

## Models of the Jovian Upper Atmosphere

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Recent developments in photochemical models of the upper atmosphere of Jupiter and Titan are reviewed. Measurements of the Jovian Lyman alpha airglow favor a homopause value of approximately  $10^7 \text{ cm}^2 \text{ s}^{-1}$  for the eddy diffusion coefficient. A relatively hot exosphere as implied by the electron density measurements results in an extended atmosphere of hydrogen. Larger than solar C/H and N/H ratios are obtained on reinterpretation of the sunlight reflected from Jupiter; and substantially lower ultraviolet photoabsorption cross sections measured for methane and ethane influence the distribution of  $\text{CH}_4$ ,  $\text{NH}_3$ , and their photochemical products. Possible coupling between  $\text{PH}_3$  and  $\text{NH}_3$  may inhibit ultraviolet destruction of  $\text{NH}_3$  on Jupiter. The red color of the Great Red Spot and other minor spots may be due to the presence of red phosphorus crystals formed after photolysis of  $\text{PH}_3$ . The detection of such gases as  $\text{PH}_3$ ,  $\text{GeH}_4$ , and CO in the stratosphere of Jupiter gives an indication of the presence of thermochemical nonequilibrium processes, and a strong vertical mixing may be required to explain their large observed upper atmospheric abundances. This argument is further strengthened by a laboratory finding that  $\text{C}_2\text{H}_2$  can efficiently scavenge photolysis products of  $\text{PH}_3$ . Other alternate mechanisms to account for the presence of CO in the stratosphere are the oxygen atom transfer from the Galilean satellites to Jupiter either by radial diffusion, or along magnetic flux tubes, or on ablation of meteoroidal material. Subsequent reactions of the thermal oxygen atoms with photolysis products of methane lead to the production of CO. Finally, the discussion of reducing atmospheres is extended to include Titan. It is found that if  $\text{NH}_3$  has outgassed from Titan and if the surface temperature during the initial phases of its evolution was  $150^\circ\text{K}$  or greater, due perhaps to a  $\text{CH}_4\text{-H}_2$  greenhouse, it is inevitable that Titan would have accumulated a thick atmosphere of nitrogen over geologic time. The pressure-induced thermal opacity of 20 bars of nitrogen can also explain the recently measured  $200^\circ\text{K}$  surface temperature of Titan. On the other hand, the composition of Titan's atmosphere would be far less certain if the surface temperature were as low as  $100^\circ\text{K}$ .

### INTRODUCTION

It is generally assumed that the escape of even the lightest of planetary gases, hydrogen and helium, is inhibited from the cold exospheres of the outer planets. Even under conditions of the relatively hot exosphere now being proposed for Jupiter [Atreya and Donahue, 1976; Hunten and Veverka, 1976] as a consequence of Pioneer measurements of the Jovian electron density profile and  $\beta$ -Sco occultation light curves, hydrogen is not permitted to escape from Jupiter. Consequently, it is expected that the atmosphere of Jupiter should represent conditions of the primordial solar nebula from which the planets were presumably accreted. This paper is devoted to a review of the photochemical processes taking place in such an atmosphere. In the ensuing discussion the term upper atmosphere is assumed to imply the visible atmosphere above the ammonia cloud tops. The models of the upper atmosphere are dependent upon a number of basic atmospheric parameters such as the temperature structure and mixing coefficients and on laboratory measurements of rate constants for chemical reactions and the line strengths of numerous important spectroscopic lines. Figure 1 [from Hunten, 1976] summarizes the current knowledge about the Jovian thermal structure as inferred from the ground-based, suborbital, satellite, and planetary spacecraft observations. The temperature is about  $170^\circ\text{K}$  at the 1-bar level. It decreases with decreasing pressure, undergoes an inversion between the 10- and 100-mbar levels, and then rises again to a stratopause (1 mbar) value of  $150^\circ\text{--}170^\circ\text{K}$ . The mesosphere is isothermal, presumably at  $170^\circ\text{K}$ . The temperature is expected to rise again above the homopause to an exospheric value between  $850^\circ\text{K}$  [Hunten, 1976] and  $1050^\circ\text{K}$  [Atreya and Donahue, 1976]. The eddy diffusion coefficient for vertical mixing,  $K$ , is in a far less satisfactorily understood

state than the temperature structure. The value can be deduced from a knowledge of the column abundance of atomic hydrogen above the methane absorption level [Hunten, 1969; Wallace and Hunten, 1973]. The atomic hydrogen column abundance has been inferred from the measurements of Jovian Lyman alpha albedo, whose reported values, until recently, ranged from 0.4 kR (Pioneer 10 and 11 measurements of Carlson and Judge [1974]) to 4 kR (rocket measurements of Moos and Rottman [1972]). Recent high-resolution measurements of the Jovian Lyman alpha airglow from OAO-Copernicus over two observing seasons give a value consistently between 1.2 and 1.6 kR [Atreya et al., 1977a]; and the latest rocket observations by the Johns Hopkins group [Giles et al., 1976] gave values lower than 2 kR. The low value measured on Pioneer flybys may have been due to a different solar flux or anomalous and/or local conditions. The eddy coefficient inferred from these values (0.4–4 kR) of Lyman alpha albedo has then a range between  $10^6$  and  $5 \times 10^9 \text{ cm}^2 \text{ s}^{-1}$  at the homopause. It is evident that the value of this important parameter is far from certain, and we expect that a determination by the Voyager ultraviolet experiment [Broadfoot et al., 1977] will settle this question. The principle of this aspect of the experiment on Voyager is that because of the large mass of methane its density will drop off rapidly above the homopause; therefore the level at which absorption in methane sets in is a good indicator of the homopause level where the eddy diffusion coefficient equals the molecular diffusion coefficient. In this review, the eddy mixing coefficient is treated as a parameter with a prejudice for a value around  $3 \times 10^7 \text{ cm}^2 \text{ s}^{-1}$  favored by the recent Copernicus [Atreya et al., 1977a] and rocket [Giles et al., 1976] observations. The tropospheric value of the eddy coefficient is deduced from the interpretation of ultraviolet albedo [Tomasko, 1974]. Values range from a high of approximately  $2 \times 10^4 \text{ cm}^2 \text{ s}^{-1}$  to a low of  $2 \times 10^2 \text{ cm}^2 \text{ s}^{-1}$

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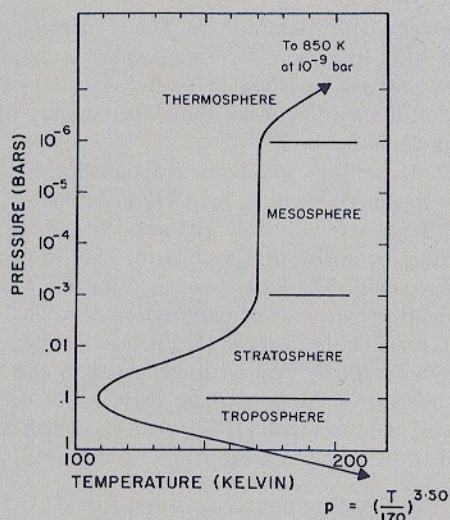


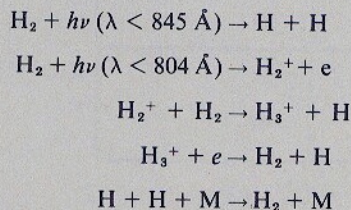
Fig. 1. Adopted temperature profile for Jupiter [Hunten, 1976]. For levels deeper than 1 bar the ideal-gas adiabat is represented by the formula given by Hunten [1976]. There is some evidence for a temperature maximum at  $\sim 200^\circ\text{K}$  in the mesosphere. (Reprinted by permission of the University of Arizona Press.)

according to a recent study by Sagan and Salpeter [1976]. The bulk composition of the Jovian atmosphere expected on the basis of solar abundance of elements is represented in a diagram shown in Figure 2. The volume mixing ratios of gases are shown as a function of atmospheric number density (90%  $\text{H}_2$  and 10% He). The horizontal bars represent approximately the pressure levels at which the thermodynamic considerations would place  $\text{NH}_3$ ,  $\text{NH}_4\text{SH}$ , and  $\text{H}_2\text{O}$  (water and ice crystal) clouds. So far, only the presence of visible solid ammonia crystal clouds around the 0.6-bar level has been definitely established. The water/ice clouds are anticipated to be present around the 4- to 5-bar level; and either the region between 1 and 4 bars is cloud free or the  $\text{NH}_4\text{SH}$  clouds are optically thin (M. Sato and J. E. Hansen, personal communication, 1978). In this paper, only photochemically active species,  $\text{CH}_4$ ,  $\text{NH}_3$ ,  $\text{PH}_3$ , and  $\text{CO}$ , and possible coupling between various chemical schemes will be considered.

#### HYDROGEN AND METHANE PHOTOCHEMISTRY

Continuous absorption of solar photons below  $845 \text{ \AA}$ , absorption in the Lyman bands of  $\text{H}_2$  (below  $1109 \text{ \AA}$ ) and Werner bands (below  $1009 \text{ \AA}$ ), and dissociative photo-ionization below  $805 \text{ \AA}$  eventually lead to the production of two hydrogen atoms as shown below:

##### Hydrogen photochemistry



Another source of H atoms above the ammonia cloud layer is the photolysis of  $\text{CH}_4$  below  $1600 \text{ \AA}$  and  $\text{NH}_3$  between  $1600$  and  $2300 \text{ \AA}$  as discussed in the subsequent sections. Once they are produced, the hydrogen atoms are removed, principally by transport. The loss due to the three-body recombination mechanism in the lower dense atmosphere ( $\text{H} + \text{H} + \text{M} \rightarrow \text{H}_2 + \text{M}$ ;

$k = 8 \times 10^{-33}(300/T)^{0.6} \text{ cm}^6 \text{ s}^{-1}$ ) is relatively slow. The average downward flux of H atoms on Jupiter is about  $7 \times 10^9 \text{ cm}^{-2} \text{ s}^{-1}$  with the production rate due to absorption in the Lyman and Werner bands contributing less than 15% [Strobel, 1975]. The distribution of atomic hydrogen is determined by solving the standard continuity and transport equation involving both eddy and molecular diffusion terms. The  $\text{CH}_4$  source of H is discussed below.

The photochemistry of methane has been reviewed recently by Strobel [1975]. Therefore only a brief overview emphasizing advances made since Strobel's review will be presented in this paper. The  $\text{CH}_4$  photochemical reactions in the reducing Jovian environment are shown schematically in Figure 3. Photolysis of methane takes place shortward of  $1600 \text{ \AA}$ , most of the dissociation being caused by solar Lyman alpha. The principal dissociation product is  $\text{CH}_2(b^1B_1)$ , which radiates to the  $^1A_1$  state and subsequently reacts preferentially with  $\text{H}_2$  to form the methyl radical  $\text{CH}_3$ . Reaction of  $^1\text{CH}_2$  with  $\text{CH}_4$  also leads to the production of  $^3\text{CH}_2$ , which in turn reacts with  $\text{CH}_3$  to give ethylene,  $\text{C}_2\text{H}_4$ . Ethylene is also produced on reaction of  $\text{CH}_4$  with  $\text{CH}$ , the other photolysis product of  $\text{CH}_4$ .  $\text{CH}_3$  reacts equally efficiently with H atoms and with itself, yielding, in the presence of a third body,  $\text{CH}_4$  and ethane,  $\text{C}_2\text{H}_6$ , respectively. Since the three-body rate of recombination of H to form  $\text{H}_2$  is much slower than the rate of reaction of  $\text{CH}_3$  with H, the consequential availability of large H atom concentrations results in a preferential reaction of  $\text{CH}_3$  with H to recycle  $\text{CH}_4$  instead of formation of  $\text{C}_2\text{H}_6$ . Photolysis of both  $\text{C}_2\text{H}_4$  (below  $2000 \text{ \AA}$ ) and  $\text{C}_2\text{H}_6$  (below  $1600 \text{ \AA}$ ) produces acetylene,  $\text{C}_2\text{H}_2$ .  $\text{C}_2\text{H}_6$ , however, is a relatively stable molecule, since its photolysis is inhibited by large concentrations of  $\text{CH}_4$ , which absorbs in the same spectral range as  $\text{C}_2\text{H}_6$ , and the activation energy of chemical reactions involving  $\text{C}_2\text{H}_6$  in the Jovian atmosphere is large.

The calculated distributions of hydrogen, helium, methane, and its photolysis products are shown in Figure 4. The profiles are shown for various eddy coefficients, and a constant temperature of  $150^\circ\text{K}$  is assumed. Methane remains mixed to a higher altitude in the case where the eddy diffusion coefficient  $K$  is taken to vary as  $[M]^{-1}$ , where  $[M]$  is the atmospheric density ( $K \approx 5 \times 10^9 \text{ cm}^2 \text{ s}^{-1}$  at the homopause).  $K$  is taken as being proportional to  $[M]^{-1/2}$  ( $K \approx 3 \times 10^7 \text{ cm}^2 \text{ s}^{-1}$  at the homopause) in the nominal case as explained earlier. The hydrocarbon distributions are taken from Strobel [1975]. Three important considerations would change the distributions.

1. Newly measured laboratory cross sections of  $\text{CH}_4$  and  $\text{C}_2\text{H}_6$  [Mount et al., 1977; Mount and Moos, 1978] are substantially different from those adopted in the models shown. The photoabsorption cross sections of  $\text{CH}_4$  beyond  $1475 \text{ \AA}$  are found to be up to 200 times smaller than the earlier values of Watanabe et al. [1953]. Absorption cross sections of  $\text{C}_2\text{H}_6$  at room temperature are found to be the same as the low values of Okabe and Becker [1963]. The absorption cross sections are found to be 20% lower at  $200^\circ\text{K}$  than at room temperature.

2. A reinterpretation of the Jovian methane observations by Wallace and Hunten [1978] on the basis of a combination of a reflecting layer model and a homogeneous scattering layer model yields a C/H ratio on Jupiter enriched by a factor of 3–4 over the solar value. J. E. Hansen (personal communication, 1978), on analyzing the observations of sunlight reflected from Jupiter's atmosphere in terms of multiple-scattering models, finds  $\text{CH}_4$  to be 2–2.5 times larger than it would be for an atmosphere of solar composition. On the other hand, a re-



analysis of the spectral line formation processes in the visible and infrared ranges by *Combes* [1978] yields a result which essentially confirms a solar C/H ratio for Jupiter. It is evident that the CH<sub>4</sub> abundance on Jupiter is far from certain, and the current best guess would place the C/H ratio somewhere between solar and 3 times solar.

3. The temperature above the homopause does not appear to be constant and cold. It is expected to rise to an exospheric value in excess of 850°K.

As a consequence of the decreased absorption cross sections the photolysis of CH<sub>4</sub> would occur to greater depths. However, increased CH<sub>4</sub> abundance would mean that the altitude of photolysis would be higher. The net result is therefore little change in the distributions of CH<sub>4</sub> and its products from those shown in Figure 4. Only the mixing ratios would be increased in accordance with the increase in the C/H ratio over the solar value. Since most of the photolysis of CH<sub>4</sub> occurs near the homopause and in the mesosphere, where the temperature is presumably constant, a temperature increase above the homopause would have little influence, if any, on CH<sub>4</sub> photochemistry. The hydrogen and helium abundances above the homopause, on the other hand, would follow a distribution dictated by the scale height due to increased temperature re-

sulting in an extended atmosphere. The H<sub>2</sub> density at 1000 km would be  $1 \times 10^{10} \text{ cm}^{-3}$  for an exospheric temperature of 1050°K [*Atreya and Donahue*, 1976]. Before leaving the subject of CH<sub>4</sub> photolysis a few ideas about the stability of methane will be discussed below.

Several mechanisms involving reactions of CH<sub>3</sub> with H<sub>2</sub> have been suggested for recycling CH<sub>4</sub> on Jupiter. These suffer from their large activation energies and from the fact that the cross section for absorption by CH<sub>3</sub> of long-wavelength UV radiation is small. The latter can, in principle, recycle CH<sub>4</sub>, since the activation energy of the reaction of excited CH<sub>3</sub> with H<sub>2</sub> is not formidable. *Strobel* [1969] has suggested that the heavier hydrocarbons may be transported to the hot, high-pressure interior of Jupiter, where they would be thermally decomposed and react with H<sub>2</sub> to form CH<sub>4</sub>, which can then be convected to the upper atmosphere.

#### PHOTOCHEMISTRY OF AMMONIA

After carbon the most abundant element in the solar system is nitrogen. On Jupiter, nitrogen is presumably present in the form of ammonia, whose stability poses a dilemma. As we shall see, photochemical considerations indicate that all of the ammonia on Jupiter should have been irreversibly converted

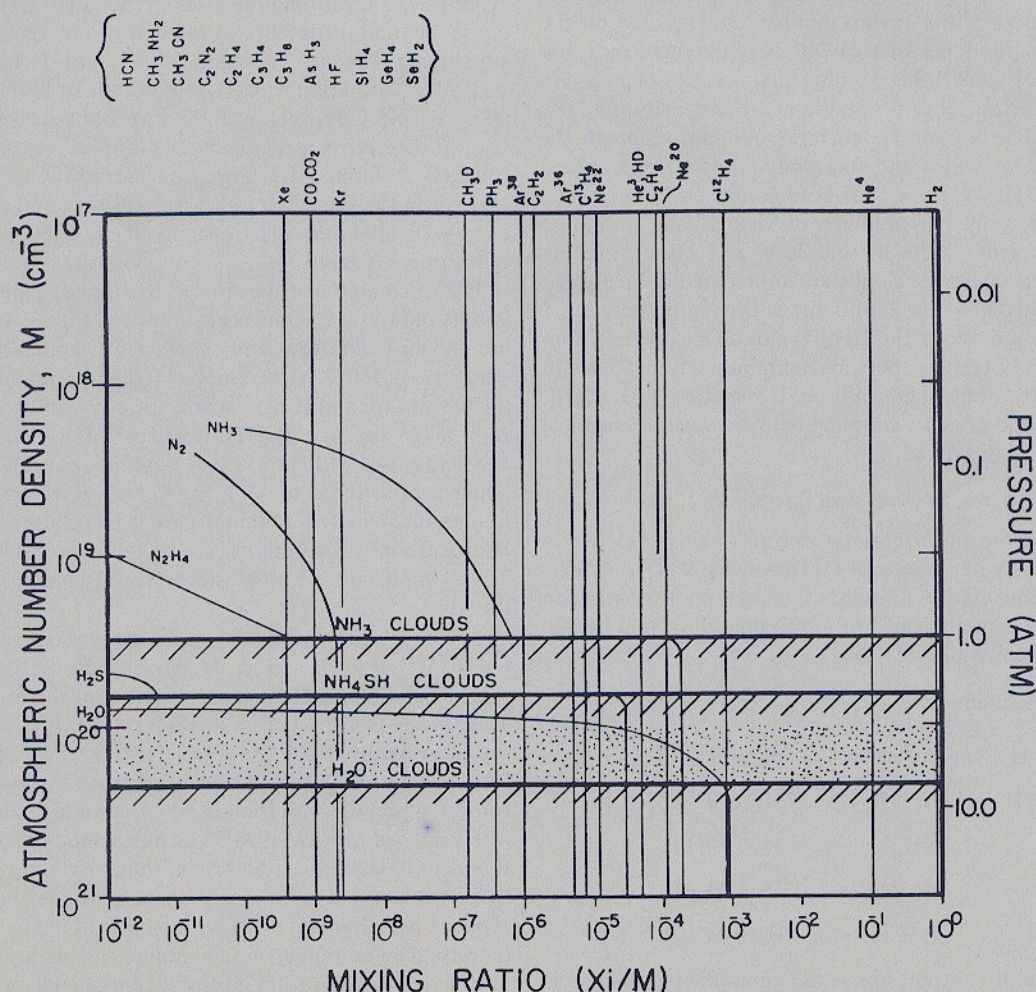


Fig. 2. Atmospheric composition of Jupiter, showing volume mixing ratios as a function of pressure and atmospheric number density of the various gaseous species anticipated to be present in the atmosphere of Jupiter. Some of these species have been detected, while others are expected on the basis of solar system composition. Various products of ammonia radical and methane chemical reactions and several hydrides likely to be formed in the atmosphere are trace constituents and are thus lumped together with mixing ratios of  $\leq 10^{-7}$ . The pressure levels where the NH<sub>3</sub>, NH<sub>4</sub>SH, and H<sub>2</sub>O (water/ice) clouds are expected to be formed are shown by heavy horizontal bars.



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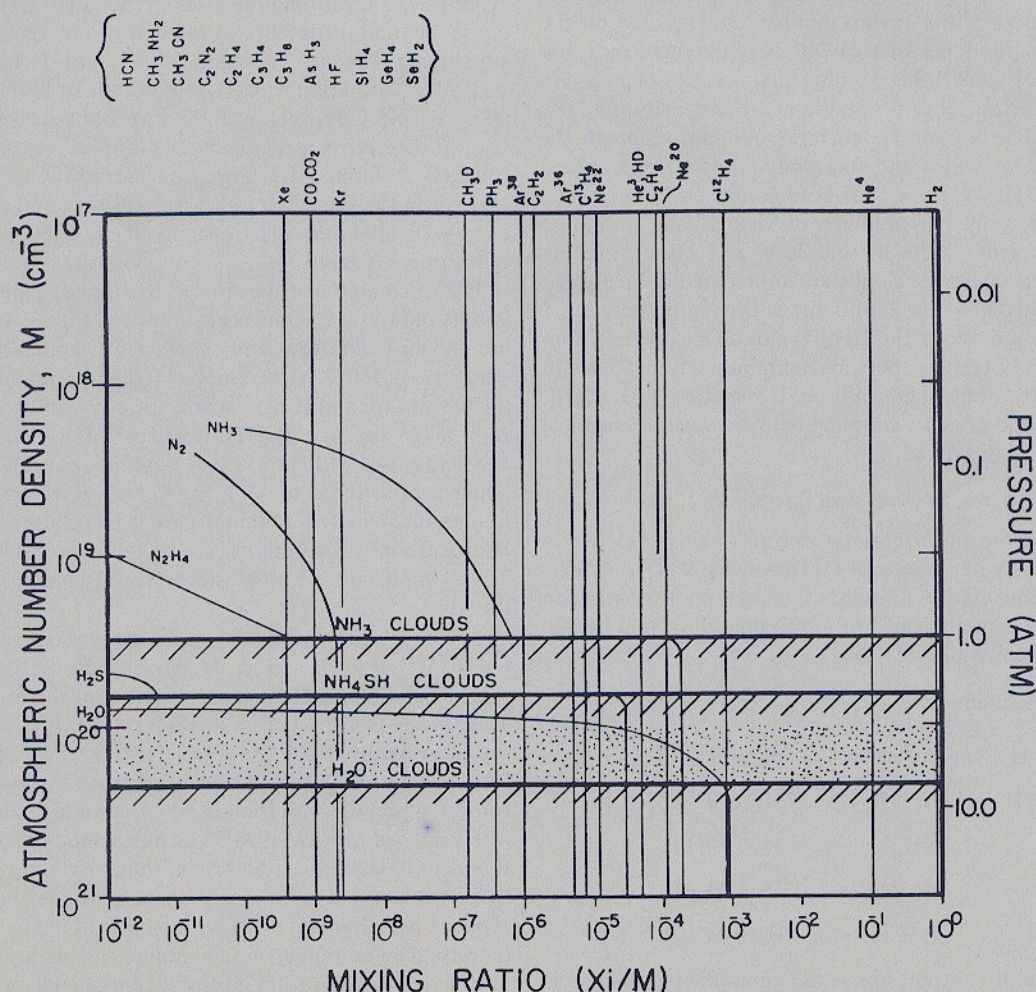


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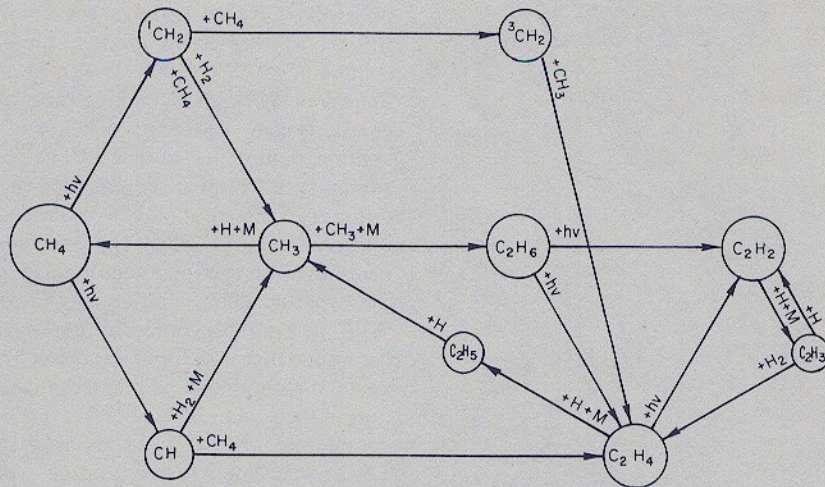


Fig. 3. Principal reactions in the hydrocarbon photochemistry [from Strobel, 1975].

to hydrazine,  $N_2H_4$ , and nitrogen,  $N_2$ , in less than 60 million years, or about 1% of geologic time. Yet the various measurements of  $NH_3$  on Jupiter place its present-day abundance close to or greater than the solar value. It is apparent that some mechanisms must be operative to recycle ammonia on Jupiter. The most recent study of the Jovian ammonia photochemistry is by Atreya *et al.* [1977b], and the review by Strobel [1975] discusses the problem prior to the Pioneer flybys of Jupiter in 1973-1974. For all practical purposes, photolysis of  $NH_3$  is confined to a few scale heights above the  $NH_3$  cloud tops.  $NH_3$  absorbs solar radiation between 1600 and 2300 Å. For these reasons,  $NH_3$  photolysis may be assumed to be entirely separated from the methane photolysis. As we shall see later, a weak coupling between the two systems is likely in a narrow altitude region, producing some significant trace species. The photochemistry of ammonia on Jupiter is adapted from the

work of Atreya *et al.* [1977b] and is shown schematically in Figure 5. Photolysis of  $NH_3$  in the 1600- to 2300-Å range leads to the formation of the amidogen radical,  $NH_2$ , and H. Up to 30% of the  $NH_3$  is recycled by reaction of  $NH_2$  with H. Reaction of  $NH_2$  with itself produces hydrazine,  $N_2H_4$ . Assuming that  $N_2H_4$  remains in the vapor phase, it undergoes photolysis in the same spectral interval as  $NH_3$  or reacts with H. In either case the hydrazyl radical,  $N_2H_3$ , will be produced. The self-reactions of  $N_2H_3$  can lead to  $NH_3$  or  $N_2H_4$  and  $N_2$ . The recycling of  $NH_3$  by this path is, however, quite inefficient and insignificant in comparison to the production of  $N_2$ . The final products of this gas phase photochemistry are  $N_2$  and  $N_2H_4$ . A crucial intermediate step for the completion of this cycle, however, is the presence of  $N_2H_4$  in the gaseous phase. For the relevant altitude range the Jovian temperature varies from approximately 165° to 110°K. The vapor pressure of  $N_2H_4$ ,

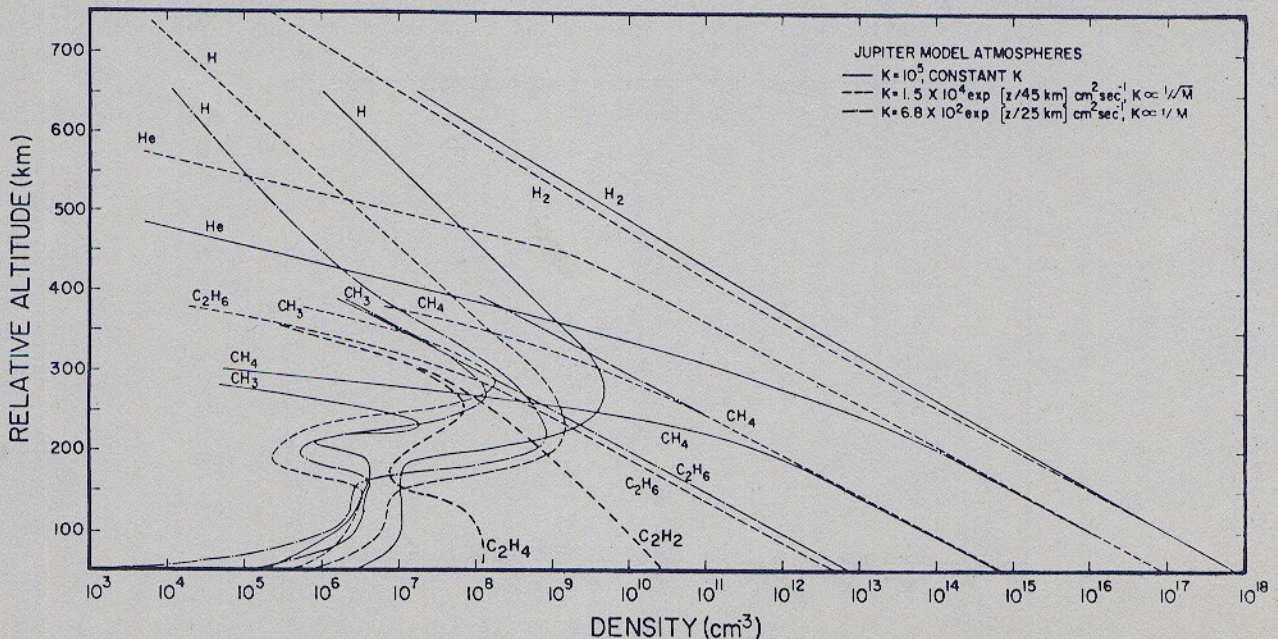


Fig. 4. Model atmospheres of Jupiter (hydrocarbon densities from Strobel [1975]) for  $K = 10^5 \text{ cm}^2 \text{ s}^{-1}$ ,  $K \propto M^{-1/2}$ , and  $K \propto M^{-1}$ , where  $M$  is the atmospheric number density. The  $K \propto M^{-1/2}$  curves represent the nominal case (see text) for which distribution of all relevant species is shown. Thermospheric temperature is assumed constant at 150°K, and the He/ $H_2$  mixing ratio is taken as 0.1. The height scale refers to the altitude above (or below) the level at which atmospheric density is  $10^{19} \text{ cm}^{-3}$ .



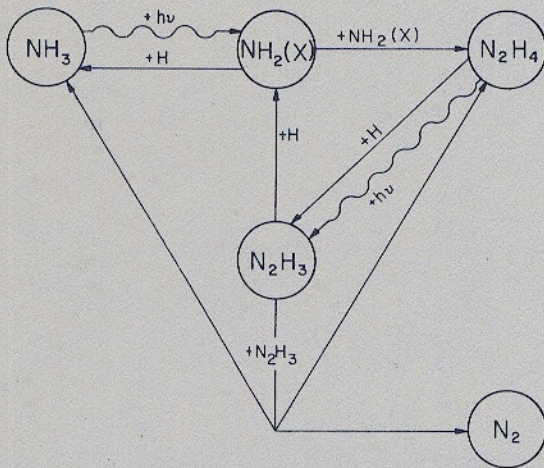


Fig. 5. Schematic representation of the Jovian ammonia photochemistry [from *Atreya et al.*, 1978]. (Reprinted by permission of the American Association for the Advancement of Science, Copyright 1978.)

over the same range of temperature varies by a factor of nearly  $10^9$ . Figure 6, taken from *Atreya et al.* [1977b], illustrates this fact. The distribution of  $\text{NH}_3$  and its photolysis products is shown assuming that all of  $\text{N}_2\text{H}_4$  is in the vapor phase. The distribution of the ultimate product  $\text{N}_2$  is shown also for the case when the  $\text{N}_2\text{H}_4$  distribution is dictated by its actual saturation vapor pressure curve. As our experience with the processes of condensation in the terrestrial troposphere indicates, a certain degree of supersaturation is quite likely. An examination of the calculated and saturation  $\text{N}_2\text{H}_4$  vapor mixing ratios in Figure 6, however, reveals that condensation of  $\text{N}_2\text{H}_4$ , especially near the top of the curve, is inevitable. The realistic  $\text{N}_2$  distribution in the Jovian atmosphere is then expected to be somewhere between the two profiles shown, i.e., a maximum  $\text{N}_2$  mixing ratio between  $10^{-9}$  and  $10^{-11}$ . The distributions are also highly dependent upon the choice of eddy diffusion coefficient and the Jovian latitude and solar zenith angle. Changing  $K$  from  $2 \times 10^4$  to  $2 \times 10^3 \text{ cm}^2 \text{ s}^{-1}$  at the cloud top results

in a sevenfold decrease in the column abundance of  $\text{NH}_3$ , while  $\text{N}_2$  increases by almost a factor of 100. With a tropospheric  $K$  of  $2 \times 10^2 \text{ cm}^2 \text{ s}^{-1}$ , as suggested by *Sagan and Salpeter* [1976], an  $\text{N}_2$  mixing ratio of  $10^{-7}$  is calculated. Calculations also yield nearly a factor of 100 increase in the  $\text{NH}_3$  column abundance above 30 km from equator to pole. In summary, it should be emphasized that the calculations shown in Figure 6 represent globally averaged results, while the actual observations will differ appreciably from these profiles depending upon the solar zenith angle, geographic location, and the eventual determination of the eddy diffusion coefficient. With the available choices in the values of  $K$ , one can expect an  $\text{N}_2$  abundance on Jupiter ranging from respectable to marginal. It should also be pointed out that a recent reinterpretation of the Jovian  $\text{NH}_3$  observations by J. E. Hansen (personal communication, 1978) yields an  $\text{NH}_3$  abundance on Jupiter 1.5–2 times larger than would be expected for an atmosphere in which the solar ratio of elements prevailed. It should be noted, however, that this result applies to the total  $\text{NH}_3$  abundance on Jupiter and not to the ammonia at and above the cloud tops. The value at the cloud top is determined by the saturation vapor curve appropriate to the temperature there. Consequently, an increased abundance of  $\text{NH}_3$  on Jupiter should have practically no influence on the profiles discussed above.

As was mentioned above, condensation of a certain amount of hydrazine will occur regardless of the presence of condensation nuclei, whose distribution in Jupiter's stratosphere is not known at the present time. Once the crystals grow to a critical size, condensation will take place. It is interesting to note that the 100-mbar region of maximum hydrazine condensation is precisely the region where the temperature inversion in the atmosphere of Jupiter has been observed. It is quite likely that the whitish hydrazine haze is the substance of which Axel dust [Axel, 1972] is composed. It is evident from the above discussion of ammonia photochemistry on Jupiter that photolysis converts most of  $\text{NH}_3$  to  $\text{N}_2\text{H}_4$  and  $\text{N}_2$ . Taking into consideration transport and convection, all of ammonia above and below the clouds would have been irreversibly

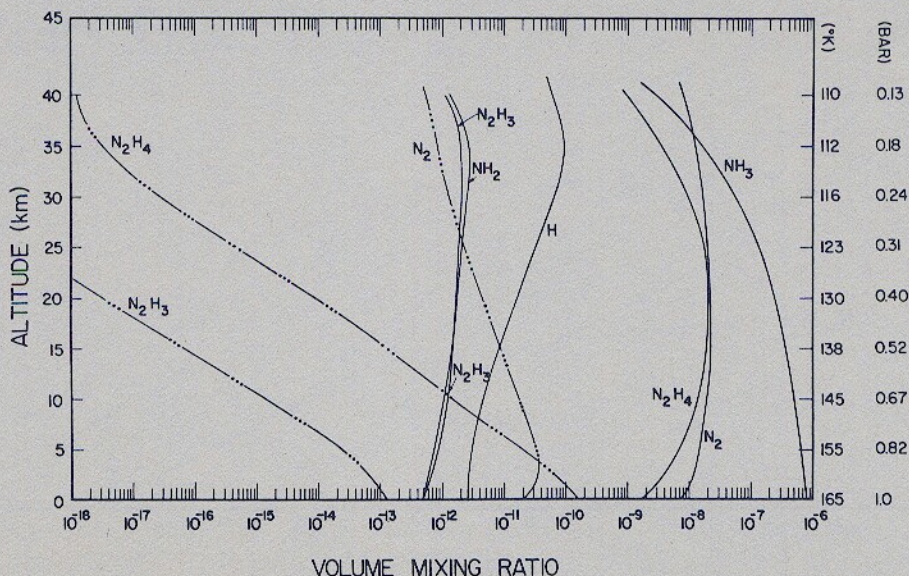
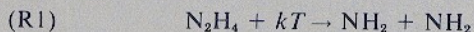


Fig. 6. Altitude profiles of volume mixing ratios of ammonia and its photochemical products for the *Hunten* [1976] temperature profile and the  $K \propto M^{-1/2}$  atmospheric model (solid curves). The temperatures and pressures shown on the right ordinate correspond to the altitudes shown on the left. The rate constant  $k_4$  is that of *Stief and Payne* [1976]. The dot-dashed curves for  $\text{N}_2\text{H}_4$  and  $\text{N}_2\text{H}_3$  assume a saturation vapor mixing ratio. The resultant  $\text{N}_2$  mixing ratio profile is shown by a dot-dashed curve [from *Atreya et al.*, 1977b]. (Reprinted by permission of Academic Press.)

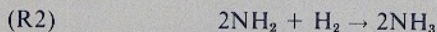


converted to other forms in 60 million years. Several mechanisms to explain the presence of ammonia in the present-day Jupiter atmosphere have been proposed. The most likely ones are listed below.

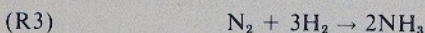
1. Once condensed, hydrazine would rain out of the atmosphere and be convected to the hotter interior, where it can be thermally dissociated into  $\text{NH}_2$  radicals which would subsequently react with  $\text{H}_2$  to form  $\text{NH}_3$  without the activation energy barrier present in the cold visible atmosphere. Once formed,  $\text{NH}_3$  will be convected to the upper atmosphere to replenish the  $\text{NH}_3$  lost by UV photolysis. The process is



followed by



2.  $\text{N}_2$  also can be convected to the deep interior, and at approximately the 3000-bar pressure level, it can react with  $\text{H}_2$  in a termolecular reaction without the difficulty of formidable activation energy in the upper atmosphere.



3.  $\text{NH}_2(X)$  formed in the ground state on photolysis of  $\text{NH}_3$  in the upper atmosphere can be excited to the  $A$  state by visible light between 4000 and 9000 Å. The excited  $\text{NH}_2(A)$  can react with  $\text{H}_2$  to yield  $\text{NH}_3$  and avoid the difficulty of the large activation energy involved in the reaction of  $\text{NH}_2(X)$  with  $\text{H}_2$  at the cold Jovian temperatures. For this mechanism to be of significance in recycling ammonia, however, the average absorption cross section for  $\text{NH}_2$  between 4000 and 9000 Å must be at least 1000 times greater than that available.

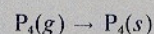
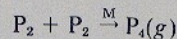
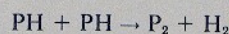
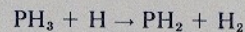
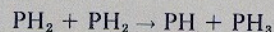
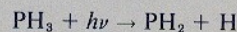
4. Phosphine,  $\text{PH}_3$ , which has been observed in the upper atmosphere of Jupiter, may scavenge  $\text{NH}_2$  radicals to form  $\text{NH}_3$  [Strobel, 1977] provided the rate of the  $\text{PH}_3$ - $\text{NH}_2$  reaction is faster than reaction of  $\text{NH}_2$  with itself to give  $\text{N}_2\text{H}_4$ . No measurements of the relevant rate constants under conditions of Jovian temperatures are yet available to permit an evaluation of the importance of this mechanism.

#### PHOTOCHEMISTRY OF PHOSPHINE

A brief overview of the problem of phosphine is presented, since it is relevant to the problem of  $\text{NH}_3$  and the possible coupling between the C-N-P systems discussed below. Phosphine,  $\text{PH}_3$ , has been detected in the visible atmosphere by Ridgway [1974] and Larson *et al.* [1977]. Prinn and Lewis [1975] argued that its presence in the upper atmosphere requires some nonequilibrium chemical processes, since  $\text{PH}_3$  is thermochemically stable only where the temperature rises above 800°K.  $\text{PH}_3$  can be oxidized by  $\text{H}_2\text{O}$  to form  $\text{P}_4\text{O}_6$  between 800° and 300°K. Prinn and Lewis therefore invoked the hypothesis of a strong vertical mixing coefficient ( $K = 10^6 \text{ cm}^2 \text{ s}^{-1}$  from the stratosphere to the 20-bar level and below) so that the time constant for transport of  $\text{PH}_3$  to the upper atmosphere would be much shorter than the oxidation time constant. The strong atmospheric vertical mixing proposed here may be indicative of the conditions in the Great Red Spot (GRS), which is presumably a violent anticyclonic hurricane-like feature with persistent thunderstorms. In other parts of the atmosphere, vertical atmospheric mixing is not that strong [Prinn and Lewis, 1975], and this may also explain the red coloration of the GRS, caused presumably by condensation of triclinic red phosphorus crystals,  $\text{P}_4(S)$ , formed on the photolysis of  $\text{PH}_3$  as shown below. The question of coloration of

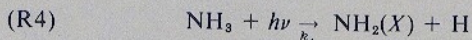
the spots on Jupiter will be addressed further in a subsequent section.

Phosphine photochemical scheme

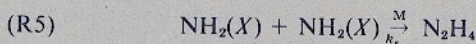


#### $\text{NH}_3$ - $\text{PH}_3$ - $\text{CH}_4$ COUPLING

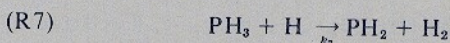
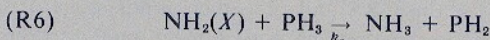
As one would expect, photolysis of  $\text{PH}_3$  in the upper atmosphere takes place in the same spectral range as the photolysis of  $\text{NH}_3$ . This implies that the solar photons between 1600 and 2300 Å must be shared between the two species. Photolysis rates of individual species,  $\text{NH}_3$  and  $\text{PH}_3$ , are accordingly reduced. One should note, however, that since  $[\text{PH}_3] < [\text{NH}_3]$ , the presence of  $\text{PH}_3$  does not appreciably reduce the  $\text{NH}_3$  destruction rate. Strobel [1977] has, however, proposed that  $\text{PH}_3$  may inhibit destruction of  $\text{NH}_3$  in another way.  $\text{NH}_2$  radicals are formed on photolysis of  $\text{NH}_3$ .  $\text{NH}_2$  can either react with itself to form  $\text{N}_2\text{H}_4$  or react with  $\text{PH}_3$  to recycle  $\text{NH}_3$ .  $\text{PH}_3$  also reacts with  $\text{H}$  to give  $\text{PH}_2$ :



followed by



or



$\text{PH}_3$  can efficiently scavenge  $\text{NH}_2$  in (R6) provided the rate of this reaction is much faster than that of (R5) and the activation energy of (R7) is large. This chain of reactions can also recycle  $\text{NH}_3$  destroyed in UV photolysis. Lee *et al.* [1976] find, contrary to the kinetics inferred from Norrish and Oldershaw's [1961] measurements, a small activation energy for the rate constant  $k_7$ . The rate and activation energy of (R6) at the cold Jovian temperatures are not known. In view of the serious lack of knowledge about the key steps in this scheme it is best to view this coupling between  $\text{PH}_3$  and  $\text{NH}_3$  as being potentially important.

In a recent laboratory study of ultraviolet photolysis of  $\text{PH}_3$  in the presence of  $\text{C}_2\text{H}_2$  or  $\text{C}_2\text{H}_4$ , Vera-Ruiz and Rowland [1978] find that these hydrocarbons act as efficient scavengers of  $\text{PH}_2$ ,  $\text{PH}$ , and  $\text{P}_2$ , thus inhibiting the formation of red phosphorus  $\text{P}_4(s)$ . These simulation experiments assumed too high an abundance for  $\text{C}_2\text{H}_4$ , so one ought to be concerned only with  $\text{C}_2\text{H}_2$  as the potential scavenger. Moreover, the experiment was conducted at room temperature, and the activation energies of the reactions of  $\text{PH}_2$ ,  $\text{PH}$ , and  $\text{P}_2$  with  $\text{C}_2\text{H}_2$  have not been measured. In view of the low Jovian temperatures in the 20- to 80-mbar region the temperature dependence of these rate constants may be important. If these scavenging reactions with  $\text{C}_2\text{H}_2$  do proceed at such low temperatures, the Prinn and Lewis [1975] hypothesis of strong vertical mixing will be



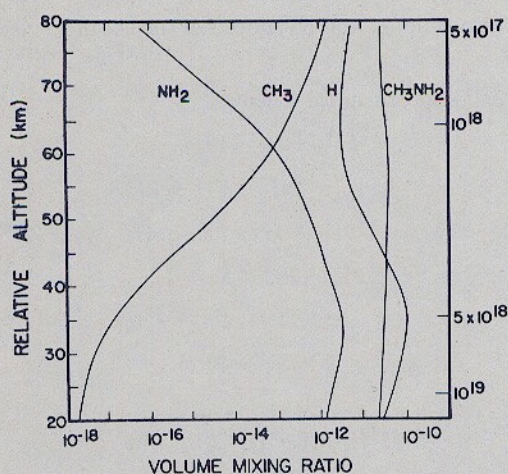


Fig. 7. Volumetric mixing ratios for  $\text{CH}_3\text{NH}_2$  and related radicals. Total atmospheric number densities are shown on the right ordinate [from Kuhn *et al.*, 1977].

strengthened even further. In regions of strong vertical mixing ( $K = 10^6 \text{ cm}^2 \text{ s}^{-1}$ ), such as the GRS,  $\text{PH}_3$  will be photolyzed higher in the atmosphere with a rate approximately 300 times the downward flux of  $\text{C}_2\text{H}_2$ . Consequently, in this region, scavenging of the photolysis products of  $\text{PH}_3$  by  $\text{C}_2\text{H}_2$  would not occur, and the  $\text{PH}_3$  photochemical chain would terminate with the formation of red phosphorus. In other parts of the atmosphere, with a substantially smaller vertical mixing, the  $\text{PH}_3$  photolysis rate could be comparable to the downward flux of  $\text{C}_2\text{H}_2$ , thus leading to an efficient scavenging of  $\text{PH}_2$ ,  $\text{PH}$ , and  $\text{P}_2$ , and production of red phosphorus would be inhibited. This is an attractive hypothesis, but one must keep in mind that the Great Red Spot is really not unique in its red coloration. If the red phosphorus crystals really are the chromophores for the GRS and the other minor spots, the concept of strong vertical mixing must not be limited to the GRS alone.

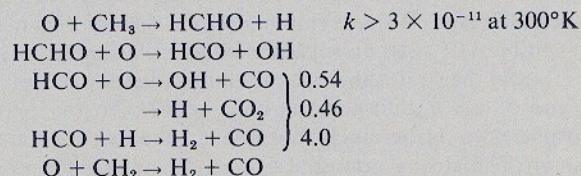
In addition to the  $\text{NH}_3$ - $\text{PH}_3$ - $\text{C}_2\text{H}_2$  coupling, it is expected that in a narrow altitude region between 58 and 68 km above the ammonia cloud tops where the abundances of  $\text{NH}_2$  and  $\text{CH}_3$  radicals are nearly comparable, reaction between these radicals would lead to the production of methylamine,  $\text{CH}_3\text{NH}_2$  [Kuhn *et al.*, 1977]. The maximum  $\text{CH}_3\text{NH}_2$  mixing ratio is found to be  $3 \times 10^{-11}$ , and its distribution is illustrated in Figure 7. Many more minor constituents may result on coupling of the C-N-P chemical schemes; however, it is not readily apparent whether their abundances can be explained by photochemical considerations. Indeed, after irradiating a gas mixture simulating a Jovian atmosphere with UV light, Khare *et al.* [1978] find production of numerous organics such as nitrogenous compounds, hydrogen cyanide, methyl cyanide, and a series of alkanes, alkenes, benzenes, and aromatics. Most of these species are produced in relatively small mixing ratios ( $\ll 10^{-7}$ ). Some of the important trace species formed as a result of coupling of  $\text{CH}_4$  and  $\text{NH}_3$  photochemistry are lumped together and illustrated at the top of Figure 2.

#### PHOTOCHEMISTRY OF CARBON MONOXIDE

The presence of carbon monoxide in the upper atmosphere of Jupiter, as recently established by observations of Beer [1975], Beer and Taylor [1978], and Larson *et al.* [1978], appears to be another example of the result of nonequilibrium processes in Jupiter. CO is thermochemically stable at 1100°K.

Prinn and Barshay [1977] have proposed a strong vertical mixing, with  $K = 2 \times 10^8 \text{ cm}^2 \text{ s}^{-1}$  in Jupiter's deep interior. CO will be formed there on oxidation of  $\text{CH}_4$  and will then be transported by mixing to the visible atmosphere. Hubbard [1970] has exploited the fact that Jupiter has a strong internal source of heat to argue in favor of a model in which Jupiter is a convective fluid throughout most of its interior. On the basis of theories of free convection, Prinn and Barshay [1977] derive a value between  $10^8$  and  $10^9 \text{ cm}^2 \text{ s}^{-1}$  for  $K$ , in agreement with the value invoked to explain the presence of CO in the upper atmosphere. However, it is not certain where the spectroscopic lines are formed. Beer and Taylor [1978] find a low CO rotational temperature of  $125^\circ \pm 25^\circ$ , implying a stratospheric origin of CO. Larson *et al.* [1978], on the other hand, associate a high rotational temperature of  $150^\circ$ - $300^\circ\text{K}$  with their CO observation. Strobel and Yung [1978] have proposed an alternate mechanism for explaining the presence of CO which argues for a stratospheric source. They suggest that the Galilean satellites can provide a source of oxygen atoms to the upper atmosphere of Jupiter. Subsequent reactions of oxygen atoms with hydrocarbons in the Jovian atmosphere will lead to the production of spectroscopically detectable amounts of CO. The oxygen atoms can be removed from the Galilean satellites, particularly Europa, Ganymede, and Callisto, whose surfaces are presumably covered with varying degrees of water ice, on sputtering of their surfaces by high-energy charged particles. This hypothesis was first suggested by Matson *et al.* [1974] for explaining sodium in the Io torus. Once ejected, the oxygen atoms are readily ionized by photo-ionization and proton or electron impact ionization and are swept away by Jupiter's magnetic field. After random motions across the field lines, a fraction of these ions diffuse radially inward to Jupiter. For instance, with a flux of  $10^8$  oxygen atoms  $\text{cm}^{-2} \text{ s}^{-1}$  from Ganymede calculated by Yung and McElroy [1977] the corresponding globally averaged flux entering the upper atmosphere of Jupiter is  $4 \times 10^4 \text{ cm}^{-2} \text{ s}^{-1}$  according to Strobel and Yung [1978]. Similarly, the flux of oxygen ions entering Jupiter from Europa could be as large as  $2 \times 10^7 \text{ cm}^{-2} \text{ s}^{-1}$ . These energetic  $\text{O}^+$  ions lose most of their energy in collision and charge transfer with  $\text{H}_2$  until they are thermalized. The chain of reactions of thermal O atoms important near and below the homopause is shown below. Oxygen atoms react preferentially with methyl radicals formed during the photochemical cycling of  $\text{CH}_4$  and produce formaldehyde,  $\text{HCHO}$ . Subsequent reactions of  $\text{HCHO}$  with O lead eventually to the formation of CO. Oxygen atoms also react with  $\text{CH}_2$  radicals to form CO directly; this mechanism, however, is insignificant because of low  $\text{CH}_2$  abundances.

#### Carbon monoxide formation



We wish to point out that in addition to the radial diffusion proposed by Strobel and Yung [1978], oxygen ions can also enter Jupiter's ionosphere along the magnetic flux tubes connecting the Galilean satellites to Jupiter. The concept of atom-molecule transfer from the satellites to the parent planets was first suggested by Goldreich and Lynden Bell [1969]. On the basis of this idea, Atreya *et al.* [1974] in their pre-Pioneer



paper suggested possible transfer of  $\text{Na}^+$  ions from Io to Jupiter's ionosphere along the magnetic flux tubes connecting Io to Jupiter. Indeed, the sharp layers observed in the lower ionosphere of Jupiter [Fjeldbo, 1976] are quite indicative of possible long-lived metallic ions, such as  $\text{Na}^+$ . If the oxygen ions did indeed slide along the flux tubes, they would be deposited at the feet of the flux tubes of the individual satellites in the polar regions of Jupiter and would subsequently diffuse over the entire planet. The concept of ion transfer from satellites to the parent planet, although it is intriguing, needs further investigation, since one should note that Jupiter acts as a strong centrifugal accelerator so that the ions are carried around by magnetic field lines much faster than their Kepler ion velocity. This may prevent the ions from entering Jupiter unless there is some as yet unknown satisfactory method of avoiding this problem.

Prather *et al.* [1978] have recently discussed meteoroidal ablation as a possible source of oxygen atoms at high altitudes in Jupiter. Assuming an influx of meteoroidal material of the order of  $3.4 \times 10^{-13} \text{ g cm}^{-2} \text{ s}^{-1}$  and a composition of the material similar to that entering the terrestrial atmosphere (i.e., carbonaceous chondrites), they anticipate an influx of  $5 \times 10^9 \text{ cm}^{-2} \text{ s}^{-1}$  of  $\text{H}_2\text{O}$ . The flux of  $\text{H}_2\text{O}$  required to produce the observed amount of CO is only  $5 \times 10^7 \text{ cm}^{-2} \text{ s}^{-1}$  [Prather *et al.*, 1978]. Water is subsequently photolysed to provide the required oxygen atoms. A laboratory experiment involving flash vaporization of minerals, rocks, and carbonaceous chondrites by Nd pulsed laser coupled with a time of flight mass spectrometer appears to support the above hypothesis [Sill and Lincoln, 1978]. Surprisingly, however, the flash vaporization of the carbonaceous chondrite material resulted in, in addition to  $\text{H}_2\text{O}$ , a direct production of CO. Further experiments by actually simulating the Jovian atmosphere and then examining the abundance fractions of the products of flash vaporization of the material are required to resolve this dilemma. In conclusion, it should be said that until a direct relationship between the source of the oxygen atoms and the effect has been established by more sophisticated experiments, the numerous hypotheses proposed above are equally attractive.

#### TITAN

Titan has been an object of considerable interest among planetary scientists. Because of recent measurements of Conklin *et al.* [1977] at a wavelength of 3 mm its surface is once again thought to be warm, of the order of  $200^\circ\text{K}$ . The unpublished results of T. C. Owen and J. J. Caldwell (personal communication, 1978) cast some doubt on the validity of these measurements. They find, from 6-cm very long aperture (VLA) measurements, a lower limit of  $90^\circ\text{K}$  and an upper limit of  $170^\circ\text{K}$ , the lower value being more heavily weighted. It is evident that at the present time, the question of the surface temperature of Titan remains unresolved and its value could range anywhere from  $90^\circ$  to  $200^\circ\text{K}$ . Since Titan's atmosphere is presumably a reducing one and because of the recent resurgence of interest, a paragraph here is devoted to the latest developments in the photochemistry of Titan. In a recent evolutionary model of the atmosphere of Titan, Atreya *et al.* [1978] have proposed that if ammonia outgassed from Titan, photochemical considerations similar to those mentioned earlier in this paper concerning Jupiter indicate that approximately 20 bars of  $\text{N}_2$  would have accumulated over geologic time in the Titanian atmosphere. A crucial requirement in this chemical scheme is the presence of sufficient amounts of the intermediate product  $\text{N}_2\text{H}_4$  in the gas phase to undergo pho-

tolysis. Such photolysis would proceed from the beginning provided the primordial surface temperature of Titan were  $150^\circ\text{K}$  or greater. However, the blackbody radiation temperature for Titan is  $86^\circ\text{K}$ , and it can be raised to  $150^\circ\text{K}$  by a greenhouse effect provided by 0.45 bar  $\text{CH}_4\text{-H}_2$  atmosphere [Pollack, 1973]. A smaller greenhouse effect would be provided by ammonia itself [Atreya *et al.*, 1978; Kuhn and Atreya, 1979]. Methane has been detected above the clouds [Traffon, 1972], and much greater amounts of  $\text{CH}_4$  are expected to be present below the clouds. Thus it appears quite likely that Titan's surface temperature could have been raised to  $150^\circ\text{K}$  in the early phases of its evolution. In this event the  $\text{NH}_3$  photochemistry would terminate with the production of  $\text{N}_2$  which over 5 billion years can accumulate to a thick  $\text{N}_2$  atmosphere. Hunten [1978] has calculated that the pressure-induced thermal opacity of 21 bars of  $\text{N}_2$  with a pinch of  $\text{H}_2$  (produced in the photochemistry of  $\text{CH}_4$  and  $\text{NH}_3$ ) is sufficient to explain the recently measured high ( $203^\circ\text{K}$ ) surface temperature of Titan. On the other hand, if the surface temperature were indeed of the order of  $100^\circ\text{K}$ , as given by the VLA measurements, it is not readily apparent what the composition of Titan would be. We know from our understanding of the terrestrial cloud physics that in a dust free environment, i.e., in the absence of appropriate nuclei, ice will not form at temperatures above  $-40^\circ\text{C}$ , and generally in the atmosphere of the earth a large degree of supercooling prevails [e.g., Mason, 1957]. If such a degree of supercooling exists on Titan, it should be possible, even at very low temperatures of  $100^\circ\text{--}110^\circ\text{K}$ , for  $\text{NH}_3$  photochemistry to proceed in the formation of  $\text{N}_2$ ; the efficiency, however, may be substantially diminished. A good surface temperature measurement, although it is extremely important, is not likely to resolve the question of the surface pressure of Titan satisfactorily. In addition to the uncertainty in the surface temperature, there are also no measurements of the critical quantity in the model—the saturation vapor pressure of hydrazine at very low temperatures. The saturation vapor pressure in the above model was calculated on the basis of the Clausius Clapeyron equation which reproduces satisfactorily the measured values at higher temperatures.

#### CONCLUSIONS

Photochemical models depend upon various critical parameters, some atmospheric, others obtained from laboratory studies. The models presented in this paper therefore are only as good as the information about atmospheric temperature structure, mixing coefficients, dynamical considerations, laboratory rate constants, and various thermodynamic quantities which go into constructing these models. Consequently, the models inevitably admit a wide range of possibilities for the distributions of gases in the atmospheres of Jupiter and Titan. It is imperative that laboratory measurements of such quantities as relevant rates of chemical reactions under Jovian conditions, data on line strengths, and ion sputtering coefficients for the various satellite surfaces be carried out simultaneously with the planetary observations. Both the interpretation of planetary observations and the construction of theoretical models will benefit from such endeavors. It is evident that photochemical models can only explain a fraction of what has been observed so far in the upper atmosphere of Jupiter. A number of nonequilibrium processes are expected to be operative and dynamics may play an important role in determining the distribution of some of the gases. We hope to be able to learn a great deal about the atmospheres of the outer



planets and their satellites from the observations to be carried out on the Voyager and Galileo projects.

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