles of the mixing ratio of NH_3 and H_2S predicted using the warm solar *P-T* profile of Atreya and Romani (1984). The solid lines correspond to the case where the abundance of H_2S has been increased to 1.56×10^{-4}, while the dashed lines correspond to the results for an H_2S abundance of 1.57×10^{-4}. Mixing ratio is defined here with respect to H_2. Formation of a condensate is indicated by the change in the slope of the mixing ratio profiles.

tively. Between 200 K and 150 K, formation of NH_4SH further reduces the abundance of NH_3 from 3×10^{-6} to 1×10^{-6}. The base of the NH_3 cloud layer is shifted from 160 K (8 bar, solar H_2S) to 130 K (4 bar).

If the mixing ratio of H_2S is increased by half a percent to 1.57×10^{-4}, NH_3 aloft disappears to be replaced by an excess of H_2S (*dashed lines* in Fig. 2). No change occurs in the locations of the water and NH_4SH cloud bases. Between 200 K and 150 K, the mixing ratio of NH_3 decreases from 1.3×10^{-6} to less than 10^{-11}; the mixing ratio of H_2S aloft is 5×10^{-8} resulting in an H_2S cloud at 1.6 bar (94 K). Increasing the abundance of H_2S by an additional half percent leads to an H_2S excess of order 10^{-6} and a somewhat higher cloud base pressure. Note that solid state phase transitions in H_2S are not accounted for in the saturation vapor pressure expressions used here (Giauque and Blue 1936), so that the predicted location of the H_2S cloud is uncertain.

The delicate balance illustrated here depends on the NH_3/H_2S ratio at the base of the water cloud. We can find a similar balance, for example, in the case of enhanced abundances of O and N (20 × solar as observed for CH_4) with an H_2S mixing ratio of 2.7×10^{-3}. With 20 × solar H_2O, the water cloud forms at 192 bar (416 K) and remains liquid through the NH_4SH cloud base at 53 bar (282 K).

We propose that the temporal variations observed in the microwave brightness temperatures are a manifestation of a compositional inhomogeneity in the Uranian atmosphere arising from the effects of the large-scale circulation on the chemical balance between NH_3 and H_2S. For example, latitudinal variations in the precipitation pattern for water clouds need only produce percent-level changes in the NH_3/H_2S ratio at the base of the NH_4SH cloud in order to shift the composition from excess NH_3 near the equator to excess H_2S near the poles. Baines and Bergstralh (1986) have suggested the presence of an H_2S cloud in the polar regions.

Why should the NH_3/H_2S ratio on Uranus exist in such a delicate balance? A possible mechanism is the photochemical conversion of NH_3 to N_2 in the upper troposphere such as occurs on Jupiter (Strobel 1973). A balance is maintained between the upward flux of NH_3 and the downward flux of N_2 followed by thermochemical conversion back to NH_3. In regions where NH_3 is in excess above the NH_4SH cloud, the integrated loss of NH_3 is approximately equal to the number of ultraviolet photons available to dissociate NH_3 (10^{10} photons cm^{-2} s^{-1} averaged over the planet). This balance requires vertical velocities of order 10^{-3} cm s^{-1} at 10 bar, typical of stratospheric conditions. A steady state would be achieved over the lifetime of the planet. If the primordial N/S ratio on Uranus were much greater than unity, then a substantial fraction of the nitrogen would be currently in the form of N_2. At present, no observational limits on the N_2 abundance in the range 10^{-4} exist.

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