EQUILIBRIUM AND NONEQUILIBRIUM CHEMISTRY OF SATURN'S ATMOSPHERE: IMPLICATIONS FOR THE OBSERVABILITY OF PH₃, N₂, CO, AND GeH₄

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ABSTRACT

Results are presented for the first comprehensive set of thermochemical equilibrium calculations for several hundred gases in Saturn's hot deep atmosphere. The thermochemical kinetics of the important destruction reactions for the most abundant equilibrium gases are incorporated in a simple chemical-dynamical model to provide predictions of nonequilibrium trace gas abundances in the cool upper atmosphere. A baseline model assuming an adiabatic lapse rate in Saturn's troposphere, 2.5 times solar elemental abundances (except for H₂ and He, where the Voyager data are used), and a vertical eddy diffusion coefficient of K = 2 × 10⁸ cm² s⁻¹, was employed; the sensitivity of the results to variations in elemental abundances and K values was studied. The most abundant nonequilibrium trace gas derived from Saturn's deep atmosphere is predicted to be N₂; other important nonequilibrium species include PH₃, CO, GeH₄, HCN, and CH₃NH₂. Only PH₃ has been observed on Saturn. The observation of PH₃ at 1–3 times solar abundance and the observed upper limit for the GeH₄ mixing ratio of 10⁻¹⁰ presents an apparent paradox: the predicted GeH₄ mixing ratio consistent with this amount of PH₃ is over 70 times greater than its observed upper limit. This paradox is resolved if we take into account the destruction of GeH₄ by reaction with H atoms from NH₃ and PH₃ photolysis and the photochemical destruction of GeH₄ above the clouds, and the fact that we see well below the uppermost clouds on Jupiter but not on Saturn. While vertical mixing from Saturn's deep atmosphere is predicted to be the major source of N₂, PH₃, HCN, and CH₃NH₂ in Saturn's visible atmosphere, photochemical reactions may effectively compete with vertical mixing as a source of CO.

Subject headings: planets; abundances — planets; atmospheres — planets: Saturn

I. INTRODUCTION

The observations of the disequilibrium species PH₃, CO, and GeH₄ on Jupiter (see, e.g., Beer and Taylor 1978; Fink, Larson, and Trefers 1978; Larson, Trefers, and Fink 1977; Larson, Fink, and Trefers 1978; Ridgway, Larson, and Fink 1976, and references therein) and of PH₃ on Saturn (Larson et al. 1980; Courtin et al. 1984) can be used to deduce the strength of vertical mixing in the deep atmospheres of these planets (Prinn and Barshay 1977). These deductions are particularly valuable in the study of the atmospheres of Jupiter and Saturn because they refer to regions of their atmospheres which cannot be sampled by entry probes and which are inaccessible to remote sensing techniques.

Extensive thermochemical calculations of the chemistry of Jupiter’s atmosphere (Lewis 1969; Barshay and Lewis 1978; Fegley and Lewis 1979) show that the observed PH₃, CO and GeH₄ abundances are many orders of magnitude larger than those predicted at complete thermochemical equilibrium in the cool, visible regions of Jupiter’s atmosphere. The observed PH₃, CO, and GeH₄ abundances can, however, be supplied by sufficiently rapid vertical mixing of gas from the hot (800–1300 K) region in Jupiter’s deep atmosphere where their abundances are much greater. Such vertical mixing would have to be rapid enough to transport gas parcels upward to cooler regions before thermochemical reactions destroying the unstable molecules could proceed appreciably. In fact, Prinn and Barshay (1977) demonstrated that the observed CO volume mixing ratio of 10⁻⁸ is compatible with the kinetics of the relevant destruction reactions and with eddy diffusion coefficients (and thus vertical mixing rates) independently estimated from considerations of Jupiter’s emitted heat flux (Stone 1976; Flasar and Gierasch 1977).

This (putative) rapid vertical mixing should also be a source of other disequilibrium species which are transported upward before they are destroyed by thermochemical reactions (e.g., oxidation, sulfurization, hydrogenation, etc.). Adopting this philosophy, Barshay and Lewis (1978) and Fegley and Lewis (1979) proposed a number of other potentially observable chemical probes of Jupiter’s deep atmosphere including AsH₃, H₂Se, HCl, HF, InBr, TII, and SbS. Prinn and Olaguer (1981) extended this approach by using kinetic data for homogeneous gas-phase and heterogeneous iron-catalyzed reactions between N₂ and H₂. They predicted that N₂ may be the most abundant chemical probe of the deep atmosphere with a volume mixing ratio of 0.6–10 × 10⁻⁶, depending on whether iron-catalyzed reactions reforming NH₃ are effective in Jupiter’s deep atmosphere.

However, despite the now extensive body of spectroscopic data for Saturn, no comprehensive thermochemical-dynamical model is available for the deep atmosphere of this planet. Such a model would have great utility for interpreting existing spectroscopic data, for guiding future observations, and for planning experiments on an entry probe mission.

In this paper we present the results of the first set of comprehensive thermochemical calculations on the chemistry of several hundred gases in Saturn’s atmosphere. Kinetic calculations for selected gas-phase and heterogeneous reactions are also presented. The results of these calculations are then used for several purposes: (a) interpreting the abundance of the observed PH₃ in terms of vertical mixing from specific atmospheric levels, (b) predicting other potentially observable
chemical probes of Saturn’s deep atmosphere, (c) placing upper limits on gas abundances from deep atmospheric sources, (d) contrasting the inferred chemistry and dynamics of the deep atmospheres of Jupiter and Saturn, and (e) evaluating models for the origin and composition of Saturn.

II. THERMOCHEMICAL MODEL OF SATURN’S ATMOSPHERE

A variety of evidence (e.g., infrared, microwave, and radio-wavelength observations) indicates that Saturn, like Jupiter, has a deep convective atmosphere. Compositional models also indicate that Saturn’s deep atmosphere is convective (see Hubbard and Stevenson 1984, and references therein). Assuming that the temperature gradient in the atmosphere beneath the tropopause is adiabatic, and taking $T_0 = 136$ K at $P_0 = 1$ bar (Prinn et al. 1984), the temperature-pressure profile in Saturn’s deep atmosphere was calculated stepwise using the relationship

$$\log_{10} \left( \frac{P_{n+1}}{P_n} \right) = \frac{C_p}{R} \log_{10} \left( \frac{T_{n+1}}{T_n} \right),$$

(1)

where $C_p$ is the temperature-dependent heat capacity of atmospheric gas, $n = 0, 1, 2, \ldots$, and $R$ is the universal gas constant. The atmospheric composition must be known before equation (1) can be used.

Prinn et al. (1984) critically reviewed the available Earth-based, Earth-orbital, and Voyager spectroscopic observations of Saturn’s atmosphere. This summary shows that while Saturn’s atmosphere has approximately solar composition, it is apparently slightly depleted in He and is enriched in ice- and rock-forming elements relative to their solar composition values as defined by Cameron (1982). Based on this critical review, we have adopted a chemical model for Saturn’s atmosphere with $\text{H}_2$ and $\text{He}$ volume mixing ratios of 0.932 and 0.068 respectively. The carbon mixing ratio is set equal to the observed $\text{CH}_4$ mixing ratio, which is about 2.5 times the solar value, and the mixing ratios of all other elements are also set equal to 2.5 times their solar composition values. (The effects of selected variations in these mixing ratios has also been investigated and will be discussed later). This chemical model was also used to calculate a depth scale for the calculated Saturn adiabat assuming hydrostatic equilibrium. Thus, in finite difference form,

$$Z_{n+1} - Z_n = C_p(T_{n+1} - T_n)/(\mu g),$$

(2)

where $Z$ is depth, $\mu$ is the molecular weight of the atmospheric gas (2.15 g mole $^{-1}$), and $g$ is the mean gravitational acceleration over the entire planet (1117 cm s $^{-2}$). The starting point is $T_0 = 136$ K, $Z_0 = 0$ km.

The chemical elements which are included in our calculations were chosen on the basis of their solar abundance and volatility. Detailed calculations of thermochemical equilibrium were done for the elements H, O, C, N, S, Fe, P, F, Ge, and Se. Scaling of the calculations presented by Lewis (1969), Barshay and Lewis (1978), and Fegley and Lewis (1979) for Jupiter were done for many other elements which are less interesting because of lower abundances or lower volatilities or both. Thus, for example, it is quite easy to show that Mg, Si, Na, and K are totally condensed out of the Jovian atmosphere at levels hundreds of kilometers beneath the visible cloud tops, then the same situation will prevail on Saturn. Analogously, volatile but extremely minor constituents of the Jovian atmosphere such as $\text{Hg}$, InBr, and TII will also be present on Saturn at abundances which are easily calculated by scaling (see, e.g., calculations in § 4.1 of Prinn et al. 1984). In this fashion a total of 44 elements and approximately 700 compounds (see Appendices to Barshay and Lewis 1978 and Fegley and Lewis 1979) has been considered.

The thermochemical equilibrium calculations were done by simultaneously considering the constraints of mass balance and chemical equilibrium. Calculations were done at temperatures ranging from 300 to 3000 K along the calculated Saturn adiabat. A detailed description of the general method used is given by Barshay and Lewis (1978). Thermodynamic data were taken from several standard sources, such as the JANAF Tables (Stull and Prophet 1971–1985); Kelley (1960); Kelley and King (1961); Stull, Westrum, and Sinke (1969); Wagman et al. (1968); and Glushko et al. (1978–1982). The results of these calculations are summarized in Figures 1–4, in which volume mixing ratios of various gases along the Saturn adiabat are plotted as a function of inverse temperature. In order to simplify the graphical representations, not all the gases included in the calculations are plotted. However, the most abundant gases for each element are always plotted, and the gases not illustrated are generally $\leq 10^{-6}$ of the abundance of that element.

III. RESULTS OF THERMOCHEMICAL EQUILIBRIUM CALCULATIONS

The calculated equilibrium mixing ratios of the most abundant carbon-bearing gases are illustrated in Figures 1 and 2. Methane is the most abundant carbon-bearing gas at all temperatures less than 3000 K. The free radical CH$_4$ is the second most abundant gas at $T > 2060$ K, CO is the second most abundant gas at 2060 $> T > 1100$ K, and $\text{C}_2\text{H}_6$ is the second most abundant gas at $T < 1100$ K. No other carbonaceous gases have mixing ratios greater than $10^{-18}$ at temperatures of 1000 K or lower.

Both $\text{C}_2\text{H}_4$ and $\text{C}_2\text{H}_6$ have been observed in Saturn’s atmosphere and have mixing ratios of $8 \times 10^{-8}$ and $4 \times 10^{-6}$ respectively at pressures less than 20 mbar (Prinn et al. 1984). As Prinn et al. (1984) further point out, the $\text{C}_2\text{H}_2$ and $\text{C}_2\text{H}_4$ mixing ratios and their rapid increase at higher pressures are compatible with photochemical sources for these gases. Our calculations show that comparable mixing ratios for $\text{C}_2\text{H}_6$ and $\text{C}_2\text{H}_2$ in thermochromic equilibrium with atmospheric gases are not reached until temperatures greater than 3000 K, over 3000 km beneath the visible cloud tops. Thus, a major deep atmospheric contribution to the observed abundances of $\text{C}_2\text{H}_2$ and $\text{C}_2\text{H}_6$ is not expected. Finally, hydrocarbons with three or more carbon atoms, and other organic compounds (e.g., acids, alcohols, aldehydes, esters, ketones, etc.) with two or more carbon atoms have negligible mixing ratios in thermochromic equilibrium at any temperature.

The calculated equilibrium abundances of the important hydrogen, oxygen, nitrogen, sulfur, and fluorine compounds are also given in Figures 1 and 2. While $\text{H}_2$, $\text{H}_2\text{O}$, $\text{NH}_3$, $\text{H}_2\text{S}$, and HF are the predicted major gases of $\text{H}$, O, N, S, and F respectively, only H$_2$ and NH$_3$ have been observed on Saturn. The absence of H$_2$O and H$_2$S in Saturn’s upper atmosphere can be plausibly explained by condensation to form clouds of aqueous NH$_3$, water ice, and NH$_3$SH (Weidenschilling and Lewis 1973; Prinn et al. 1984; Atreya and Romani 1985). Larson et al. (1980) point out that their upper limit to Saturn’s water abundance (<2 cm amagat) is consistent with the H$_2$O saturated vapor pressure at the assumed temperature (175 K) of the 5 $\mu$m line-forming region (Fink and Larson 1978). Prinn et al. (1984) note that as a result of condensation the H$_2$S...
Fig. 1.—Equilibrium abundances of some carbon-containing gases along the model adiabatic (P, T)-profile in Saturn's atmosphere. The horizontal scales indicate temperature and depth along the Saturnian adiabat.

mixing ratio decreases very rapidly above the NH$_4$SH cloud base (224 K, 4.7 bars for 2.5 times solar N and S abundances) with a scale height $h \approx 3$ km. Solar UV photolysis would reduce the H$_2$S abundance in Saturn's upper atmosphere even further. Finally, HF is removed by condensation at 330 K to form NH$_4$F(s), which will probably dissolve in the predicted aqueous NH$_3$ clouds.

N$_2$ is the second most abundant nitrogen-bearing gas at all temperatures less than 3000 K and is potentially the most abundant nonequilibrium species in the upper atmosphere (Prinn and Oulaguer 1981). The thermochemical kinetics of N$_2$ formation and destruction reactions and the relative contributions of thermochemical and photochemical (Atreya, Kuhn, and Donahue 1980) N$_2$ sources will be considered later. All other N species which could potentially be mixed up to visible levels have very low abundances. The deep atmospheric

Fig. 2.—As in Fig. 1 but for H$_2$, He, and oxygen-, nitrogen-, and sulfur-containing gases
sources for some of these gases (e.g., for HCN and CH$_3$NH$_2$) may be comparable nevertheless to the predicted photochemical sources (Kaye and Strobel 1984) and are therefore of interest. For example, Lewis and Fegley (1984) suggested that rapid vertical mixing provides the dominant contribution to tropospheric HCN and CH$_3$NH$_2$ on Jupiter.

The calculated equilibrium abundances of phosphorus compounds are shown in Figure 3. It is immediately apparent that if complete thermochemical equilibrium is attained, then the abundance of PH$_3$ in the visible atmosphere will be negligible. However, the observations reviewed by Prinn et al. (1984) show PH$_3$ mixing ratios of 0.2–2 × 10$^{-6}$, which are 32–33 orders of magnitude larger than the PH$_3$ mixing ratio predicted assuming thermochemical equilibrium in the visible atmosphere. The PH$_3$ observations are direct evidence for the existence of a potent disequilibrating mechanism such as rapid vertical mixing.

Sufficiently vigorous vertical mixing should also have a noticeable effect on the GeH$_4$ abundance. Figure 4 displays the calculated equilibrium abundances of Ge- and Se-bearing gases. Prinn et al. (1984) note that the observed GeH$_4$ mixing ratio on Jupiter of ~7 × 10$^{-10}$ (Kunde et al. 1982; Fink, Larson, and Trefers 1978) could be supplied by vertical mixing from the 800 K level (Fegley and Lewis 1979). Taking this temperature as the quench level for thermochemical reactions destroying GeH$_4$ leads to the prediction that rapid vertical mixing on Saturn should supply a GeH$_4$ abundance equivalent to a mixing ratio of 6 × 10$^{-9}$ (see Fig. 4) in the visible atmosphere. However, GeH$_4$ has not been observed in Saturn’s atmosphere, and the upper limit of 10$^{-10}$ for the GeH$_4$ mixing ratio determined by Larson et al. (1980) is 60 times smaller than the abundance predicted by this simple analogy with Jupiter. This apparent discrepancy suggests that significant differences may exist between the vertical mixing rates or the
chemistry in the deep atmospheres of Jupiter and Saturn. In order to explore this possibility, we must examine the thermochemical kinetics of the reactions involved in the formation and destruction of PH$_3$, N$_2$, CO, and GeH$_4$.

IV. KINETICS OF THERMOCHEMICAL REACTIONS IN SATURN’S DEEP ATMOSPHERE

The attainment of thermochemical equilibrium for a gas requires that the time constant $t_{\text{chem}}$ for the fastest reactions producing and destroying it is much shorter than the time constant $t_{\text{conv}}$ for transporting the gas to a cooler region of the atmosphere where these reactions will be kinetically inhibited. Typically, $t_{\text{chem}}$ increases more rapidly with increasing altitude (i.e., decreasing temperature) than $t_{\text{conv}}$. Prinn and Barshay (1977) define the altitude $Z = Z^*$ at which $t_{\text{chem}} = t_{\text{conv}}$ as the quench level for the gas. At lower levels in the atmosphere $Z < Z^*$, $t_{\text{chem}} < t_{\text{conv}}$ holds, and thermochemical equilibrium is reached. Conversely, at higher altitudes in the atmosphere $Z > Z^*$, $t_{\text{chem}} > t_{\text{conv}}$ holds, and there is insufficient time to reach thermochemical equilibrium. For reactions with sufficiently large activation energies, once $t_{\text{chem}} \approx t_{\text{conv}}$, vertical mixing over a very small altitude increment compared to the atmospheric density scale height $H$ results in thermochemical reactions being quenched at the equilibrium concentrations prevailing at level $Z^*$.

The quench level $Z^*$ differs for each species considered. We derive $Z^*$ by identifying the level where $t_{\text{chem}} = t_{\text{conv}} \approx H^2/K$, where $K$ is the vertical eddy diffusion coefficient. The quantity $K$ is taken as $2 \times 10^8$ cm$^2$ s$^{-1}$ in our baseline model. This value is consistent with $K$ values of $10^{-7}$–$10^{-8}$ cm$^2$ s$^{-1}$, estimated for Saturn’s deep atmosphere using the theory for free convection and a knowledge of Saturn’s internal heat flux (Prinn et al. 1984). Note that this $K$ value refers to the region 1000–2000 km below the visible clouds. Values of $K$ for the visible part of the atmosphere are different and are discussed later. Alternatively, we can define $Z^*$ as the level at which the equilibrium mixing ratio of the species equals its “quenched” mixing ratio, as observed in the visible atmosphere, and proceed to estimate $K$ from the formula

$$K = H^2/t_{\text{chem}}(Z^*) .$$

Here we are interested in particular in the thermochemical kinetics of the gases PH$_3$, CO, GeH$_4$, and N$_2$. Prinn and Barshay (1977) and Prinn and Olaguer (1981) assumed that the rate-determining reactions for the gas-phase conversion of CO to CH$_4$ and of N$_2$ to NH$_3$ are

$$\text{CO} + \text{H}_2 = \text{CH}_2\text{O} ,$$
$$\text{CH}_2\text{O} + \text{H}_2 = \text{CH}_3 + \text{OH} ,$$
$$\text{N}_2 + \text{H}_2 = \text{NH} + \text{NH} .$$

The corresponding equations for the CO and N$_2$ chemical lifetimes are

$$t_{\text{chem}}(\text{CO}) \approx [\text{CO}] / k_5[H_2][\text{CH}_2\text{O}] \approx 1/K_4 k_5[H_2]^2 ,$$
$$t_{\text{chem}}(\text{N}_2) \approx 1/k_6[H_2] ,$$

where the square brackets denote the number concentrations of the particular molecules, $K_4$ is the equilibrium constant for reaction (4), and $k_5$ and $k_6$ are the rate constants for reactions (5) and (6) given by the equations

$$k_5 \approx 2.3 \times 10^{-10} \exp (-36,200/T) \text{ cm}^3 \text{ s}^{-1} ,$$
$$k_6 \approx 8.45 \times 10^{-8} \exp (-81,515/T) \text{ cm}^3 \text{ s}^{-1} .$$

The relevant number concentrations used in equations (7) and (8) are taken from the results of the thermochemical equilibrium calculations and our atmospheric model. We emphasize that there may exist more rapid (but as yet unidentified) gas-phase destruction reactions for CO and N$_2$ than (4) and (5). To place an upper limit on their destruction rates we also consider the case when reactions (4), (5), and (6) are catalyzed by metallic iron particles.

Heterogeneous iron-catalyzed reactions for N$_2$ + H$_2$ were considered using the computational method described by Prinn and Olaguer (1981). Calculations were done for iron particles with radii of 1, 2, 4, and 6 $\mu$m; coalescence and sedimentation limit the upward transport of larger particles, and coagulation constrains the population of smaller particles. Figure 5 shows that the predicted N$_2$ mixing ratio for heterogeneous catalysis increases with decreasing $K$. If we increase $t_{\text{conv}}$ (i.e., decrease the vertical eddy diffusion coefficient $K$), we also increase $t_{\text{chem}}$ because less vigorous vertical mixing results in lower densities of the metallic iron catalyst in the relevant portion of the atmosphere. The points where $K = wH$ (the product of the Stokes sedimentation velocity $w$ and the atmospheric density scale height $H$) for each particle radius are marked with arrows in Figure 5.

We are unaware of any relevant experimental data for heterogeneous iron-catalyzed reactions converting CO to CH$_4$. Therefore, heterogeneous catalysis of CO destruction was modeled by using the same $t_{\text{chem}}$ values (for a given particle radius and $K$ value) calculated for the N$_2$ + H$_2$ reactions. Because the presence of iron metal “clouds” on Saturn is only hypothetical (the iron may be sequestered in the core), and because the efficiency of iron catalysis may be reduced by various surface coatings on iron particles (e.g., FeS and Fe$_3$P), we regard the catalyzed N$_2$ and CO abundance profiles as firm lower limits. (Note also that the calculated base of the iron metal “cloud” on Saturn is at 4700 K and 560 km and our ability to accurately model cloud physics in such conditions is open to question.)

The rate-determining reaction and the corresponding rate constant and chemical time constant for destruction of HCN are taken from Prinn and Fegley (1981):

$$\text{HCN} + \text{H}_2 = \text{CH}_2\text{O} + \text{NH} ,$$

$$t_{\text{chem}}(\text{HCN}) \approx 1/k_1[H_2] ,$$

$$k_1 \approx 1.08 \times 10^{-8} \exp (-70,456/T) \text{ cm}^3 \text{ s}^{-1} .$$

The thermochemical destruction of PH$_3$ proceeds via the overall reaction

$$4\text{PH}_3 + 6\text{H}_2\text{O} \rightarrow \text{P}_2\text{O}_6 + 12\text{H}_2 .$$

Prinn et al. (1984) suggested one possible mechanism for this reaction in the gas phase

$$\text{PH}_3 = \text{PH} + \text{H}_2 ,$$
$$\text{H}_2\text{O} = \text{OH} + \text{H} ,$$
$$\text{H}_2 = \text{H} + \text{H} ,$$
$$\text{PH} + \text{OH} = \text{PO} + \text{H}_2 ,$$
$$\text{PO} + \text{OH} = \text{PO}_2 + \text{H} ,$$

where M is another atom or molecule and reaction (18) is the rate-determining step. The chemical lifetime of PH$_3$ is there-
fore given by

\[ t_{\text{chem}}(\text{PH}_3) \approx \frac{[\text{PH}_3]}{(k_{18} [\text{PH}] [\text{OH}])} = (K_{17} [\text{H}_2])^{\frac{1}{2}} (k_{18} K_{15} K_{16} [\text{H}_2 \text{O}]) \]  \( (21) \)

where the \( K \)'s are known equilibrium constants and we estimate the rate constant \( k_{18} \approx 10^{-9} \text{ cm}^3 \text{ s}^{-1} \) at temperatures above 1000 K.

The thermochemical destruction of \( \text{GeH}_4 \) principally proceeds by the net reaction

\[ \text{GeH}_4 + \text{H}_2 \text{S} \rightarrow \text{GeS} + 3\text{H}_2 \]  \( (22) \)

although an analogous reaction

\[ \text{GeH}_4 + \text{H}_2 \text{Se} \rightarrow \text{GeSe} + 3\text{H}_2 \]  \( (23) \)

is also important (see Fig. 4). We propose a simple mechanism for reaction (22),

\[ \text{GeH}_4 = \text{GeH} + \text{H}_2 + \text{H} \]  \( (24) \)
\[ \text{H}_2 \text{S} = \text{H} + \text{SH} \]  \( (25) \)
\[ \text{GeH} + \text{SH} \rightarrow \text{GeS} + \text{H}_2 \]  \( (26) \)

where reaction (26) is the rate-determining step. In this case the chemical lifetime of \( \text{GeH}_4 \) is given by

\[ t_{\text{chem}}(\text{GeH}_4) \approx \frac{[\text{GeH}_4]}{(k_{26} [\text{GeH}] [\text{SH}])} = K_{17} [\text{H}_2]^2 (k_{26} K_{24} K_{25} [\text{H}_2 \text{S}]) \]  \( (27) \)

with \( k_{26} \) also estimated as \( 10^{-9} \text{ cm}^3 \text{ s}^{-1} \) at temperatures above 1000 K. The proposed mechanisms for the conversion of \( \text{PH}_3 \) to \( \text{P}_2\text{O}_6 \) and of \( \text{GeH}_4 \) to \( \text{GeS} \) are difficult to evaluate in the absence of laboratory data on the kinetics of reactions (14) and (22). However, we can use the estimated expressions for the \( \text{PH}_3 \) and \( \text{GeH}_4 \) chemical lifetimes and our baseline chemical-dynamical model to predict their expected abundances on Jupiter, where both gases have been observed. The predicted \( \text{PH}_3 \) and \( \text{GeH}_4 \) mixing ratios are \( 5 \times 10^{-7} \) and \( 6 \times 10^{-10} \) (see Fig. 6). The observed \( \text{PH}_3 \) and \( \text{GeH}_4 \) mixing ratios are \( 6 \pm 2 \times 10^{-7} \) and \( 7 \pm 2 \times 10^{-10} \) (Larson, Fink, and Trefers 1978; Kunde et al. 1982). The agreement between the predicted and observed values indicates that our treatment of these two gases is a reasonable first approximation.

V. RESULTS

The results of our chemical-dynamical model for Saturn are presented in Table 1. The predicted \( \text{PH}_3 \) mixing ratio is identical to that observed by Hanel et al. (1981) and very close to that (0.9 \( \times 10^{-7} \)) observed by Larson et al. (1980). However, the predicted \( \text{GeH}_4 \) mixing ratio of \( 7 \times 10^{-9} \) is about 70 times larger than the upper limit given by Larson et al. (1980). Our calculations also predict a CO mixing ratio of 0.07–1.3 \( \times 10^{-10} \) and an \( \text{N}_2 \) mixing ratio of 0.2–2 \( \times 10^{-6} \), depending on whether iron-catalyzed heterogeneous reactions are effective (see Fig. 5). Neither CO nor \( \text{N}_2 \) has yet been observed on Saturn, but the levels predicted here are undoubtedly beyond current capabilities of remote sensing, particularly given the infrared inactivity of \( \text{N}_2 \).

The apparent discrepancy between the predicted and observed \( \text{GeH}_4 \) abundances could be due to several possible effects. Uncertainty in the estimated rate constant for reaction (26) could lead to an overestimate of the amount of \( \text{GeH}_4 \) transported into Saturn's upper atmosphere by rapid vertical mixing. Alternatively, our neglect of \( \text{GeH}_4 \) loss by conversion to \( \text{GeS} \) could also lead to an overestimate of the \( \text{GeH}_4 \) abundance. Heterogeneous catalysis of \( \text{GeH}_4 \) destruction by different types of cloud particles, which would again lead to lower \( \text{GeH}_4 \) abundances, is also a possible explanation. However, the calculated \( \text{GeH}_4 \) abundances are relatively insensitive to the

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exact value of $k_{26}$; varying $k_{26}$ from $10^{-7}$ to $10^{-11}$ cm$^3$ s$^{-1}$ changes the calculated GeH$_4$ abundances by only a factor of 1.6. Also, GeSe is a minor species relative to GeS over most of the temperature range where thermochemical reactions are expected to be rapid. The two gases do not have equal abundances until below 670 K, by which level Ge(s) condensation is the major GeH$_4$ loss mechanism. Finally, the good agreement between the predicted and observed GeH$_4$ abundances on Jupiter suggests that heterogeneous catalysis of GeH$_4$ destruction is not significant on that planet nor, by inference, on Saturn. The same types of condensate cloud particles are calculated to condense on Saturn, and there is no compelling reason to believe that the same types of particles should be more effective as catalysts on Saturn than on Jupiter. There is also no evidence for heterogeneous catalysis of PH$_3$ destruction on Saturn and not on Jupiter.

The (apparent) partitioning of He into Saturn’s core may indicate similar behavior for ice- and rock-forming elements on Saturn. Thus, Saturn’s atmosphere may be depleted in Ge instead of having a Ge abundance of 2.5 times solar as assumed in our calculations. Again, credible arguments suggest that this proposed mechanism is not significant for Ge. Both P and Ge are rock-forming elements which are expected to be accreted in their solar P/Ge ratio. Thus, if rock-forming elements were depleted by partitioning into Saturn’s core, equal P and Ge depletions would be expected. The observation of PH$_3$ in Saturn’s atmosphere shows that equal P and Ge depletions have not occurred. Selective Ge partitioning into Saturn’s core cannot be unambiguously ruled out. However, Stevenson (1982) has argued that accretion of icy planetesimals after Saturn’s formation has enriched the upper atmosphere in heavier constituents, which presumably includes rock constituents like Ge.

Another alternative is that the reported GeH$_4$ upper limit is not representative of its global tropospheric abundance on Saturn. This could be due to observational problems or to the fact that Saturn’s 5 μm spectral window is not associated with “hot spots” in the planetary cloud cover, as is the case on Jupiter. Larson et al. (1980) report that Saturn’s 5 μm brightness temperature (190 K, vs. 300 K for Jupiter) originates not

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**Table 1**

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* Predictions assume solar composition and $K = 2 \times 10^8$ cm$^3$ s$^{-1}$.
* Predictions assume 2.5 times solar composition and $K = 2 \times 10^8$ cm$^3$ s$^{-1}$.
* Predictions assume $k_{26} = k_{26} \approx 10^{-9}$ cm$^3$ s$^{-1}$.
* Jupiter values from Prinn and Barshay 1977.
* Jupiter values from Prinn and Oelugay 1981.
from deep in the atmosphere but from levels immediately above the visible cloud tops. If the reported GeH₄ upper limit is valid, it may indicate that GeH₄ destruction occurs above the visible clouds on both Jupiter and Saturn by another irreversible process such as solar UV photolysis or reactions with H atoms from NH₃ or PH₃ photolysis. Mahncke and Noyes (1935) studied the UV absorption spectrum of GeH₄ and reported absorption coefficients for the 160–170 nm region. The absorption is apparently continuous, and the ultimate photochemical decomposition products are metallic Ge and H₂. Interestingly, the absorption cross section of GeH₄ is large in the wavelength region longward of the strong C₂H₆ and CH₄ absorptions at ≤160 nm but shortward of the strong C₂H₂, PH₃, and NH₃ absorptions above 170 nm.

A one-dimensional chemical-dynamical model was used to model GeH₄ photolysis in the 140–180 nm region at a latitude of 30° in Saturn’s upper atmosphere. The solar UV flux digitized in 5 nm increments was obtained by scaling to Saturn the data of Heath and Thekaekara (1972). Absorption coefficients σ for CH₄, C₂H₂, C₂H₆, NH₃, PH₃, and GeH₄ were taken from Mount, Warden, and Moos (1977), Mount and Moos (1978), Strobel (1973), Sullivan and Holland (1966), Kley and Welge (1965), Halmann (1965), and Mahncke and Noyes (1935). The available GeH₄ absorption coefficients were extrapolated down to σ = 7 × 10⁻²⁴ cm² at 180 nm and taken constant at σ = 10⁻¹⁷ cm² at ≤160 nm. Vertical distribution profiles for C₂H₂, C₂H₆, C₂H₄, PH₃, and NH₃ were taken from Prinn et al. (1984). The PH₃ profile T1 was used above the 100 mbar level, and a constant PH₃ mixing ratio of 1 × 10⁻⁶ was assumed at lower levels. A GeH₄ mixing ratio of 7 × 10⁻⁹ at the lower boundary (1.7 bars) was used.

Calculations of τchem for GeH₄ photolysis were done at 10 km increments in the 30–500 mbar region (which was also studied by Kaye and Strobel 1984). These photolysis lifetimes were computed ignoring the self-absorption of GeH₄, an assumption we justify a posteriori. The results show τchem = 5.7 × 10⁴–4.5 × 10⁵ s in the 30–500 mbar region with most of the GeH₄ photolysis occurring in the upper 30 km of this region. These τchem values are longer than the convective mixing times τconv = 4H²/K calculated from the three vertical eddy diffusion coefficient profiles in the upper atmosphere model of Kaye and Strobel (1984). (Profile A represents slow vertical mixing, K ≈ 10⁴ cm² s⁻¹, near the NH₃ cloud level; profile B represents rapid vertical mixing, K ≈ 10³ cm² s⁻¹, up to just below the tropopause but decreasing to 10⁴ cm² s⁻¹ just above the tropopause; and profile C with K = 10⁵ cm² s⁻¹ independent of altitude.) Consequently, except in the upper 30 km of this region, photolysis is not an important loss mechanism for GeH₄. Hydrogen abstraction by reaction with H atoms,

\[ H + \text{GeH}_4 \rightarrow \text{GeH}_3 + \text{H}_2, \quad (29) \]

appears to be in comparison a much more important loss mechanism for GeH₄.

Austin and Lampe (1977) and Choo, Gaspur, and Wolf (1975) both reported values for k₂₉ at 300 K. Unfortunately, these two determinations disagree by a factor of 215. We have therefore done calculations with both values by adopting the estimated activation energy (Austin and Lampe 1977) of 2.5 kcal mol⁻¹ for SiH₄ abstraction for reaction (29) as well. The two derived expressions for k₂₉ are denoted “fast” (Choo, Gaspur, and Wolf 1975) and “slow” (Austin and Lampe 1977):

\[ \text{“fast” } k_{29} = 2.7 \times 10^{-8} \exp \left( -1258/T \right) \text{ cm}^3 \text{ s}^{-1}, \quad (30) \]

\[ \text{“slow” } k_{29} = 1.2 \times 10^{-10} \exp \left( -1258/T \right) \text{ cm}^3 \text{ s}^{-1}. \quad (31) \]

Using these two values, together with the upper atmosphere model, vertical eddy diffusion coefficient profiles, and H atom concentration profiles of Kaye and Strobel (1984), we estimate the chemical lifetime of GeH₄ due to hydrogen abstraction in Saturn’s upper atmosphere from \( t_{\text{chem}} = 1/k_{29}[\text{H}] \).

The chemical lifetime of GeH₄ due to photolysis and hydrogen abstraction is plotted in Figure 7, where the “long” and “short” \( t_{\text{chem}} \) profiles correspond to the “slow” and “fast” expressions for \( k_{29} \), and the \( t_{\text{conv}} \) profiles A, B, C refer to the three vertical eddy diffusion coefficient profiles of Kaye and Strobel (1984). Hydrogen abstraction is an efficient GeH₄ destruction mechanism in the 30–500 mbar region of Saturn’s upper atmosphere if vertical mixing is relatively slow (profiles A and B) and if the “fast” expression for \( k_{29} \) is appropriate.

GeH₄ concentration profiles were calculated for the three \( t_{\text{conv}} \) profiles using the “short” \( t_{\text{chem}} \) values. Since GeH₄ is not an important source of H atoms, its profile can be derived simply from the formulae

\[ f(z) = f(0) \exp \left( -z/H \right), \quad (32) \]

\[ h = [-1/2H + (1/4H^2 + 1/Kt_{\text{chem}}^{1/2})^{-1}]^{-1}. \quad (33) \]

(Prinn et al. 1984), where \( f \) is the mixing ratio of GeH₄, \( z \) is altitude, \( h \) is the mixing ratio scale height, and the GeH₄ mixing ratio is 7 × 10⁻⁹ at \( z = 0 \)(1.7 bars). The \( t_{\text{chem}} \) and \( t_{\text{conv}} \) profiles in Figure 7 were extrapolated down to the 1.7 bar level in Saturn’s atmosphere in these calculations. Figure 8 displays the resulting GeH₄ concentration profiles and shows that GeH₄ mixing ratios less than 10⁻¹⁰ are obtained in cases A and B but not C (where \( K = 10^5 \text{ cm}^2 \text{ s}^{-1} \) throughout the region considered). Self-absorption of UV by GeH₄ is negligible for each of the profiles shown. Essentially no dropoff in GeH₄ is obtained in cases A and C for the “long” \( t_{\text{chem}} \) profiles (Fig. 7), and the concentration profile for case B for the “long” \( t_{\text{chem}} \) is very similar to case C for the “short” \( t_{\text{chem}} \). Note that, even in the unlikely case of no depletion, GeH₄ is not a dominant source of UV opacity. Thus, for relatively slow vertical mixing and the faster of two hydrogen abstraction rate constants, we conclude that substantial GeH₄ depletions can be produced several tens of kilometers above the NH₃ cloud base on Saturn (located at 1.7 bars, 162 K for 2.5 times solar composition; Prinn et al. 1984).

The final alternative which we have considered is that vertical mixing in Saturn’s deep atmosphere is slower than on Jupiter. In this case, less GeH₄ would be transported into the upper atmosphere. The effects of varying eddy diffusion coefficients on the “quenched” abundances of PH₃ and GeH₄ are illustrated in Figure 6. The PH₃ abundance is independent of the assumed eddy diffusion coefficient until \( K \approx 3 \times 10^9 \text{ cm}^2 \text{ s}^{-1} \); however, the GeH₄ abundance decreases with decreasing \( K \) over the entire range considered. An eddy diffusion coefficient of \( 5 \times 10^2 \text{ cm}^2 \text{ s}^{-1} \) is large enough to provide the solar abundance of PH₃ in Saturn’s upper atmosphere (consistent with the lower range of the PH₃ observations summarized by Prinn et al. 1984) but gives only 25% of the calculated GeH₄ abundance in our baseline model. This GeH₄ mixing ratio, 2 × 10⁻⁹, is still 20 times larger than the reported GeH₄ upper limit; a GeH₄ mixing ratio of 2 × 10⁻¹⁰ consistent with the
Fig. 7.—Comparison of GeH₄ chemical lifetime $t_{\text{chem}}$ due to hydrogen abstraction and photo-dissociation with convective mixing times $t_{\text{conv}}$ in Saturn's upper atmosphere. The three separate diagrams correspond to the three vertical eddy diffusion coefficient profiles in Kaye and Strobel (1984). The "long" and "short" $t_{\text{chem}}$ profiles correspond to two different rate constants for hydrogen abstraction from GeH₄ (see text).

Fig. 8.—GeH₄ concentration profiles in Saturn's upper atmosphere. Three profiles corresponding to the "short" $t_{\text{chem}}$ profiles for the three assumed vertical eddy diffusion coefficient profiles are shown. The "long" $t_{\text{chem}}$ profiles yield essentially no GeH₄ depletion except for case B, which is very similar to curve C (see text).
The upper limit requires \( K = 1 \text{ cm}^2 \text{s}^{-1} \). Values of \( K \) as low as 1–500 cm\(^2\) s\(^{-1}\) are totally at odds with the values needed to explain transport of heat from the interior. Even if such values of \( K \) were possible, it is clear that we could not explain simultaneously the observed PH\(_3\) and GeH\(_4\) abundances using the same \( K \) value.

The abundances of two other potential chemical probes (CO and HCN) show large variations with changes in the assumed eddy diffusion coefficient and in principle are thus very useful for constraining vertical mixing rates. The calculated abundance profiles as a function of the assumed eddy diffusion coefficients are given in Figure 5 for CO, HCN, and N\(_2\). The predicted CO mixing ratio corresponding to \( K = 2 \times 10^{4} \text{ cm}^2 \text{s}^{-1} \) in our baseline model is \( 1.3 \times 10^{-10} \) for gas-phase destruction and \( 7 \times 10^{-12} \) for iron-catalyzed destruction. A Jupiter-like CO mixing ratio of \( 10^{-9} \) would require \( K > 2 \times 10^{10} \text{ cm}^2 \text{s}^{-1} \), which is very unlikely. No CO abundance estimates are available for Saturn, and in any case there is a plausible competing source for CO to that discussed in this paper. In particular, Prather, Logan, and McElroy (1978) and Strobel and Yung (1979) described models for CO production in Jupiter’s upper atmosphere utilizing meteoritic debris and the Galilean satellites, respectively, as sources of extra-Jovian oxygen. It is certainly plausible that Saturn’s rings may act as extra-Saturnian oxygen sources and that similar mechanisms to those proposed by Prather et al. and Strobel and Yung may operate on Saturn. Thus, spectroscopic observations of CO on Saturn (or Jupiter) cannot unambiguously be interpreted in terms of a vertical mixing source unless vertical distributions can be measured or inferred from the observations.

Observational upper limits (Larson et al. 1980; Tokunaga et al. 1981) are available for HCN on Saturn. The more stringent upper limits of Tokunaga et al. (1981) correspond to an HCN mixing ratio of \( 7 \times 10^{-9} \) in Saturn’s troposphere and \( 8 \times 10^{-9} \) in Saturn’s stratosphere. From Figure 5 we see that these upper limits correspond to \( K < 4 \times 10^{14} \text{ cm}^2 \text{s}^{-1} \). This is not a useful upper bound to the eddy diffusion coefficient in Saturn’s deep atmosphere, since the eddy vertical transport velocity is certainly constrained to be less than the sound speed \( v_s \) (\( \approx 3.0–4.3 \times 10^{5} \text{ cm s}^{-1} \) in the 1000–2000 K region), so the eddy diffusion coefficient is certainly constrained by

\[
K < v_s H \approx 1–3 \times 10^{13} \text{ cm}^2 \text{s}^{-1},
\]

where \( v_s \) is calculated for a solar composition H\(_2\) + He gas. Using expression (34), the maximum HCN abundance which can be provided by vertical mixing corresponds to a mixing ratio of \( \approx 5 \times 10^{-9} \), which is already 20%–80% smaller than the spectroscopic upper limits.

Kaye and Strobel (1984) predicted HCN abundances produced by solar UV photolysis in Saturn’s upper atmosphere. Their predictions yield HCN mixing ratios less than \( 10^{-12} \) at the 300 mbar level in Saturn’s atmosphere, depending on their assumed eddy diffusion coefficient profiles. These mixing ratios are comparable to HCN mixing ratios predicted for vertical mixing with \( K = 3 \times 10^{10} \text{ cm}^2 \text{s}^{-1} \) and are over 100 times smaller than the predicted HCN mixing ratio of \( 2 \times 10^{-10} \) in our baseline model (in which \( K = 2 \times 10^{8} \text{ cm}^2 \text{s}^{-1} \)). Therefore, it appears that vertical mixing may dominate photochemistry as a source of HCN in Saturn’s troposphere. Assuming that HCN and CH\(_3\)NH\(_2\) remain in conditional chemical equilibrium with each other, vertical mixing will supply more CH\(_3\)NH\(_2\) than HCN by several orders of magnitude (see Fig. 2). Kaye and Strobel (1984) also included CH\(_3\)NH\(_2\) in their calculations and found calculated column densities \( \approx 10^{2–3} \) times smaller than their calculated HCN column densities. Thus, it also appears that vertical mixing may dominate photochemistry as a source of tropospheric CH\(_3\)NH\(_2\).

Atreya, Kuhn, and Donahue (1980) predicted N\(_2\) mixing ratios in Saturn’s upper atmosphere by considering solar UV photolysis of NH\(_3\). They calculated N\(_2\) mixing ratios of \( 1.8 \times 10^{-10} \) to \( 6 \times 10^{-9} \) (depending on the amount of NH\(_3\) and N\(_2\)H\(_4\) supersaturation) at the visible cloud tops. By contrast, the predicted N\(_2\) mixing ratios in our baseline model (which has 2.5 times solar NH\(_3\)) are in the range \( 0.2–2 \times 10^{-6} \) depending on whether heterogeneous catalysis is effective. The homogeneous gas-phase reactions which we have considered for N\(_2\) do not yield mixing ratios less than \( 10^{-6} \) for all K values considered (Fig. 5). The heterogeneous iron-catalyzed reactions do yield lower N\(_2\) mixing ratios, but eddy diffusion coefficients greater than \( 10^{13} \text{ cm}^2 \text{s}^{-1} \) are required to get N\(_2\) mixing ratios as low as those produced photochemically (for reasonable Fe particle sizes which could be transported into the upper atmosphere). Therefore, we also conclude that the dominant source of N\(_2\) in Saturn’s troposphere (as on Jupiter) is vertical mixing.

Finally, we have also considered possible chemical probes of other elements by scaling the calculations of Barshay and Lewis (1978) and Fegley and Lewis (1979) to Saturn. This exercise suggests that very few additional chemical probes with potentially observable abundances are expected on Saturn. The “short list” of probes and their maximum predicted mixing ratios (for our 2.5 times solar composition baseline model) are as follows: H\(_2\)Se (\( \sim 10^{-8} \)), AsH\(_3\) (\( \sim 10^{-9} \)), InBr (\( \sim 10^{-10.5} \)), TI (\( \sim 10^{-10.5} \)), and SbS (\( \sim 10^{-10.3} \)).

VI. CONSTRAINTS ON THE COMPOSITION OF SATURN’S ATMOSPHERE

The relative abundances of some chemical probes such as PH\(_3\), CO, and N\(_2\) are also potentially useful for constraining the composition of Saturn’s bulk atmosphere. Current models for the formation of Saturn lead to the prediction that Saturn’s bulk composition is enriched in ice- and rock-forming elements to varying amounts (see, e.g., Stevenson 1982). The available spectroscopic data reviewed by Prinn et al. (1984) also show that Saturn’s upper atmosphere is enriched in CH\(_3\)H\(_2\), NH\(_3\), and PH\(_3\) by factors of 2.5, 1–3, and 1–4 times, respectively, relative to the solar composition values. Thus it is worthwhile considering cases where ice- and rock-forming elements such as C, N, O, P, and Ge are enriched by factors greater than 2.5 relative to solar composition. As shown by Prinn et al. (1984), this is easily accomplished by examination of the equilibria involved to define scaling laws which relate the enriched cases to our baseline case. If the enrichment factor for elements heavier than H and He relative to our baseline model is \( E \), and the enrichments are not so large as to influence the mixing ratios of H\(_2\) and He, then the equilibria CO and N\(_2\) mixing ratios both simply increase by a factor of \( E^2 \). According to equations (7) and (8) the O and N\(_2\) chemical lifetimes are independent of \( E \), so the CO and N\(_2\) mixing ratios predicted for a given K value also increase simply by a factor of \( E^2 \).

Because the assumed net reaction (22) for GeH\(_4\) destruction involves equimolar amounts of GeH\(_4\) and H\(_2\)S, increases in the assumed elemental abundances do not alter the calculated GeH\(_4\) abundance profile (Fig. 4). According to equation (27), the chemical lifetime of GeH\(_4\) varies as \( E^{-1} \), which produces a
decrease in the GeH₄ mixing ratio predicted for a given K value (Fig. 6), but the effect is relatively small. By contrast, the equilibrium PH₃ mixing ratios for E > 1 increase as E below the P₂O₅ condensation level and decrease as E > 5/6 above this level despite the increased P abundance. In addition, according to equation (21) the PH₃ chemical lifetime varies as E⁻¹, which leads to a further decrease in the PH₃ mixing ratio predicted for a given K value. The results for E = 4 and 20 for PH₃ are shown in Figure 6. For E = 4, eddy diffusion coefficients less than ~10⁷ cm² s⁻¹ yield less PH₃ by vertical mixing than in the baseline model. The situation is even more extreme in the E = 20 case, where all values of K < 10⁻⁵ cm² s⁻¹ yield less PH₃ than in the baseline model. In fact, the latter model for the composition of Saturn's atmosphere is inconsistent with the observed PH₃ abundance range in Saturn's atmosphere except for very rapid vertical mixing (K > 10⁶ cm² s⁻¹). Mixing rates this rapid in the E = 20 case would also yield CO and N₂ mixing ratios greater than 10⁻⁶.6 and 10⁻³.2 respectively.

VII. CONCLUDING REMARKS

The results of our thermochemical equilibrium and kinetic calculations show that the most abundant nonequilibrium species mixed up from Saturn's deep atmosphere are predicted to be N₂, PH₃, GeH₄, and CO. Other less abundant nonequilibrium species produced in the same way are HCN and CH₃NH₂. Vertical mixing appears to be the dominant source of all these species (except perhaps CO) in Saturn's troposphere. Because the abundances of these nonequilibrium species in the upper atmosphere depend on the thermochemistry and dynamics of the very deep atmosphere, they can be regarded as “chemical probes” of these deep, otherwise inaccessible, levels within the planet.

Three chemical probes, PH₃, CO, and GeH₄, have been observed on Jupiter, and our thermochemical kinetic calculations for PH₃ and GeH₄ satisfactorily account for their observed abundances on that planet. However, only PH₃ has been observed on Saturn, and the GeH₄ abundance is reported to be less than 10⁻¹⁶ (mixing ratio). The apparent paradox on Saturn is that the predicted GeH₄ abundance is 70 times larger than this reported upper limit. To resolve this paradox, we have shown that destruction of GeH₄ by reaction with H atoms (from NH₃ and PH₃ photodissociation) and by photodissociation is sufficiently rapid to deplete this gas at least above the tropopause on both Jupiter and Saturn. We propose that this depletion, combined with the fact that the spectroscopic observations at 5 μm on Saturn apply to much higher levels in the atmosphere than on Jupiter, is a possible reason why GeH₄ has not yet been observed on Saturn.

Although Courtin et al. (1984) and Fink et al. (1983) reported that the 5 μm flux is from the 170–190 K, 2 bars level, both groups also found NH₃ mixing ratios less than solar. This is in apparent conflict with the microwave data of Klein et al. (1978) indicating NH₃ mixing ratios of solar or greater beneath the NH₃ cloud base (153 K, 1.4 bars for solar NH₃, 162 K, 1.7 bars for 2.5 times solar NH₃). Thus, as Fink et al. (1983) conclude, the penetration depth of Saturn's 5 μm flux is still unclear.

It is possible to deduce vertical mixing rates in Saturn's deep atmosphere by using the above chemical probes. Our calculations show that CO, GeH₄, and HCN are most useful for this purpose, while N₂ has a relatively flat abundance profile versus assumed eddy diffusion coefficients and is less sensitive in this regard. At the moment a vertical eddy diffusion coefficient K > 10⁶ cm² s⁻¹ appears adequate to explain the PH₃ levels on Saturn. Observations of (any of) the other chemical probes mentioned above will be required to constrain the K value better.

Note added in manuscript 1985 July 31.—Noll, Knacke, and Tokunaga (Goddard Institute for Space Studies Conf. on Outer Planets, 1985 May) reported the detection of CO on Saturn at a mixing ratio of 3 ± 2 × 10⁻⁹. This abundance implies unrealistically rapid vertical mixing (K ≈ 2.5 × 10¹¹ cm² s⁻¹) if the CO is solely due to rapid vertical mixing. If the CO mixing ratio is indeed this large, then the major source must be CO production in Saturn's upper atmosphere.

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