

## Predicted chemistry of the deep atmosphere of Uranus before the Voyager 2 encounter

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The Voyager 2 spacecraft will encounter Uranus in January 1986, and will provide the first spacecraft observations of that planet. It carries an infrared interferometer spectrometer (IRIS) which has already detected a variety of infrared active gases in the atmospheres of Jupiter, Saturn and Titan<sup>1-4</sup>. Some of the detected gases are not in chemical equilibrium but have sources in the deep atmosphere. IRIS observations of these non-equilibrium gases, in particular PH<sub>3</sub> (mixing ratio  $X_{\text{PH}_3} \approx 6 \times 10^{-7}$ ) and GeH<sub>4</sub> ( $X_{\text{GeH}_4} \approx 7 \times 10^{-10}$ ) on Jupiter<sup>1</sup> and PH<sub>3</sub> ( $X_{\text{PH}_3} \approx 1 \times 10^{-6}$ ) on Saturn<sup>5</sup>, can be used to deduce the strength of convective mixing in the deep atmospheres of Jupiter and Saturn<sup>5,6</sup>. Similar deductions could be made about convective mixing rates in the deep atmosphere of Uranus if models of the equilibrium chemistry and thermochemical kinetics were available to help interpret IRIS observations of the visible Uranus atmosphere. We describe here the results of comprehensive thermochemical equilibrium and chemical kinetic calculations for Uranus. We predict that the most abundant non-equilibrium trace gas derived from the deep atmosphere of Uranus is N<sub>2</sub>; other important non-equilibrium species include HCl, HF, GeH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, PH<sub>3</sub>, H<sub>2</sub>Se, CH<sub>3</sub>SH, CO, CH<sub>3</sub>NH<sub>2</sub>, CH<sub>3</sub>OH, and CO<sub>2</sub>. Some of these species are detectable potentially by the Voyager instruments.

We assume that Uranus, like Jupiter and Saturn, has a deep convective atmosphere. Use of this assumption also leads to reasonable interior structure models<sup>7</sup>, but this is still uncertain because of the apparent lack of a large internal heat source on Uranus<sup>8</sup>. The present results refer to an arbitrary but plausible compositional model in which H<sub>2</sub> and the noble gases (He, Ne, Ar, Kr, Xe) are present in solar abundance<sup>9</sup>, H<sub>2</sub>O, NH<sub>3</sub>, H<sub>2</sub>S and many 'heavy' elements (atomic number  $\geq 3$ ) are enriched 100 times relative to solar abundance, and CH<sub>4</sub> is enriched  $\approx 10$  times. This model, which is based on the low-temperature equilibrium condensation sequence outlined by Lewis<sup>10</sup> and Prinn and Fegley<sup>11</sup>, is one of several that we are investigating. It is consistent with deductions from visible<sup>12</sup> and infrared<sup>13</sup> spec-

troscopy and interior structure models<sup>7</sup> that Uranus is enriched in 'heavy' elements relative to solar abundances.

We constructed an adiabatic temperature-pressure profile for our model Uranus atmosphere taking temperature  $T = 74$  K at pressure  $P = 1$  bar (ref. 13). Thermochemical equilibrium calculations were done for several hundred compounds of the elements H, He, O, C, N, S, Fe, Mg, Si, Na, Cl, K, F, P, Ge, Se, Ne, Ar, Kr, Xe, Ca, Al and Ti. The thermochemical kinetics of the important destruction reactions for selected gases were also studied. Homogeneous gas phase and heterogeneous Fe-catalysed destruction reactions for N<sub>2</sub> and CO were included in our model. The specific techniques used to construct our model and the thermodynamic and chemical kinetic data sources are described in detail elsewhere<sup>5,6,11,14-18</sup>.

The calculated equilibrium mixing ratios of important gases as functions of temperature and pressure are illustrated in Fig. 1. The abundances of two major gases H<sub>2</sub>O and NH<sub>3</sub> are appreciably reduced by the formation of dilute NH<sub>3</sub>-H<sub>2</sub>O solution clouds at 595 K. By the 275 K level the NH<sub>3</sub> abundance is less than the H<sub>2</sub>S abundance and it is quantitatively removed from the atmosphere by precipitation of NH<sub>4</sub>HS(s) as first suggested by Prinn and Lewis<sup>19</sup>.  $X_{\text{NH}_3}$  varies from about 10<sup>-9</sup> at 200 K to 10<sup>-14</sup> at 160 K, compatible with the observations of Gulikis *et al.*<sup>20</sup> that NH<sub>3</sub> is depleted in this region of the uranian atmosphere. Atreya and Romani<sup>21</sup> and Stevenson<sup>22</sup> also noted that formation of NH<sub>3</sub>-H<sub>2</sub>O solution clouds would consume large amounts of NH<sub>3</sub>. The excess H<sub>2</sub>S may condense slightly higher in the atmosphere at 166 K but is probably photolysed to S<sub>8</sub>(s) on a short timescale, while CH<sub>4</sub>(s) condenses at 77 K. The equilibrium abundances of other gases such as HCl, HF, H<sub>2</sub>Se, GeH<sub>4</sub> and P<sub>4</sub>O<sub>6</sub> are reduced significantly by precipitation reactions lower in the atmosphere (see Fig. 1).

Larger enhancements of H<sub>2</sub>O will yield solution cloud condensation at higher temperatures (and deeper levels) of the uranian atmosphere until the H<sub>2</sub>O critical point of 647 K is reached. Because the initial clouds are very dilute NH<sub>3</sub>-H<sub>2</sub>O solutions which have critical points slightly lower than that of pure water<sup>23</sup>, the 647 K level is the upper temperature limit to a NH<sub>3</sub>-H<sub>2</sub>O solution cloud base on Uranus. Latent heat effects due to solution condensation will also decrease as the cloud-base temperature approaches the critical point for the first formed (dilute NH<sub>3</sub>-H<sub>2</sub>O) solution<sup>24,25</sup>.

The observations of PH<sub>3</sub> and GeH<sub>4</sub> on Jupiter<sup>1</sup> and of PH<sub>3</sub> on Saturn<sup>5</sup> at concentrations orders of magnitude greater than their equilibrium abundances in the cool visible regions of the jovian and saturnian atmospheres have been interpreted in terms of rapid convective mixing from the hot deep atmospheres where

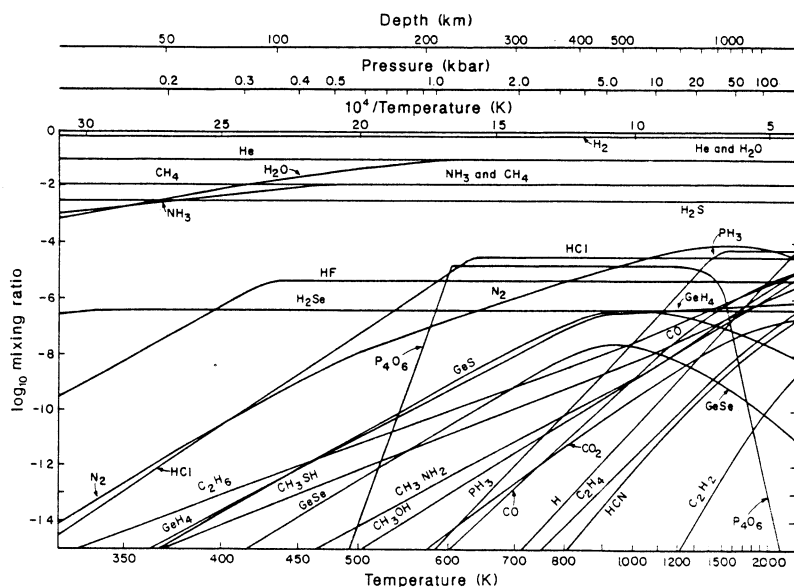


Fig. 1 Equilibrium abundances of important gases along the model adiabat in the atmosphere of Uranus. The horizontal scales indicate temperature, depth below the 300 K level and pressure along the adiabat. The constant abundances of the noble gases ( $X_{\text{Ne}} = 1.5 \times 10^{-4}$ ,  $X_{\text{Ar}} = 6.1 \times 10^{-6}$ ,  $X_{\text{Kr}} = 2.4 \times 10^{-9}$  and  $X_{\text{Xe}} = 3.4 \times 10^{-10}$ ) are not plotted. Precipitation of NH<sub>4</sub>Cl(s), NH<sub>4</sub>F(s), NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub>(s), Ge(s) and GeSe(s) at 629 K, 430 K, 602 K, 868 K and 339 K, respectively, depletes HCl(g), HF(g), P<sub>4</sub>O<sub>6</sub>(g), Ge and Se gases. Solution of H<sub>2</sub>S(g) and HF(g) in the ammonia-water clouds is a minor effect. All compounds of Fe, Mg, Si, Na, K, Ca, Al, Ti are condensed phases over the ( $P, T$ ) range considered.

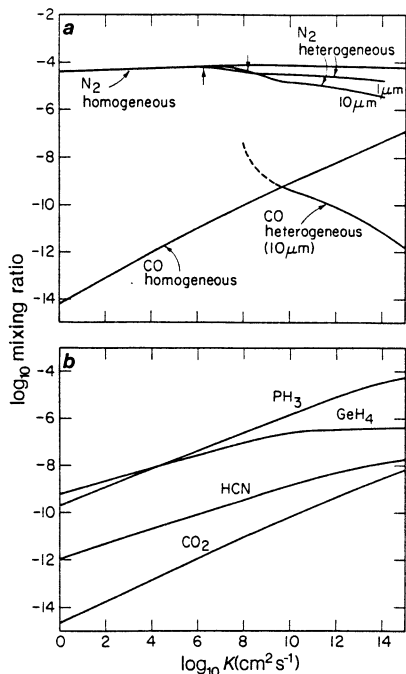


Fig. 2 *a*, Predicted  $N_2$  and CO mixing ratios in the observable Uranian atmosphere as a function of the vertical eddy diffusion coefficient  $K$ . Homogeneous gas-phase and heterogeneous iron-catalysed reactions are considered. Curves for catalysis on iron cloud particles with radii of  $10\ \mu\text{m}$  (CO) and  $1\ \mu\text{m}$  ( $N_2$ ) are shown. The dotted line on the CO heterogeneous curve indicates the predicted trend in the absence of homogeneous gas-phase reactions. Actual CO mixing ratios for  $K < 5 \times 10^9\ \text{cm}^2\ \text{s}^{-1}$  will follow the homogeneous curve. *b*, As *a* but for  $PH_3$ ,  $GeH_4$ , HCN and  $CO_2$ . Homogeneous gas-phase reactions only are considered.

these species are more abundant<sup>5,6,14</sup>. We have applied a similar model to Uranus to predict concentrations of non-equilibrium gases such as  $N_2$ ,  $GeH_4$ ,  $PH_3$ , CO,  $CO_2$ , and HCN in the Uranian upper atmosphere as a function of the rates of the relevant homogeneous and heterogeneous destruction reactions and the (assumed) strength of convective mixing in the deep Uranian atmosphere. Iron-catalysed heterogeneous  $N_2(g)$  and  $CO(g)$  destruction reactions were considered using the model of Prinn and Olaguer<sup>17</sup>. This treatment gives firm lower limits to the  $N_2$  and CO mixing ratios, because Fe(liquid) condenses at 6,000 K ( $2.4 \times 10^7$  bar) so Fe particles in the 1,000–2,000 K region are unlikely. The results of these calculations are illustrated in Fig. 2 where the predicted mixing ratios are plotted as a function of the vertical eddy diffusion coefficient  $K$ .

No observational estimates are available for the vertical eddy diffusion coefficient  $K$  in the deep Uranian atmosphere. However, various *a priori* estimates of  $K$  are possible. Assuming that free convection is a dominant mode for vertical heat transport in the deep Uranian atmosphere, we can estimate  $K$  from the relationship,  $K \approx H(\phi/\rho\gamma)^{1/3}$  where  $H$  is the pressure scale height,  $\gamma$  is the ratio of the heat capacity at constant pressure to the gas constant,  $\rho$  is the atmospheric density, and  $\phi$  is the upward heat flux carried by free convection. Taking  $\phi \approx 10\text{--}100\ \text{erg}\ \text{cm}^{-2}\ \text{s}^{-1}$  from ref. 26 yields  $K \approx (5\text{--}10) \times 10^7\ \text{cm}^2\ \text{s}^{-1}$  at the 1,000 K level in our atmospheric model. These values suggest more sluggish convective mixing on Uranus than on Jupiter or Saturn where  $K \approx 10^8\text{--}10^9\ \text{cm}^2\ \text{s}^{-1}$  in the deep atmosphere<sup>6,16,27–29</sup>.

Table 1 Predicted non-equilibrium trace gas abundance in the observable atmosphere of Uranus for 100 times enriched compositional model ( $K = 10^7\text{--}10^8\ \text{cm}^2\ \text{s}^{-1}$ )

Gas	Quench temperature (K)	Predicted mixing ratio
$N_2$	1,205–1,390	$(5.0\text{--}6.3) \times 10^{-5}$
$PH_3$	1,058–1,102	$(1.0\text{--}2.3) \times 10^{-7}$
$GeH_4$	775–810	$(5.0\text{--}10) \times 10^{-8}$
CO	846–885	$(3.2\text{--}10) \times 10^{-11}$
HCN	1,299–1,357	$(1.6\text{--}3.5) \times 10^{-10}$
$CO_2$	787–832	$(3.2\text{--}10) \times 10^{-12}$

Table 1 shows the predicted abundances of  $N_2$ , CO,  $PH_3$ ,  $GeH_4$ , HCN and  $CO_2$  in the observable Uranus atmosphere for  $K \approx 10^7\text{--}10^8\ \text{cm}^2\ \text{s}^{-1}$ . Specific kinetic calculations were not done for other potential non-equilibrium gases such as  $C_2H_6$ ,  $CH_3SH$ ,  $CH_3NH_2$  and  $CH_3OH$ , but quench temperatures of  $\approx 1,000$  K may not be unreasonable for these gases<sup>30</sup>; the resulting abundances can then be estimated from Fig. 1. Since precipitation of  $NH_4Cl(s)$  and  $NH_4F(s)$  may be very difficult to quench, HCl and HF are likely to be in equilibrium; however, if the low  $NH_3$  mixing ratios ( $< 10^{-6}$ ) inferred by Gulkis *et al.*<sup>20</sup> hold throughout the Uranian atmosphere there will not be enough  $NH_3$  to react with the HCl and HF, so their equilibrium concentrations could be much higher than indicated in Fig. 1. Non-ideal gas behaviour may increase the pressure-dependent  $N_2$  abundance; at our highest  $N_2$  quench temperature (1,390 K), the pressure may be three times too high<sup>31</sup> and thus the predicted  $N_2$  abundance nine times too small, while at lower temperatures the required corrections becomes smaller.

Once the Voyager observations are in hand, the inverse process, namely deduction of  $K$  values from the observed abundances of  $PH_3$ ,  $GeH_4$  and so on, will be possible using Fig. 2.

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