

VERTICAL DISTRIBUTION OF DISEQUILIBRIUM SPECIES IN JUPITER'S TROPOSPHERE

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(Received 29 July, 1983)

Abstract. Sources of organic matter and inorganic tracers on Jupiter, including solar UV photolysis, lightning discharges, and convective quenching of hot gases from the lower atmosphere, are reviewed in light of Earth-based and Voyager data with the purpose of predicting the tropospheric steady-state abundances and vertical distributions of HCN, CH₂O, and other species.

It is concluded that a steady-state mole fraction of HCN in the Jovian troposphere of only $\sim 10^{-12}$ could be maintained by vertical transport of hot gases from the deep atmosphere. The observed HCN abundance (roughly $X_{\text{HCN}} = 10^{-9}$) appears to be due to photochemical reactions.

After HCN, the most abundant organic disequilibrium species in the troposphere is probably C₂H₆, derived from direct photolysis of CH₄ at high altitudes, with a mole fraction of $\sim 10^{-10}$ at the H₂O cloud level. Inorganic tracers of disequilibrium processes are also briefly summarized.

1. Introduction

Since the pioneering laboratory work by S. L. Miller in the 1950's (Miller and Urey, 1959), it has been well established that disequilibrating energetic processes, such as UV photolysis and electrical discharges, may cause enormous increases in the compositional complexity of simple chemical systems. One leading result of such simulations has been the demonstration of the richness of diversity of organic species produced by the action of disequilibrating energy sources on chemically reducing gas mixtures, especially those containing H₂, CH₄, NH₃, H₂O, H₂S, and PH₃. Numerous discussions of laboratory experiments involving the chemistry of such a system have explicitly claimed relevance of these experiments to natural processes on the Jovian planets. Most notable have been claims of large abundances of organic matter in the Jovian atmosphere, of the production of the colors of the Jovian clouds from polymerization of organic matter, of the suitability of the Jovian atmosphere for the support of accidentally introduced terrestrial organisms, and even of the spontaneous generation of indigenous Jovian life forms (Ponnamperuma, 1976; Sagan and Salpeter, 1976; and references in these papers).

That region of Jupiter's atmosphere which appears most hospitable to life as we know it is the vicinity of the water cloud layer near 0 °C. It is our purpose in the present review to apply our present knowledge of disequilibrating processes on Jupiter to the task of estimating the abundances of a number of biologically and chemically interesting species

in the upper troposphere, especially including their abundance in the region of liquid water stability.

There is inherent in any attempt to quantify such an area of research a curious two-edged character to the work that must be recognized and respected. This duality arises from the fact that pioneering work on the qualitative behavior of very complex systems is proceeding in parallel with carefully quantitative studies of greatly simplified portions of these same systems. It is obvious from a perusal of the literature that there are insufficient kinetic and mechanistic data available on the processes of interest to permit a theoretical model to describe all the richness of behavior observed in the laboratory. For this reason qualitative and semi-quantitative 'prospecting' through the available parameter space in search of previously unreported phenomena may still be rewarding. On the other hand, the vast increase in our knowledge of Jupiter and the growing body of data on the *efficiencies* (if not the *mechanisms*) of production of interesting molecules in the laboratory combine to offer the opportunity to construct global-average vertical distribution models which reasonably approximate Jovian conditions. Thus qualitative considerations may be subjected to quantitative discipline, while at the same time planetary studies may reveal parameter ranges deserving of more intensive laboratory study. Most important, however, is the explicit connecting of laboratory data to observable properties of Jupiter. This can be done if the laboratory 'simulations' are carried out under conditions sufficiently similar to those on Jupiter so that the efficiencies of the observed processes may be scaled to Jovian conditions. When this is done, it may be found that certain of the processes which are of apparent importance based on purely qualitative criteria will be quantitatively negligible.

The observable property most directly related to the importance of a disequilibrating mechanism is the abundance of its products. Second, those mechanisms which provide detectable amounts of products are of far greater interest if the products are chemically *distinctive* (diagnostic of the process), *complex* in structure, or *colored*.

In order to estimate the abundance and vertical distribution of such products, it is necessary not only to identify their major sources, but also to quantify their loss mechanisms. Only then can their steady-state abundances be estimated. Some disequilibrium species, such as H_2Se , are vulnerable to UV dissociation and condensation as NH_4HSe at high altitudes, but most disequilibrium species, especially those produced by UV photolysis and lightning, are principally depleted by thermochemical reactions in the lower troposphere: thus the major role of convective vertical transport in such models. Vertical mixing both dilutes locally produced disequilibrium species and carries them down to dense, hot levels in the lower atmosphere. There, chemical equilibration rapidly destroys these molecules and reconstitutes their component elements into methane, ammonia, etc. Studies of the planetary thermal state of Jupiter (Hubbard, 1973) and the attendant atmospheric mixing required to transport the large observed heat flux (Stone, 1976) lead to valuable estimates of the tropospheric vertical mixing rate. Treating the transport of heat by Prandtl mixing length theory (by assuming that the internal heat flux is transported upward by dry free convection), the mean vertical wind speed w is related to the gas constant R , the heat capacity C_p , the density ρ , and the heat flux F

by

$$w \simeq \left(\frac{RF}{C_p \rho} \right)^{1/3}. \quad (1)$$

For a heat flux near $10^4 \text{ erg cm}^{-2} \text{ s}^{-1}$, $w \sim 3 \times 10^2 \text{ cm s}^{-1}$. Applying this approximation to a dry portion of the Jovian atmosphere (such as the region where $T > 300 \text{ K}$) gives us an estimate of the overturn rate of the atmosphere. The eddy diffusion coefficient K ($\text{cm}^2 \text{ s}^{-1}$), which models vertical mixing as a globally-averaged one-dimensional random walk, is related to the mean vertical displacement Δz of a parcel of atmosphere after time interval Δt by $K = (\Delta z)^2 / \Delta t$. The mean vertical wind speed w is then $\Delta z / \Delta t$, whence $K \sim w \Delta z$. Turbulent cells usually have size scales comparable to the pressure scale height, H , of the atmosphere: $\Delta z \sim H = RT / \mu g$, where μ is the mean molecular weight and g is the acceleration due to gravity. In Jupiter's upper troposphere, H is on the order of 30 km ($3 \times 10^6 \text{ cm}$). Thus, for $w \sim 3 \times 10^2$, K would be about $wH = 10^9 \text{ cm}^2 \text{ s}^{-1}$.

The time scale Δt for dry free-convective overturn through a vertical displacement of one scale height is roughly $\Delta t = H^2 / K$, which is about 10^4 s . The overturn time scale is important because it provides a limit on the length of time over which disequilibrium products may accumulate in their production region. If we know the rate of formation of these species, then the overturn time permits us to calculate the maximum concentration of these products in their source region.

There also exists an entirely independent estimate of the overturn rate of the atmosphere. This estimate is based on an analysis of the stability of CO in the lower troposphere (Barshay and Lewis, 1978) that suggests that the observed CO abundance of about $X_{\text{CO}} = 10^{-9}$ near the tropopause could be provided by quenching of hot CO-bearing gas from the 1000 K level in the lower atmosphere. Prinn and Barshay (1977) have analyzed the homogeneous gas phase thermochemical kinetics of CO destruction in Jupiter's atmosphere and present arguments that, if the source of the observed CO is indeed quenched gas mixed rapidly upward, then the eddy diffusion coefficient near the 1000 K level must be on the order of $2 \times 10^8 \text{ cm}^2 \text{ s}^{-1}$. This is reassuringly close to the value estimated by mixing length theory. A value of K near 10^8 to 10^9 should apply to the entire region of the lower troposphere up to the level of water condensation.

In principle, other independent estimates of the eddy diffusion coefficient at various levels in the deep Jovian atmosphere can also be made. For example, the observed abundances of PH_3 and GeH_4 could be used to estimate K values. Unfortunately no experimental data are available for the thermochemical kinetics of the PH_3 oxidation and GeH_4 sulfurization reactions which destroy these species in Jupiter's atmosphere. However, Fegley and Prinn (1983a) have analyzed the PH_3 oxidation reaction using estimated rate constants. They find that the eddy diffusion coefficient of $2 \times 10^8 \text{ cm}^2 \text{ s}^{-1}$ deduced from the observed CO abundance implies that the PH_3 oxidation is quenched at approximately 1300 K. This result is consistent with the

proposed quench levels for both CO and N₂ (Prinn and Barshay, 1977; Prinn and Olaguer, 1981).

Gierasch (1976) has suggested that latent heat release from H₂O condensation may stabilize the upper troposphere and decrease the eddy mixing rate significantly (K between 10^5 and 10^6 cm² s⁻¹). We will assume a moist adiabat with saturation of H₂O and NH₃ allowed. These gases are assumed to have solar elemental abundance ratios.

The horizontal scale of motions, L_h , is taken as the radius of deformation, L_r :

$$L_h \approx L_r = \left(\frac{\alpha g H^2 \partial\theta/\partial z}{f^2} \right)^{1/2}, \quad (2)$$

where α is the compressibility ($1/T$ for an ideal gas), H is the scale height, f the Coriolis parameter ($\sim 10^{-4}$ s⁻¹ at typical latitudes), and θ is the potential temperature. Taking for $\partial\theta/\partial z$ a finite potential T difference of ~ 1.5 K over a temperature range of about 140 K and taking the adiabatic lapse rate $\Gamma = 2$ K km⁻¹, we have $\Delta\theta = 1.5$ K, and $\Delta z = \Delta T/\Gamma = 70$ km, whence $L_h = 10^8$ cm.

The Rossby number, $u/fL_h = R_0$, can be estimated for large-scale motions by using $u \simeq 10^3$ cm s⁻¹ as the typical horizontal wind speed (this ignores higher mean speeds due to smaller-scale motions), whence $R_0 = 0.1$. A lower limit on the effective eddy diffusion parameter is then

$$K = \frac{H}{L_h} R_0 u H \simeq \frac{\Delta(z)^2}{L_h} R_0 u = 5 \times 10^7 \text{ cm}^2 \text{ s}^{-1}. \quad (3)$$

Thus, it is far from obvious to us that a mean value of K much less than 10^8 is found over the 280 to 140 K region.

In order to maximize the stabilizing effect, one could restrict the potential temperature change to a narrow altitude interval to try to make a thin stable layer. Let us say that nearly all the $\Delta\theta$ (1.3 K) takes place due to the condensation of 90% of the water vapor between the ~ 280 and 254 K levels. Then $\Delta T = 26$ K, $\Delta z = 26/\Gamma \simeq 10$ km, and $L_h = 3.5 \times 10^7$ cm. The Rossby number is 0.3, and K evaluated over this Δz interval is then 10^7 cm² s⁻¹. The mixing time across this 'stable layer' is $\tau_{\text{mixing}} = (\Delta z)^2/K = 10^5$ s, compared to the mixing time over the two scale heights from the H₂O clouds to the NH₃ clouds *in the absence* of condensation, $(2H)^2/K = (6 \times 10^6)^2/2 \times 10^8 = 1.8 \times 10^5$ s. The difference due to the 10^5 s delay added by H₂O condensation is not very impressive: indeed, vertical motions may penetrate this thin stable layer and reduce or even remove this small correction. Further, we have neglected small-scale motions, which will enhance vertical mixing even further.

If, as suggested by the observations of Bjoraker *et al.* (1981) and Dossart and Encrenaz (1982), the water abundance in the troposphere is much less than solar, then this argument is strengthened.

In any case, the temperature structure will be sharply changed at pressures below about 2 bars, where the infrared opacity of the atmosphere drops to low enough levels to permit heat to be lost efficiently by radiation into space. The bulk of the heat load

then need not be carried by convection, and the mean vertical wind speed must decrease markedly. The eddy diffusion coefficient K must likewise decrease rapidly from the ~ 2 b level to the tropopause (at a few hundred mb).

At higher altitudes, well above the temperature minimum at the base of the stratosphere, K will increase again due to dissipation of energy by upward-propagating waves. In that regime, K will depend on the gas number density n roughly as $K \sim n^{-1/2}$. We are not concerned here with the details of the composition, structure, and motions at high altitudes; however, it is important to realize that there exists a minimum value of K in the vicinity of the 200 mb level.

We shall give one simple argument by which the value of K near the tropopause can be estimated. Phosphine, PH_3 , has a mole fraction of about 10^{-6} at the tropopause, where the total gas number density is about 10^{19} cm^{-3} . It is photolysed at a rate ϕ of $\sim 10^{11} \text{ cm}^{-2} \text{ s}^{-1}$. The vertical mixing rate must be sufficient to replenish the phosphine at the rate at which it is destroyed. We can easily see that w must be at least as large as ϕ/n , which is $10^{11}/10^{13} = 10^{-2} \text{ cm s}^{-1}$. Thus K must be at least $wH = 10^4 \text{ cm}^2 \text{ s}^{-1}$. Several other lines of evidence also points to virtually identical conclusions. This subject is well reviewed in Prinn and Owen (1976). We thus take the minimum value of K as $10^4 \text{ cm}^2 \text{ s}^{-1}$.

These considerations of exposure times and of vertical mixing rates are of great value in estimating the production rates and steady-state concentrations of many disequilibrium species such as CO, HCN, etc. We shall consider a number of such organic and inorganic tracers.

We shall treat the vertical distributions of these disequilibrium species in as much detail as presently available data permit, since these distributions are a rich source of information on the chemical and dynamical properties of the atmosphere. It is especially valuable to develop a reasonable clear advance understanding of the chemical structure of the Jovian atmosphere so that analytical experiments may be designed and optimized to address chemical problems in a realistic way. Excessive pressure on spacecraft experiments to analyze for trace constituents which could not conceivably be present in abundances greater than, say, one part in 10^{12} could cripple development of an analytical instrument, while failure of the experiment designers to consider certain species which may be detectable and useful tracers could lead to an equally unfortunate loss of valuable data.

2. Mechanisms for Production of Disequilibrium Species

In this section we shall treat the general features and energetic limits of several types of sources for tropospheric disequilibrium species. We shall consider both organic and inorganic species, but with more emphasis and detail on organic matter because of its importance in connection with the origin of life. A more extensive discussion of the vertical distribution of inorganic tracers is given by Fegley and Prinn (1983a).

We shall first consider direct production of organic matter by photolysis of methane

at high altitudes. This source, though small because of the limited solar UV flux capable of photolysing methane, is quite efficient in terms of product yield per erg.

Second, we shall deal with the indirect synthesis of organic matter and the direct production of inorganic tracers by photolysis of NH_3 , PH_3 , and H_2S . In this connection, both hot-atom abstraction reactions by H atoms and thermal synthesis of recombination products will be covered, using our recent treatment of the appropriate scaling of laboratory 'simulations' of such processes to conditions prevalent of Jupiter (Lewis and Fegley, 1979).

Third, we shall include the scaling of laboratory electrical discharge experiments to Jovian conditions (Lewis, 1976). We shall incorporate the very firm upper limits on the synthesis of interesting products by lightning and thunder shock waves arising from consideration of chemical, dynamical, and energetic constraints (Lewis, 1980a b; Borucki *et al.*, 1982).

Finally, we shall use the results of detailed of the equilibrium chemistry of the lower troposphere (Barshay and Lewis, 1978; Fegley and Lewis, 1979; Fegley and Prinn, 1983a, b) to assess rapid vertical mixing of the atmosphere as a source of species that are out of equilibrium in the observable regions of the troposphere.

2.1. THE HYDROCARBON PHOTOLYSIS REGION

Only radiation shortward of $\lambda = 1650 \text{ \AA}$ is capable of dissociating methane at a finite rate. The longest wavelength at which methane can be ionized is 1000 \AA , while the ionization threshold for $\text{N}_2 + n\nu \rightarrow \text{N}_2^+ + e^-$ is 800 \AA . The available solar flux shortward of 1650 \AA is $7 \times 10^9 \text{ cm}^{-2} \text{ s}^{-1}$ averaged over the entire planet, of which about 40% is in the $\text{L}\alpha$ line of atomic H. The flux shortward of 1000 \AA is $\sim 3.4 \times 10^8 \text{ cm}^{-2} \text{ s}^{-1}$ and that below 800 \AA $\sim 1.6 \times 10^8 \text{ cm}^{-2} \text{ s}^{-1}$, of which about $0.4 \times 10^8 \text{ cm}^{-2} \text{ s}^{-1}$ is due to the $\text{L}\alpha$ line of the He^+ ion at 304 \AA . Ammonia is essentially absent throughout all except the very bottom of the methane photolysis region, due not only to depletion by condensation, but also to photolytic destruction to make molecular nitrogen. The only other major species besides CH_4 and N_2 which are available as starting materials for photochemistry in the methane photolysis region are H_2 , He, and Ne, all of which have both high ionization (dissociation) energies and negligible chemistry. Several trace species such as C_2H_2 and C_2H_6 are also possible starting materials for photochemistry in this region. Thus the species produced in this region will generally be hydrocarbons, some of which may contain nitrogen as well: The limited region of overlap between the NH_3 and CH_4 photolysis regions has been shown by Kuhn *et al.* (1977) to be a source of methyl amine (CH_3NH_2). Kaye and Strobel (1982) have also studied the coupled photochemistry of NH_3 and C_2H_2 , which is an important pathway for HCN formation.

Products formed by photolysis at high altitudes are produced in and above a slowly mixed region ($K \simeq 10^4 \text{ cm}^2 \text{ s}^{-1}$ in the stratosphere) which is surmounted by the very low density regions of CH_4 and H_2 photodissociation and H_2 and He ionization, in which K increases with height at a rate probably proportional to $n_M^{-1/2}$ (n_M is the total number density). Since most photolysis products are destroyed by thermochemical

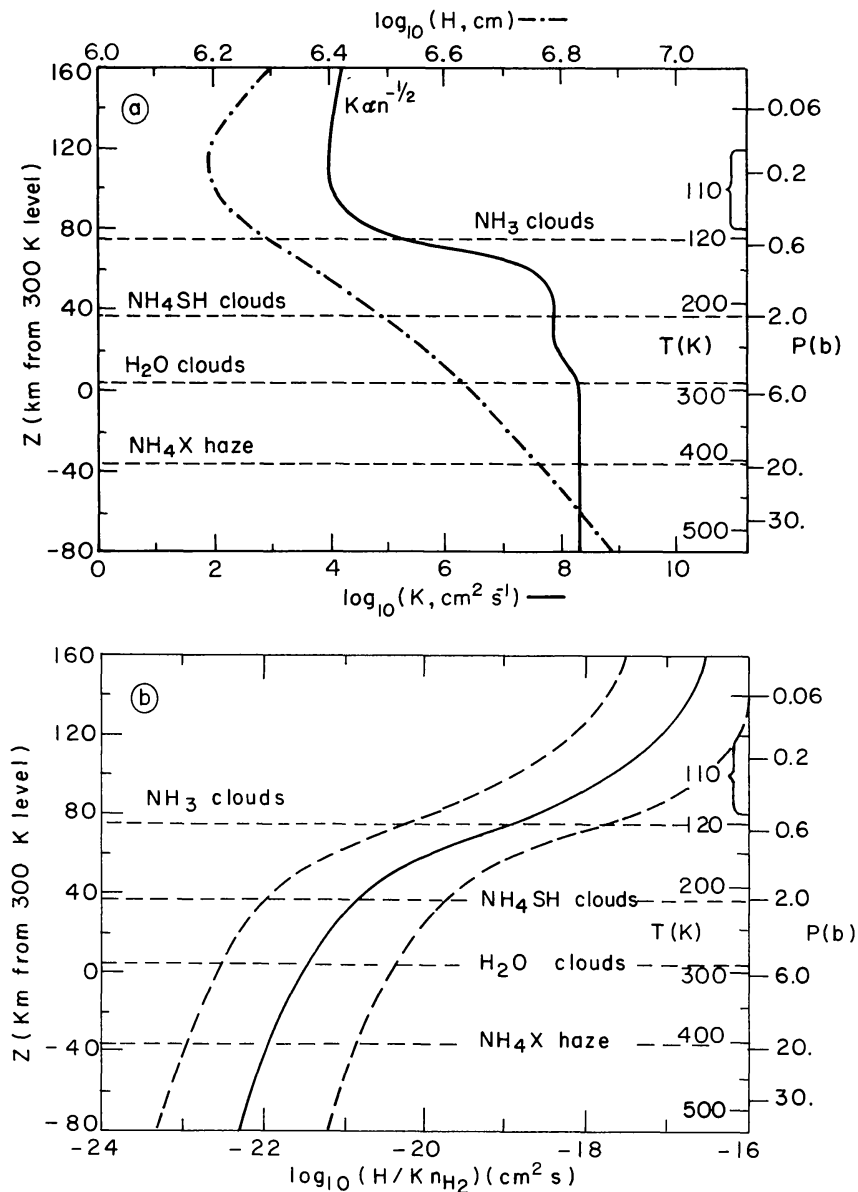


Fig. 1. Part (a) gives the values of H and K , and part (b) gives smoothed values of the parameter H/Kn_{H_2} , as functions of altitude. The steady state concentration of a species produced in the upper troposphere and destroyed by thermochemical equilibration in the lower atmosphere can be calculated by simply multiplying the source strength S ($\text{cm}^{-2} \text{s}^{-1}$) times the parameter H/Kn_{H_2} . The probable error in this parameter is about a factor of 10, with the largest errors likely in the region where K (and hence H/Kn_{H_2}) is rapidly varying. Errors in estimating H/Kn_{H_2} do not affect the relative abundances of disequilibrium species from similar source regions.

reactions deep within the atmosphere, there is a constant mean downward flux (and associated concentration gradient) of these species from the photolytic production region to the equilibrium region. The molecular hydrogen flux carried by larger scale overturn is just $\phi_{\text{H}_2} = n_{\text{H}_2} w$ ($\text{cm}^{-2} \text{s}^{-1}$), while the flux of each photolysis product i is just equal to its source strength, ϕ_i ($\text{cm}^{-2} \text{s}^{-1}$). The mole fraction of i is then $X_i = \phi_i H / Kn_{\text{H}_2}$. The values of H , K , and the factor H/Kn_{H_2} are shown in Figure 1 as functions of altitude throughout the region of interest to us.

In order to illustrate the effects of these simple considerations on the tropospheric abundance of organic products from methane photolysis, we shall use the steady-state downward flux of all (mainly C₂) hydrocarbons as calculated by Strobel (1973), $\sim 1 \times 10^9 \text{ cm}^{-2} \text{ s}^{-1}$ ($\sim 5 \times 10^{-14} \text{ g cm}^{-2} \text{ s}^{-1}$). Inserting this large a source into the Jovian mesosphere will provide a total mole fraction of all organics of $\sim 1 \times 10^{-13}$ in the 300–500 K region of the troposphere, as can be verified by reference of Figure 1. Since both K and n_{H_2} are small in the mesosphere, local mole fractions of methane photolysis products can be near 10^{-5} to 10^{-8} there without yielding a tropospheric abundance discernable at the part-per-trillion ($X_i = 10^{-12}$) level. For specific products, mechanistic and energetic considerations may permit far more stringent upper limits to be calculated.

Clearly, the solar flux in the methane photolysis region ($\lambda < 1650 \text{ \AA}$) is a very feeble source of tropospheric organic matter. The rapid increase in solar flux toward longer wavelengths provides a mean photolysis rate of $10^{11} \text{ cm}^{-2} \text{ s}^{-1}$ for NH₃ and PH₃ ($\lambda\lambda 1650$ to 2350 \AA) and $10^{12} \text{ cm}^{-2} \text{ s}^{-1}$ for H₂S ($\lambda\lambda 2350$ to 2700 \AA), and we will therefore examine other possible pathways of minor branches to the photochemistry of these species which could produce organic matter at a rate greater than that of direct CH₄ photolysis.

2.2. HOT-ATOM CHEMISTRY

Khare, Sagan, and coworkers (Khare and Sagan, 1971, 1973; Sagan and Khare, 1971a, b; Khare *et al.*, 1978) have reported UV photolysis experiments in ‘simulated Jovian atmospheres with a low hydrogen abundance’, i.e., mixtures of CH₄, NH₃, H₂S, and C₂H₆ in roughly equimolar amounts. By irradiation for very long times with an extremely intense near UV source (5.8 W at the mercury 2537 Å resonance line for up to 418.6 hr) they produced a complex mixture of sulfur, sulfides and organic matter. Since the wavelength used is absorbed only by H₂S, they attribute the formation of organic matter to indirect destruction of methane by abstraction reactions by hot hydrogen atoms from H₂S photolysis. Hydrogen atoms may be thermalized by collisions with other molecules, especially light species such as H₂. Conservation of momentum in the center-of-mass frame clearly predicts that collisions of H atoms with cold (‘stationary’) heavy molecules will remove little momentum per collision, while collisions with cold H₂ molecules leads to the loss of a large fraction of the atom’s momentum in a single collision. H atoms with $\sim 1 \text{ V}$ translational energy in a cool (0.2 eV) H₂ gas will be effectively thermalized in two collisions with H₂, but will still be ‘hot’ and reactive after 10 collisions with CH₄, NH₃, C₂H₆ and other heavy molecules (Lewis and Fegley, 1979). By ‘thermalized’, we here mean that the speed of the atom has been reduced to below 1.5 times the mean thermal speed at ambient temperatures.

In applying the results of the above experiments to Jupiter, we shall be concerned with two major scaling effects. First, we shall calculate the efficiency of the process and scale it to realistic Jovian energy fluxes and UV exposure times. Second, we shall consider the effects of the actual H₂- and He-rich Jovian atmosphere on the abundances of products formed by the hot-atom mechanism.

Scaling the yields of products from the experiments of Khare *et al.* is hindered by their failure to report even approximate yields; we are told only that 4862 cm³ NTP of H₂S (total) was irradiated, and that the products contained 95% sulfur by weight and 5% organic (H, C, N, O) matter on a sulfur-free basis. We will accordingly make the most generous possible assumption to maximize the yield of organic matter: that *all* the H₂S was converted into condensed sulfur and sulfur compounds, and that 5% of the total condensed matter was sulfur-free H, C, N, and O compounds. Then the total mass of solids would be 7 g, and the organic component would total 0.35 g. The lamp delivered 5.8 W for 1.4 × 10⁶ s, for a total energy input of 8 × 10¹³ erg. The efficiency of production of organic matter was then 4 × 10⁻¹⁵ g erg⁻¹.

The flux of UV available for photolysis of H₂S on Jupiter is 60 erg cm⁻² s⁻¹, and the time over which products may accumulate in the troposphere is related to the eddy mixing rate by

$$\tau = \frac{H^2}{K} \simeq 3 \times 10^4 \text{ s} . \quad (4)$$

The efficiency of production of organic matter made in the laboratory ‘simulation’, uncorrected for thermalization of hot H atoms by collisions with H₂, would then provide 4 × 10⁻¹⁵ g erg⁻¹ × 60 erg s⁻¹ cm⁻² × 3 × 10⁴ s = 0.7 × 10⁻⁸ g cm⁻² of organic matter after exposure for the full mixing time. The mass of atmosphere into which this matter is mixed is $P/g \geq 2 \times 10^6$ dyne cm⁻²/2500 cm s⁻², or > 800 g cm⁻², so that the *mass* fraction of organic matter at tropospheric pressures > 2 b is < 0.7 × 10⁻⁸/800 ≈ 10⁻¹¹. The highest possible mole fraction of organic matter would be reached if C₂H₂, HCN, or other small organic species were dominant: their total *mole* fraction would then be < 10⁻¹². Note that this mass fraction, some 20 times that provided by direct CH₄ photolysis, requires a very non-Jovian atmospheric composition, with hydrogen depleted by a fraction of 10⁴ or more.

Let us now consider the correction necessitated by thermalization of H atoms on Jupiter. The molar H₂ : CH₄ ratio on Jupiter is ~ 3000 : 1, and the probability that a hot H atom in collision with a CH₄ molecule will react is only 10⁻³ to 10⁻² (Steacie, 1954; Thrush, 1965). Martin and Willard (1964) report a reaction probability of 3.2 × 10⁻³. We shall use 10⁻² as an upper limit on the reactive probability, which is probably not a very serious overestimate at the low energies involved here: a typical ~ 2600 Å photon (4.9 eV), after providing 3.9 eV to break the HS–H bond, will give only ~ 1 eV kinetic energy to the H atom (Gann and Dubrin, 1967). It has been shown by Lewis and Fegley (1979) that, with proper weighting for the collisional cross sections of H₂, He, and CH₄, the fraction of hot H atoms which react with methane on Jupiter is 6 × 10⁻⁵ that found in the laboratory, where the H₂ abundance is far smaller and thermalization is very inefficient.

It is clear that simple scaling of the conditions of the laboratory ‘simulation’ to Jupiter would give an efficiency of production of organic matter of 4 × 10⁻¹⁵ × 6 × 10⁻⁵ = 2.4 × 10⁻¹⁹ g erg⁻¹. Using an overturn time of 3 × 10⁴ s at

the ~ 210 K level on Jupiter, the $60 \text{ erg cm}^{-2} \text{ s}^{-1}$ available solar flux ($2350 < \lambda < 2700 \text{ \AA}$) would provide a steady-state abundance of organics of $60 \times 3 \times 10^4 \times 2.4 \times 10^{-19} = 4 \times 10^{-13} \text{ g cm}^{-2}$, for a *weight* fraction of $\sim 5 \times 10^{-16}$, and a *mole* fraction of total organics of $\sim 5 \times 10^{-17}$. Almost all of this organic matter would be methyl mercaptan, CH_3SH , formed by reaction of hot-atom-produced CH_3 with photochemical SH.

The present practical detection thresholds for GC/MS *in situ* analysis or IR remote spectroscopy are close to 10^{-9} mole fraction, and thus the expected abundance of organic matter from this hot-atom source is several orders of magnitude too low for detection with the most sensitive available analytical techniques.

There seems little point to repeating these calculations in detail for the NH_3/PH_3 photolysis region, since the efficiency of thermalization of H abstraction will at best be the same there as in the present example, while the rate of production of hot H atoms, limited by the available solar UV of wavelength $1650 < \lambda < 2350 \text{ \AA}$, is an order of magnitude smaller than that found for H_2S photolysis.

In any case, the rate of production of organic matter by hot-atom reactions from H_2S , PH_3 , and NH_3 photolysis is negligible compared to the direct methane photolysis source.

2.3. LIGHTNING AND THUNDER

Following the reasoning of Lewis (1976, 1980a, b), we shall first estimate the likely rate of production of organic matter by lightning discharges in the Jovian troposphere, based on efficiencies measured in laboratory experiments.

We shall assume that the entire vertical heat flux near the water-cloud level (~ 280 K), which has a globally averaged value of $0.9 \times 10^4 \text{ erg cm}^{-2} \text{ s}^{-1}$, is carried by bulk atmospheric motions. We will assume (Lewis, 1976) that the efficiency for conversion of atmospheric convective heat flux into lightning is the same on Jupiter as on Earth (i.e. $\sim 10^{-4}$ erg/erg). We further assume that the efficiency of production of organic matter by lightning in a solar-composition gas ($X_{\text{CH}_4} \simeq 3 \times 10^{-4}$) is the same as in laboratory discharge experiments in *pure methane*. Laboratory experiments by Miller (1955) on 60 kV spark discharges in a 1:2:2 mixture of H_2 , CH_4 , and NH_3 showed a production efficiency of $\sim 10^{-14} \text{ g erg}^{-1}$, and Ponnampertuma and Woeller (1964) have found efficiencies ranging from 10^{-15} to $10^{-13} \text{ g erg}^{-1}$ for 0.85 to 9.4 kV discharges in pure methane. Miller (1955) found that higher spark voltages, modestly closer to the natural-lightning range, gave a *decreased* product diversity and yield. We shall therefore adopt $10^{-14} \text{ g erg}^{-1}$ as typical of laboratory results for very methane-rich gases, with the clear expectation that 3000:1 dilution with H_2 and use of 10^8 to 10^9 V discharges may greatly reduce the yield in nature.

Combining these efficiencies, then, we generously estimate that Jovian lightning might produce $10^4 \times 10^{-4} \times 10^{-14} = 10^{-14} \text{ gm cm}^{-2} \text{ s}^{-1}$ of organic matter. This upper limit is smaller than the production rate of total organics from direct methane photolysis which we calculated earlier.

Bar-Nun and coworkers (Bar-Nun and Tauber, 1972; Bar-Nun and Shaviv, 1975;

Bar-Nun, 1975, 1979) have pointed out that most of the efficiency of natural lightning strokes in effecting chemical synthesis is due to shock wave heating and subsequent rapid cooling of a sheath of gas surrounding the extremely hot (but thin) plasma core. This 'thunder' mechanism bypasses the expected inefficiency of very high-temperature processes in making complex molecules, and loses very little of its advantage in the conversion of electrical energy to shock wave energy (roughly 40% efficiency on Earth). Bar-Nun and Shaviv (1975) have reported that the efficiency of production of hydrocarbons in hydrogen-rich shocked $\text{H}_2 + \text{CO}$ gas mixtures lies between 10^{-13} and $10^{-11} \text{ g erg}^{-1}$, with almost no sensitivity to the initial CO mole fraction. This is 100 times the efficiency seen in electrical discharge syntheses, and seems to be due to the chemical instability of the $\text{CO} + \text{H}_2$ mixture, which spontaneously reacts to make hydrocarbons over a wide range of conditions. There is no reason to suppose that the chemically stable low-temperature mixture of CH_4 , H_2O , and H_2 in the Jovian atmosphere should yield complex hydrocarbons nearly this efficiently. Indeed, Lewis (1980a) has shown that the energetic cost of heating a Jovian solar-composition gas mixture to high enough temperatures for CO and hydrocarbon synthesis is so large that efficiencies of $\sim 2 \times 10^{-14} \text{ g erg}^{-1}$ are expected. The main product is CO, with N_2 , HCN, C_2H_2 and smaller traces of other gases also present. HCN and organic molecules are formed in amounts 100 times smaller than CO. For an Earthlike efficiency of production of lightning from atmospheric heat fluxes, a steady-state HCN mole fraction of 3×10^{-16} is predicted in the upper troposphere. Even if 100% of the heat flux is used with perfect efficiency to make lightning, and thunder shock energy is used solely to heat gas parcels to the optimum (P, T) conditions for synthesis of dis-equilibrium species, the resulting absolute upper limit on the HCN abundance would be only $X_{\text{HCN}} \simeq 2.5 \times 10^{-12}$. Lewis (1980a) presents results for CO, N_2 , C_2H_2 , CH_2O , CO_2 , and C_2H_6 in addition to HCN.

Voyager observations of optical flashes (Cook *et al.*, 1979) and ratio whistlers (Scarf *et al.*, 1979) associated with Jovian lightning led Lewis (1980b) to estimate lightning energy dissipation rates and conversion efficiencies that could be as low as 10^{-3} times these values. For the purpose of estimating the abundances of lightning and thunder products, however, he used a conversion efficiency of $\sim 10^{-5}$ (erg/erg). Extensive analysis of both the optical and whistler data by Borucki *et al.* (1982) has led to the conclusion that the conversion efficiency of convective energy to lightning on Jupiter is $(4 \pm 1) \times 10^{-5}$. This confirms the estimate of Lewis (1976), who preferred a Jovian efficiency somewhat less than that found on Earth ($\sim 10^{-4}$).

Using this observationally derived efficiency, we would predict a mole fraction of $\sim 1 \times 10^{-16}$ for HCN in the water cloud region.

2.4. DEEP ATMOSPHERIC MIXING

At high temperatures and pressures deep in the Jovian atmosphere the rates of chemical reactions are so large that the time scale for thermochemical equilibrium is very much shorter than the time scale for convective overturn and vertical mixing. Chemical equilibrium is therefore very closely approached. That such equilibration happens has been known for many years, because of the observed dominance of photochemically

unstable species such as CH_4 and NH_3 in the upper atmosphere. This observation leads naturally to the postulate of atmospheric overturn and equilibration at great depths (see for example, Lewis, 1969a).

The chemical composition of the atmospheres of the Jovian planets at equilibrium has been investigated in great detail for over 800 compounds of 46 elements (Lewis, 1969a; Barshay and Lewis, 1978; Fegley and Lewis, 1979; Fegley and Prinn, 1983a, b). Based on this understanding of the equilibrium state at each (Z, T, P) level, several authors have studied the thermochemical kinetics of the destruction reactions of several species that are stable at high temperatures and pressures. Prinn and Barshay (1977) have examined the kinetics for the conversion of CO to CH_4 . They find that the observed CO mole fraction of $X_{\text{CO}} \sim 10^{-9}$, which is in equilibrium at the 1150 K level, will be quenched at that temperature for a vertical mixing rate corresponding to $K = 2 \times 10^8 \text{ cm}^2 \text{ s}^{-1}$. As previously mentioned, this K value is well within the range of 10^7 to $10^9 \text{ cm}^2 \text{ s}^{-1}$ estimated from the vertical transport of Jupiter's internal heat flux (Stone, 1976; Flaser and Gierasch, 1977). Prinn and Olaguer (1981) have analyzed the kinetics for the homogeneous and heterogeneous conversion of N_2 to NH_3 . They predict that vertical motions will transport large amounts of N_2 from the 900–1700 K levels up to the visible levels in Jupiter's atmosphere. The predicted N_2 mole fractions range from 10^{-5} to 0.6×10^{-6} depending on the reactions considered (homogeneous gas phase vs heterogeneous Fe-metal catalysed reactions). Finally, Fegley and Prinn (1983a) have studied the gas phase oxidation of PH_3 to P_4O_6 . They conclude that the observed PH_4 abundance may be due to rapid vertical transport ($K = 2 \times 10^8 \text{ cm}^2 \text{ s}^{-1}$) from about the 1300 K level.

A number of other gaseous species stable in the 400–1000 K region, and having mixing ratios near or above 10^{-11} in this region have been identified by Barshay and Lewis (1978) and Fegley and Lewis (1979) as potential tracers of deep atmospheric mixing. These species include H_2Se , HF , H_3BO_3 , GeH_4 , SbH_3 , HCl , SbS , H_2Te , AsF_3 , TlI , and InBr . Of these, only GeH_4 has been detected (Fink *et al.*, 1978). In principle these tracers can provide information about atmospheric mixing rates over a wide altitude range. For example, GeH_4 , SbH_3 , and SbS abundances are potentially valuable diagnostics of atmospheric dynamics around the 1000 K level. Other gases such as H_2Se , HF , H_3BO_3 , HCl , H_2Te , AsF_3 , TlI , and InBr may provide information about mixing rates at higher levels around 300–500 K.

There are a few potential organic tracers of deep atmospheric mixing, most of which are not as abundant as the above-mentioned inorganic species at equilibrium at 1000 K. The best organic prospects are C_2H_6 (ethane), CH_3SH (methyl mercaptan), CH_3OH (methanol), CH_3NH_2 (methylamine), CH_2O (formaldehyde), C_2H_4 (ethylene), and HCN (hydrogen cyanide), all of which would require rapid quench from 2000 K or higher in order to preserve observably high abundances.

A number of these organic species may in fact remain reactive down to temperatures of 1000 K or lower, and thus be depleted in abundance, by equilibration, to unobservably low concentrations. It is a complex problem in chemical kinetics to identify the reactions responsible for their destruction, to determine their chemical lifetimes as a function of

altitude (T and P) along a Jovian adiabat, and to find the altitude above which the equilibration time is longer than the mixing time.

Another potential source of distinctive tracers of deep mixing is free radicals, especially those which are abundant at equilibrium near 1000 K or higher. Barshay and Lewis cite PH_2 , H , HS , CH_3 , and NH_2 as the most abundant radicals (mole fractions $\lesssim 10^{-12}$ at 1000 K). Recombination and reaction products formed from these radicals at lower temperatures may in some cases be diagnostic of this mode of origin. However, such species are likely to be very minor constituents. The free radicals R_i themselves will recombine via either two-body or three-body mechanisms:



where M is any third body (such as H_2), k is the bimolecular rate constant ($\text{cm}^3 \text{s}^{-1}$), and l is the rate constant for three-body recombination ($\text{cm}^6 \text{s}^{-1}$). Typical values of k and l for recombination reactions of the radicals listed above are $10^{-10} \text{cm}^3 \text{s}^{-1}$ and $10^{-30} \text{cm}^6 \text{s}^{-1}$, respectively. These rates are essentially independent of temperature, since there is zero activation energy for such reactions. The recombination time scale for bimolecular reaction is the ratio of the radical number density, n_R (cm^{-3}), to its reaction rate, kn_R^2 , or $\tau \simeq 10^{10} n_R^{-1} \text{s}$. Similarly, the time scale for three-body recombination is $n_R / (ln_R n_M)$; or $\tau = 10^{30} n_R n_M^{-1} \text{s}$. These typical reaction times will be equal where $n_M \simeq 10^{20} \text{cm}^{-3}$ (the $T \simeq 260 \text{K}$, $P \simeq 3.5 \text{b}$ level), with the three-body reaction dominant deeper in the atmosphere. The radical number density is unable to drop below a value fixed by the mixing time scale, which at the 260 K level is given by $K \simeq 5 \times 10^7 \text{cm}^2 \text{s}^{-1}$. For mixing up to the cloud tops, $(\Delta Z)^2 / K = (5 \times 10^6)^2 / 5 \times 10^7 = 5 \times 10^5 \text{s}$, so that $n_R \simeq 10^{10} / 5 \times 10^5 = 2 \times 10^4 \text{cm}^{-3}$. The atmospheric density is 10^{20}cm^{-3} , and thus $X_R = 2 \times 10^{-16}$, due solely to the lower atmospheric source. The mean vertical wind speed at this level, $w = K/H$, is 10cm s^{-1} , for a total mass flux of $10^{21} \text{cm}^{-2} \text{s}^{-1}$, and a free-radical flux of $2 \times 10^5 \text{cm}^{-2} \text{s}^{-1}$. For ionic recombination with free electrons, $k \simeq 10^{-7} \text{cm}^{-7} \text{cm}^3 \text{s}^{-1}$.

Species produced at equilibrium or by partial equilibration deep within the atmosphere, and which are not destroyed by processes at higher altitudes, will have constant mole fractions in the upper troposphere. Molecular nitrogen is an example of such a species.

The equilibrium abundances of high-temperature species at that level in the atmosphere where chemical reactions become slower than overturn are preserved up to high altitudes, where photochemically active species may be destroyed by solar UV. Photochemically unreactive and uncondensable species will have constant mole fractions from the quenching level up to the turbopause. The vertical distribution of such a quenched high-temperature species is compared to that for a typical photochemical product in Figure 2.

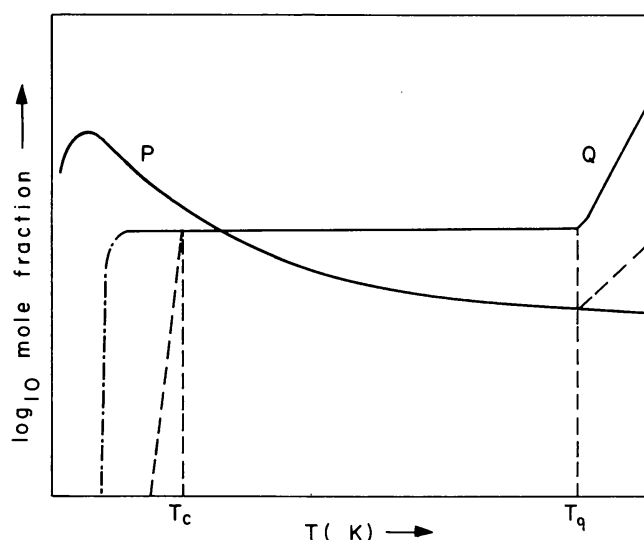


Fig. 2. Schematic vertical distributions for quenched lower-troposphere gases and photolysis products. Curve Q shows the distribution for quenched high-temperature gases. T_Q is the quench temperature, below which the chemical lifetime of the species Q is longer than the characteristic time for vertical mixing, H^2/K . The dashed extension of Q shows the effect of condensation at temperature τ , while the dot-dashed line shows schematically the effects of UV photolysis of an uncondensable but photolabile Q . Curve P shows the vertical distribution of a typical photolysis product. The dashed branch of curve P shows the distribution of a species which is *both* a photochemical and quench product which 'freezes in' at T_Q . For explanations, refer to the text and to Figure 1.

3. Vertical Distributions of Specific Compounds

In this section we treat the vertical distributions of a number of specific organic and inorganic tracers that may be synthesized in any of the process previously considered. For each species we shall, so far as possible, quantify the source strengths and the effects of vertical mixing. As in Figure 2, we shall report the mole fractions of products as a function of (Z , P , T) in the atmosphere.

The principal organic species considered are HCN, CH_2O , C_2H_2 , C_2H_4 , C_2H_6 , CH_3NH_2 , CH_3SH , CH_3OH , HCOOH , and the free radicals HCO, CN, and CH_3 . We begin with HCN, the most widely discussed.

3.1. ORGANIC COMPOUNDS

HCN

Since HCN is an important intermediate in the synthesis of aldehydes, alcohols, acids and amino acids, its possible production on Jupiter has long been a matter of interest. Sources which have been suggested include photolysis of $\text{CH}_4\text{-NH}_3$ mixtures (Ferris and Chen, 1975), hot-atom chemistry initiated by solar UV photolysis of H_2 (Sagan and Khare, 1971a, b; Khare and Sagan, 1971, 1973; Khare *et al.*, 1978), exposure of gases to high exospheric temperatures (Lippincott *et al.*, 1967), electrical discharges (Woeller and Ponnampuruma, 1969), thunder shock waves (Bar-Nun *et al.*, 1970; Bar-Nun and

Tauber, 1976; Bar-Nun, 1975, 1979; Bar-Nun and Saviv, 1975), and the coupled photochemistry of NH_3 and C_2H_2 (Kaye and Strobel, 1982).

The observational evidence regarding HCN on Jupiter has, until recently, been ambiguous. The claim by Sagan (1960) of identification of a weak absorption feature at $1.53 \mu\text{m}$ in the Jovian IR spectrum has received no observational or theoretical support. A feature in the $5 \mu\text{m}$ transmission window was tentatively assigned to either germane GeH_4 or to HCN (Munch and Neugebauer, 1971; Beer and Taylor, 1973; Larson *et al.*, 1976), in qualitative support of suggestions by Sagan and Miller (1960), Woeller and Ponnampertuma (1969) and Ponnampertuma and Molton (1973). However, Larson *et al.* (1977) have interpreted the $4.73 \mu\text{m}$ feature as largely due to PH_3 and possibly GeH_4 . Treffers *et al.* (1978) set a spectroscopic upper limit on HCN of $X_{\text{HCN}} = 1 \times 10^{-6}$, and Fink *et al.* (1978) have attributed the $4.73 \mu\text{m}$ feature to GeH_4 , with mole fraction $X_{\text{GeH}_4} = 6 \times 10^{-10}$.

Tokunaga *et al.* (1981) have reported a reasonably convincing case for the detection of several absorption lines of the ν_2 fundamental of HCN (near $13.5 \mu\text{m}$). A column abundance of $5 \times 10^{-3} \text{ cm amagat}$ was estimated, corresponding to a mole fraction near 10^{-9} . Due to the absence of self-reversed emission cores in the observed lines, the HCN is believed to be concentrated near and below the level of the tropopause: it surely is not more abundant above the temperature minimum than it is below it. This is what would be expected if HCN were made by NH_3 photolysis.

We shall first explore several possible mechanisms for involvement for nitrogen in the photochemistry of carbon, then turn to lightning and thunder production, the effects of rapid vertical mixing, and condensation by formation of NH_4CN (Lewis, 1969b).

Photochemical destruction of NH_3 and N_2H_2 at high altitudes leads to efficient conversion of NH_3 into N_2 . Molecular nitrogen cannot be photolysed directly to make N atoms, but instead only photoionizes to $\text{N}_2^+ + e^-$. The photoionization threshold for N_2 is 796 \AA , shortward of the H_2 cutoff, and N_2 must compete with H_2 (and with CH_4) for these photons (Huffman *et al.*, 1963). The fraction of the 800 \AA photons absorbed by N_2 is only 8×10^{-7} , or $500 \text{ cm}^{-2} \text{ s}^{-1}$. The N_2^+ ion can undergo dissociative recombination via $\text{N}_2^+ + e^- \rightarrow \text{N}^* + \text{N}^*$, where the N atoms carry off the excess neutralization energy remaining after breaking the N–N bond as translational kinetic energy. There are known reactions by which N atoms can attack simple hydrocarbons to produce HCN, although these reactions are not in general very fast: Abell (1976) quotes rate constants near 10^7 for $\text{N} + \text{C}_2\text{H}_2$ or $\text{N} + \text{C}_2\text{H}_4$ at 150 K . To avoid the complexities of a detailed model, we shall assume the following to calculate a firm upper limit on the HCN production rate by this mechanism: that every N_2^+ ion yields two HCN molecules with perfect efficiency. The maximum HCN production rate is then $10^3 \text{ cm}^{-2} \text{ s}^{-1}$. From Figure 1 we calculate a tropospheric HCN mole fraction varying from 10^{-15} at the NH_3 cloud level to 10^{-19} near the 300 K level.

A second, somewhat more direct, method of achieving participation of nitrogen in the chemistry of carbon would be to find a means of producing atomic nitrogen in the ammonia photolysis region. Methane screens ammonia from UV shortward of 1650 \AA with great effectiveness, since the ammonia abundance above the tropopause and in the

methane absorption layer is very severely limited by both NH_3 condensation and long-wave ($2350 > \lambda > 1650 \text{ \AA}$) UV photolysis. The overwhelming majority of the NH_3 never sees a photon of $\lambda < 1650 \text{ \AA}$, equivalent to 7.55 eV. The least demanding mechanism for making N is $\text{NH}_3 \rightarrow \text{N} + \text{H}_2 + \text{H}$, which has an absolute minimum enthalpy requirement of $176.04 \text{ kcal mole}^{-1}$, or 7.69 eV. In reality, so much energy is carried off by H and H_2 in ammonia photolysis that the only reaction of importance in this wavelength region is $\text{NH}_3 \rightarrow \text{NH}_2 + \text{H}$ (103.1 kcal; 4.5 eV), and the cross section for $\text{NH}_3 \rightarrow \text{NH} + \text{H}_2$ (92.0 kcal; 4.28 eV) is at best very small and poorly known. Schnepf and Dressler (1960) found NH to be produced at longer wavelengths. It is therefore clear that atomic N production from NH_3 photolysis is not a viable source of HCN.

The high kinetic energy of the H atoms ejected during NH_3 photolysis provides another possible mechanism. Consider that the loss of 4.50 eV (the dissociation energy, D^0 , of $\text{H}_2\text{-H}$) from incident photons carrying 5.30 to 7.55 eV leaves 0.80 to 3.50 eV available for excitation of the products. Conservation of momentum in the center-of-mass (C.M.) system shows that the departure speed of the H atom will be 16 times that of the recoil speed of NH_2 , and thus H carries 95% of the excess energy as translational kinetic energy (0.76 to 2.89 eV). The highest of these energies corresponds to the thermal speed of H at 4000 K.

Thermalization of hot H atoms in a solar-composition gas has been shown by Lewis and Fegley (1979) to occur with extreme rapidity due to efficient momentum transfer in $\text{H} \rightarrow \text{H}_2$ collisions, in each of which the hot atom loses 5/9 of its kinetic energy. The number of collisions needed to thermalize to $\sim 300 \text{ K}$ is $n = \log(300/4000)/\log(4/9)$ or 3 collisions. The fraction of hot H atoms which are able to abstract hydrogen from methane to make CH_3 (and thus initiate hydrocarbon involvement in nitrogen photochemistry) is only 3×10^{-3} on Jupiter (Martin and Willard, 1964). Since the total photolysis rate of NH_3 is $\sim 10^{11} \text{ cm}^{-2}$, the maximum conceivable rate of formation of C-N bonds (as CH_3NH_2) is only $\sim 3 \times 10^8 \text{ cm}^{-2} \text{ s}^{-1}$ if every CH_3 radical so produced reacted with NH_2 . Of course the most efficient production of CH_3NH_2 actually occurs at higher altitudes, where the CH_4 and NH_3 photolysis rates are comparable although small. Kuhn *et al.* (1977) calculate a peak methyl amine mole fraction of 3×10^{-11} in the vicinity of the tropopause, varying slowly with altitude, with a production rate of about $3 \times 10^6 \text{ cm}^{-2} \text{ s}^{-1}$. The total photochemical conversion of this amount of CH_3NH_2 into HCN would provide a local mole fraction of 3×10^{-11} near the tropopause, and less at lower altitudes. Thus photolysis of *photochemically produced* CH_3NH_2 can probably be dismissed as the source of the observed HCN. Photolysis of quenched CH_3NH_2 (advected from the lower atmosphere) apparently can provide a much larger amount of HCN. This problem is clearly deserving of further study.

Laboratory studies on the production of C-N bonds due to NH_3 photolysis are very limited. Ferris and Chen (1975) and Raulin *et al.* (1979) claim a very small production of HCN from photolysis of $\text{NH}_3\text{-CH}_4$ mixtures with 1849 \AA and 1470 \AA light, amounting to $(1 \text{ to } 8) \times 10^{-4}$ HCN molecules per NH_3 photolyzed, which translates into a few times $10^7 \text{ cm}^{-2} \text{ s}^{-1}$ on Jupiter. Ferris *et al.* (1977) propose a mechanism which involves $\text{H} + \text{CH}_4$ and $\text{NH}_2 + \text{CH}_4$ abstraction reactions 'if activation energies

are low', but the mechanism they suggest does not make HCN. The activation energies for both reactions are well known, and they are 11 900 and 11 800 cal mole⁻¹, respectively (Kerr, 1976), introducing a factor $e^{-E^*/RT} \simeq e^{-50}$ into the rate at 120 K. Thus hot-atom reactions fail because of rapid thermalization on Jupiter, and thermal abstraction reactions of H and NH₂ with CH₄ fail because of large activation energy barriers. If the HCN reported by Ferris and Chen is to be attributed to hot-atom processes, then scaling to Jovian conditions would dramatically lower the expected yields by a factor of $\sim 10^{-2}$ to 10^{-4} . A production rate of $\sim 3 \times 10^7$ cm⁻² s⁻¹ for HCN via NH₃ photolysis, neglecting this downward correction, provides an HCN mole fraction of $\sim 3 \times 10^{-12}$ at the NH₃ clouds and $\sim 10^{-14}$ below the 300 K level. A more reasonable expectation would be ~ 100 times lower. A study of the effects of the hydrogen content of the initial gas mixture by Ferris and Morimoto (1981) clearly shows that the HCN yield from 1850 Å photolysis of CH₄-NH₃-H₂ mixtures declines precipitously as Jovian H₂ abundances are approached. This strongly supports the influence that hot-atom reactions are responsible for HCN synthesis in this laboratory system, and leads us to conclude that this process is negligible on Jupiter.

Kaye and Strobel (1982) have recently studied the coupled photochemistry of NH₃ and C₂H₂ which they suggest is an efficient pathway for producing HCN. Their model yields a HCN abundance comparable to that observed by Tokunaga *et al.* (1981) if vertical mixing is slow ($K \sim 10^4$ cm² s⁻¹) above the NH₃ cloud tops. It is important to check their results by experimental measurement of several of the rate coefficients that had to be estimated in their calculations.

As we remarked earlier, HCN is a characteristic product of very high temperature equilibration at moderately high pressures. The abundance of HCN over a wide range of temperatures and pressures is discussed in detail in Lewis (1980a), with lightning and thunder shock wave production in mind. A range of P, T histories from isopycnic (constant density) to adiabatic (constant entropy) was explored, and the efficiency of production of HCN, CO, and many other products was calculated for the P, T profile which optimizes the yield of organic matter per erg of energy.

Isopycnic heating leads to entry into the CO stability field (Lewis *et al.*, 1978) at too low a temperature for efficient HCN synthesis. If the heating process is adiabatic, the pressure-temperature history will follow the Jupiter adiabat, which lies at pressures several orders of magnitude too high for optimum HCN production. The optimum case is heating to 3000 K with a peak pressure near 10³ bars, where X_{HCN} can reach $\sim 2 \times 10^{-6}$. To beat the $X_{\text{HCN}} = 2 \times 10^{-6}$ figure during shock heating along a Jovian adiabat, a temperature of ~ 5000 K is required, and quenching from ~ 5000 K without loss of HCN is essential! Dilution with unshocked gas will then reduce H_{HCN} to $\sim 2.5 \times 10^{-12}$ (Lewis, 1980a).

A realistic lightning stroke would achieve a peak temperature in the leader core far too high for efficient synthesis of any interesting molecule at great expense in energy, while most of the volume compressed and heated by the resulting shock wave would be heated to a temperature far too low for efficient HCN synthesis. Clearly the grossly artificial optimum use of energy (to shock to exactly the CO/CH₄ boundary) which we

have used in our calculations gives this figure for the HCN concentration more the character of an upper limit rather than an estimate.

Simple scaling of the observed efficiency of production of organic matter in laboratory electrical discharge experiments through pure methane (10^{-14} g erg $^{-1}$) with 0.01% conversion of Jupiter's internal heat flux into lightning will provide $\sim 10^{-14}$ g cm $^{-2}$ s $^{-1}$ of total organics, of which <1% is HCN. Over the mixing timescale, only $\sim 5 \times 10^{-12}$ g cm $^{-2}$ of HCN can be produced, which upon dilution gives $X_{\text{HCN}} \simeq 6 \times 10^{-16}$.

A more detailed model of high-temperature shock synthesis by using 0.01% of the available convective energy to heat solar-composition parcels of gas to exactly the optimum pressure and temperature for highest efficiency of production of HCN, CH $_2$ O, and organic matter, gives very nearly the same results ($X_{\text{HCN}} \simeq 2 \times 10^{-16}$) (Lewis, 1980a).

No laboratory simulation of Jovian conditions has ever demonstrated an efficiency of production of organic matter from lightning higher than $\sim 2 \times 10^{-14}$ g erg $^{-1}$, the efficiency calculated theoretically. Every experiment which reports a higher yield does so *because* of the way it deviates from known Jovian conditions.

Since violent heating events produce other characteristic high-temperature species more abundantly than HCN, we may use them to establish observationally-based limits on HCN. These species include CO, CH $_3$, NH $_2$, H, and N $_2$, of which CH $_3$, NH $_2$, and H will be lost by three-body recombination reactions. The N $_2$ will not be directly observable in the infrared and would be swamped by N $_2$ from deep atmospheric mixing and photolysis of NH $_3$. It may readily be shown (Lewis, 1980a) that a high HCN abundance requires that about half the total carbon inventory be found as CO ($X_{\text{CO}} \simeq 2 \times 10^{-4}$). Thus, at best the ratio $X_{\text{HCN}}/X_{\text{CO}}$ is $\sim 2 \times 10^{-6}/2 \times 10^{-4} = 10^{-2}$ (for heating to ~ 3000 K). But CO is an *observed* species on Jupiter, with $X_{\text{CO}} = 10^{-9}$. This places an *upper limit* on X_{HCN} from this source of 10^{-11} .

The effects of convective overturn of the atmosphere, which will involve upward transport of HCN from some deep, hot quench level, cannot be precisely estimated without knowledge of the quench temperature. Assuming a similarity between the reduction of the high-temperature species CO and HCN, the CO quench temperature of ~ 1100 K derived on kinetic grounds by Prinn and Barshay (1977) may be taken as a first approximation to the HCN quench temperature. From the results of Barshay and Lewis (1978), we see that X_{HCN} at the 1100 K level on the Jovian adiabat is $\sim 10^{-12}$.

Alternatively, we may guess that the major loss process for HCN is $\text{HCN} + \text{H}_2 \rightarrow \text{CH}_2 + \text{NH}$, followed by rapid hydrogen addition to make NH $_3$ and CH $_4$. The rate constant of the reverse reaction, $\text{CH}_2 + \text{NH}$, is probably near 10^{-10} cm 3 s $^{-1}$ by analogy with numerous known radical-radical reactions, which permits an estimate of the reverse rate at each temperature for which the equilibrium constant is known. By this very crude procedure we estimate a quench temperature for HCN reduction of ~ 1200 K, for $X_{\text{HCN}} \simeq 2 \times 10^{-12}$. For extreme assumptions regarding the quench temperature, X_{HCN} could be as low as 3×10^{-16} ($T_Q = 800$ K) and as high as 2×10^{-12} ($T_Q = 1200$ K). One product of HCN reduction along the Jovian

TABLE I
HCN predicted mole fractions (at 300 K level)

Source	Expected X_{HCN}
<i>Photolysis</i>	
N_2 ionization	$< 10^{-19}$
NH_3 photolysis	~ 0
Scaling lab. data	10^{-16}
Coupled $\text{NH}_3/\text{C}_2\text{H}_2$ photolysis	$\sim 10^{-9}$
<i>Lightning</i>	
Scaling lab. data	$< 10^{-16}$
Heating to 3000 K	2×10^{-17}
Limit from X_{CO}	$< 10^{-11}$
<i>Vertical mixing</i>	
From 1100 K level	10^{-12}
Photolysis of CH_3NH_2	$< 10^{-10}$

adiabat is probably CH_3NH_2 , methylamine, which is found in equilibrium calculations to be more abundant than HCN at all temperatures below ~ 1800 K. Thus it is an explicit prediction of the vertical mixing model that $X_{\text{CH}_3\text{NH}_2}$ should be larger than X_{HCN} . Quenching near 1200 K would provide a methylamine mole fraction of

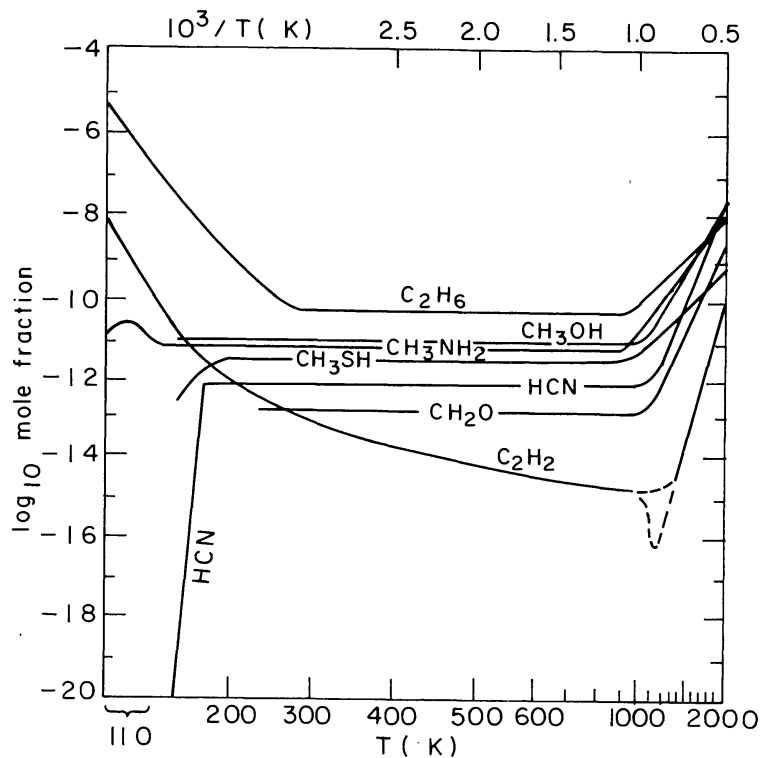


Fig. 3. Vertical distribution of selected organic species. For plausible quench temperatures of ~ 800 K to ~ 1500 K the mole fractions of all these species are generally below 10^{-10} throughout the lower troposphere. Only the very abundant photochemical products C_2H_2 and C_2H_6 will have mole fractions much above 10^{-10} in and near their source region. See the text for descriptions of the source mechanisms considered.

$\sim 1 \times 10^{-10}$, 30 times X_{HCN} . This is relevant because photochemical processing of methylamine near the tropopause may be a source of HCN: quench at ~ 1500 K would give a methylamine mole fraction of 10^{-9} , sufficient to generate all the observed HCN by photolysis near the tropopause.

The results of our calculations on HCN sources are summarized in Table I. We find that no known source except Kay and Strobel (1983) is capable of providing a mole fraction of HCN greater than roughly 2×10^{-12} . The most important known source of tropospheric HCN is most probably vertical mixing of high-temperature gases from the ~ 1200 K level in the deep atmosphere.

Our model for the vertical distribution of HCN, including all the sources considered, except Kaye and Strobel (1982), is given in Figure 3. At temperatures below 160 K HCN is regulated not by the abundance in the lower troposphere but by condensation of the solid salt NH_4CN , as described by Lewis (1969b). The entire region of the atmosphere ($160 > T > 110$ K) in which HCN is observed to be present must be supersaturated with NH_4CN . This is clearly a severe problem. The HCN, if indeed present with a mole fraction of 10^{-9} , must be confined to the lowest part of the ammonia cloud layer.

CH_2O

Photochemical mechanisms to produce CH_2O are difficult to discover, since the portion of the Jovian atmosphere exposed to solar UV is essentially devoid of water due to the low local temperatures. The most intense photochemical activity is localized near the 200 K level in regions of clearing of the NH_3 cloud layer, where H_2S is photodissociated by photons of $2350 < \lambda < 2700 \text{ \AA}$ to make SH and H, with a local rate of photolysis reaching $10^6 \text{ cm}^{-3} \text{ s}^{-1}$. The steady state abundance of H is governed principally by the rate of $\text{H} + \text{H} + \text{H}_2 \rightarrow 2\text{H}_2$ (Lewis and Fegley, 1979), which gives $n_{\text{H}} = 6 \times 10^8 \text{ cm}^{-3}$ near $T = 220$ K. The time required to achieve steady state is $6 \times 10^8 \text{ cm}^{-3} / 10^6 \text{ cm}^{-3} \text{ s}^{-1} = 600$ s, short compared to the mixing time of $\sim 10^5$ s. The abundance of water vapor at this level, given by the vapor pressure of ice, is $2.6 \times 10^{-5} \text{ b}$ ($X_{\text{H}_2\text{O}} = 1.3 \times 10^{-5}$). Oxygen participation in the photochemistry can be achieved via the abstraction reaction $\text{H} + \text{H}_2\text{O} \rightarrow \text{OH}$, and OH can combine with the prevalent organic radical, CH_3 , which is made by $\text{H} + \text{CH}_4 \rightarrow \text{H}_2 + \text{CH}_3$. However, the rate constant for H abstraction from H_2O is 2.5×10^{-8} times that for $\text{H} + \text{CH}_4$ (Kondratiev, 1972) at 220 K, and the production rate of CH_3 will be $\sim 240 \text{ cm}^{-3} \text{ s}^{-1}$ while that of OH will be near $3 \times 10^{-7} \text{ cm}^{-3} \text{ s}^{-1}$ at the same level. If *all* OH reacts via $\text{CH}_3 + \text{OH} \rightarrow \text{CH}_2\text{O} + \text{H}_2$ (a most improbable result), the concentration of CH_2O after one mixing time will be $3 \times 10^{-7} \times 10^5 = 0.03 \text{ cm}^{-3}$, for a mole fraction below 10^{-21} .

Hot atom reactions of H from H_2S photolysis with water vapor could provide a probability of reaction as high as 2×10^{-5} if every hot H atom that strikes a water molecule reacts with it. Thus the reaction rate $\text{H} + \text{H}_2\text{O} \rightarrow \text{OH} + \text{H}_2$ could reach $10^6 \text{ cm}^{-3} \text{ s}^{-1} \times 2 \times 10^{-5} = 20 \text{ cm}^{-3} \text{ s}^{-1}$. Over one mixing time this amounts to $2 \times 10^6 \text{ cm}^{-3}$ OH produced, for a potential mole fraction of reaction products $\leq 2 \times 10^{-14}$, clearly far more important than thermal sources of OH.

Direct photolysis of H_2O vapor to form reactive species is for all practical purposes impossible on Jupiter. The longest wavelength at which H_2O is capable of predissociation, $\sim 1950 \text{ \AA}$, corresponds to a wavelength at which the absorption cross section of ammonia is about $3 \times 10^{-18} \text{ cm}^2$. Weidenschilling and Lewis (1973) give a column abundance profile for NH_3 which shows that $\tau = 10^4$ for NH_3 (1950 \AA), corresponding to $3 \times 10^{21} \text{ molecules cm}^{-2}$, or 100 cm amagat, occurs far above the NH_4SH clouds near the NH_3 cloud base, where the H_2O abundance is only $\sim 10^{-9}$ b. Obviously direct photolysis of H_2O is negligible.

Shock production of CH_2O in lightning discharges is another possible mechanism. Calculations of the mole fraction of CH_2O at equilibrium in a solar composition gas over a wide range of relevant temperatures and pressures show that the maxima closely follow those found for HCN, except that CH_2O is very nearly 100 times less abundant than HCN along the entire CO/CH_4 boundary (Lewis, 1980a).

Along the Jovian adiabat $X_{\text{CH}_2\text{O}}$ ranges from about equal to X_{HCN} at lower temperatures (600 K) to about 20 times lower than X_{HCN} at 2000 to 3000 K.

Table II is constructed for CH_2O in the same way that Table I was for HCN. Again, as with HCN, the largest plausible source is vertical mixing from the lower troposphere. The vertical distribution of CH_2O , taking into account these sources, is sketched out in Figure 3. As before, a quench temperature of $\sim 1100 \text{ K}$ is assumed.

TABLE II
 CH_2O predicted mole fractions (at 300 K level)

Source	Expected $X_{\text{CH}_2\text{O}}$
<i>Photolysis</i>	
Thermal H abstraction	$< 10^{-21}$
Hot H abstraction	10^{-15}
Direct H_2O photolysis	~ 0
<i>Lightning</i>	
Heating to 3000 K	2×10^{-18}
Limit from X_{CO}	3×10^{-13}
<i>Vertical Mixing</i>	
From 1100 K level	3×10^{-13}
From 1500 K level	$< 10^{-10}$

C_2H_2

Acetylene was predicted as a major photochemical product from methane by Strobel (1969), and the acetylene abundance in the Jovian mesosphere-stratosphere estimated by Strobel (1973) has been generally confirmed by Ridgway's (1974) observations. A more detailed observational study by Orton and Aumann (1977) is in even better agreement with Strobel's model, including even an indication of a decline in C_2H_2 mole fraction downward into the troposphere. Strobel estimates a production rate of

$\sim 5 \times 10^8 \text{ cm}^{-2} \text{ s}^{-1}$ for C_2 hydrocarbons in the CH_4 photolysis region, corresponding to a local mole fraction of $\sim 10^{-8}$ in the source region, 5×10^{-11} at the NH_3 cloud tops or 10^{-13} at the 300 K level. Most of this material is C_2H_6 , not C_2H_2 .

Thunder shock waves generate good acetylene yields ($X_{\text{C}_2\text{H}_2} = 3 \times 10^{-6}$) near 3000 K on the CO/CH_4 boundary, corresponding to $X_{\text{C}_2\text{H}_2} = 3 \times 10^{-16}$ after dilution in the unshocked background gas. As before, this figure is an upper limit which assumes that 0.01% of the internal heat flux of Jupiter is used with perfect efficiency to shock gases to exactly 3000 K.

Chemical equilibrium on the Jovian adiabat will provide $X_{\text{C}_2\text{H}_2} > 10^{-12}$ only above ~ 1700 K. If we guess that equilibration reactions of C_2H_2 freeze in near 1000 K (see C_2H_6), then $X_{\text{C}_2\text{H}_2}$ is 10^{-17} above that level unless, as in the case, the photochemical source is more important.

See Figure 3 for the vertical distribution model results.

CH_3OH

Methyl alcohol may be produced from the same reactants used above to make CH_2O : $\text{CH}_3 + \text{OH} \rightarrow \text{CH}_3\text{OH}$. Following the generous spirit of the foregoing sections we shall again assume that 100% of the OH made by hot-atom reactions goes to make organic products: this time we assume that it all goes to make CH_3OH , not CH_2O (a 200% yield overall!).

Shock-produced CH_3OH at $T > 2000$ K has about the same abundance as CH_2O , but CH_3OH is more abundant than CH_2O along the Jovian adiabat (the $\text{CH}_3\text{OH}/\text{CH}_2\text{O}$ ratio is $\sim 10^4$ at 600 K; 20 at 1000 K; 2 at 2000 K). Quench from 1100 K gives $X_{\text{CH}_3\text{OH}} = 10^{-11}$, making CH_3OH a more sensitive indicator of vertical mixing than CH_2O . Thus the photochemical source of CH_3OH is clearly very unimportant by comparison. This can be seen in Figure 3.

C_2H_6

Ethane, like acetylene, which was predicted to be a major product of UV photolysis of methane in the models by Strobel (1969, 1973), is a moderately abundant product of shock wave heating (see Figure 3), and is an unusually stable high-temperature gas (Barshay and Lewis, 1978; Lewis, 1969a).

The main difference in behavior between C_2H_6 and C_2H_2 lies in the very much higher equilibrium abundance of C_2H_6 along the Jovian adiabat. Quench of the C–C bond-breaking reaction $\text{C}_2\text{H}_6 + M \rightarrow \text{CH}_3 + \text{CH}_3 + M$ occurs near 930 K, where $\tau_{\text{chem}} = 1/kn_M = 10^6 \text{ s} = H^2/K = \tau_{\text{mix}}$. The mole fraction of C_2H_6 at 930 K is $\sim 10^{-10}$, far larger than any photochemical source could provide. It is likely that, at all levels deeper than the NH_3 clouds, $X_{\text{C}_2\text{H}_6} \geq 10^{-10}$, and the photochemical contribution is negligible, as can be seen in Figure 3.

CH_3NH_2

Methylamine is a side product of the photolysis of CH_4 and NH_3 , formed in a narrow altitude interval where both species are present and undergoing photolysis (Kuhn *et al.*,

1977). The column production rate of $\sim 2.4 \times 10^7 \text{ cm}^{-2} \text{ s}^{-1}$ corresponds to $X_{\text{CH}_3\text{NH}_2} = 3 \times 10^{-11}$ in the source region, or 3×10^{-16} near the 300 K level.

Methylamine is also a prominent high-temperature product. If quenching of CH_3NH_2 removal occurs on the Jovian adiabat at the same level where CH_3CH_3 destruction quenches ($\sim 930 \text{ K}$), then the mole fraction of CH_3NH_2 in the upper troposphere will be $\sim 5 \times 10^{-12}$. Quenching at $\sim 1200 \text{ K}$ would give a mole fraction of $\sim 2 \times 10^{-10}$. As a result, the abundance of CH_3NH_2 below the tropopause will probably be dominated by the deep-mixing source, not the photochemical source. See Figure 3.

CH₃SH

Methyl mercaptan is, after sulfur and polysulfides, a significant product of H_2S photolysis. Lewis and Fegley (1979) have shown that thermal H atoms from H_2S photolysis can abstract H from methane to make CH_3 radical. Even more rapid is $\text{H} + \text{H}_2\text{S} \rightarrow \text{H}_2 + \text{SH}$, whereby almost every H_2 photolysis event produces two SH radicals. The rate constant for the reaction of H with H_2S is about 10^7 times that for $\text{H} + \text{CH}_4$ at 220 K (Kerr, 1976), so that about 10^6 SH radicals are produced per CH_3 radical. If *all* CH_3 goes to make CH_3SH , and *no* CH_3SH is lost to photolysis, the production rate of CH_3SH will be $\sim 10^6 \text{ cm}^{-2} \text{ s}^{-1}$. Since $\text{H}/Kn_{\text{H}_2} \simeq 10^{-21}$ at the NH_4SH cloud level, this yields a local steady-state concentration of $X_{\text{CH}_3\text{SH}} = 10^{-15}$ at the 220 K level, dropping to $\sim 3 \times 10^{-16}$ near the 300 K level. This is an overestimate of the CH_3SH production rate, since rapid CH_3 depletion could also take place by $\text{H} + \text{CH}_3 + M \rightarrow \text{CH}_4 + M$.

Laboratory experiments on the production of organic matter via hot atom mechanisms (see Khare *et al.*, 1978 and references therein) have been shown by Lewis and Fegley (1979) to provide $\sim 3 \times 10^{-6}$ g of organic matter per gram of sulfur when scaled to Jovian conditions, or 2×10^{-6} moles CH_3SH per mole of H_2S photolysed. Given an H_2S photolysis rate of $10^{12} \text{ cm}^{-2} \text{ s}^{-1}$ in regions of clearing of the NH_3 clouds, this gives a CH_3SH source strength of $\leq 5 \times 10^6 \text{ cm}^{-2} \text{ s}^{-1}$, for a local mole fraction of 5×10^{-15} .

Quench of CH_3SH destruction at the 1000 K level on the Jovian adiabat would leave $X_{\text{CH}_3\text{SH}} = 3 \times 10^{-12}$ throughout the upper troposphere. The vertical distribution of CH_3SH is therefore probably governed by vertical mixing from the lower atmosphere, not by photochemical production.

The calculated CH_3SH profile, given in Figure 3, clearly shows the dominance of the internal source for reasonable quench temperatures. It would be necessary for equilibrium to be closely attained down to below 500 K in order for the deep-mixing products to be reduced to an abundance below that of the photochemical product.

3.2. INORGANIC COMPOUNDS

CO

Prinn and Barshay (1977) have considered the available kinetic data regarding the reduction of CO and have concluded that the rate of reduction will become equal to the

overturn rate near the 1100 K level. Quenching from this level gives $X_{\text{CO}} = 10^{-9}$, the observed value, when $K \simeq 2 \times 10^8 \text{ cm}^2 \text{ s}^{-1}$.

Prinn and Barshay also found that interconversion of CO, CO₂, CH₂O, and CHO (and conceivably CH₃OH) occurs more rapidly than reduction of these species to methane, and hence that quasi-equilibrium between these gases will occur down to temperatures lower than 1000 K. It can readily be seen from Figure 3 that CO is by far the most stable of these species at all temperatures between 1000 and 600 K, and such reequilibration of C–O compounds cannot affect the CO abundance.

For reasons discussed above, no photochemical source of CO is considered to be of comparable importance.

CO is, however, of great importance in connection with shock wave synthesis. Reasonably efficient (0.01%) conversion of convective heat flux into lightening, with highly efficient (40%) conversion of lightning discharge energy into shock waves, all of which is used to heat gas to precisely the optimum temperature for maximum chemical efficiency ($\sim 2000 \text{ K}$) will provide, as we have seen, $10^{-12} \text{ g cm}^{-2} \text{ s}^{-1}$ of shocked gas, which upon vertical mixing will be diluted down to 4×10^{-11} of the atmospheric mass. The mole fraction of CO in the optimally shocked gas is 2×10^{-4} , or $X_{\text{CO}} = 8 \times 10^{-5}$ after dilution. Since the *observed* value of X_{CO} is 2×10^{-9} (Beer, 1975; Larson *et al.*, 1978), we much conclude that lightning and thunder synthesis are not important contributors to the CO abundance. The observed CO abundance in no way lends credence to shock synthesis scenarios, since we have seen that they are incapable of meeting the requirements imposed by observation. Figure 4 presents the CO vertical distribution results.

If, following Beer and Taylor (1978), we take the CO as a high-altitude gas, then the CO must be due to an external source and the observed CO abundance could not be used to deduce tropospheric mixing rates (Prather *et al.*, 1978; Strobel and Yung, 1979).

CO₂

The equilibrium CO₂/CO ratio varies from about 2×10^{-4} at 2000 K through 10^{-3} at 1000 K to 5×10^{-2} at 600 K. Quench of CO reduction occurs near 1100 K, and reequilibration of CO to produce an increased mole fraction of CO₂ below 1100 is possible kinetically, although it is unlikely that reequilibration is significant below $\sim 800 \text{ K}$. Quench of CO₂ at 800 K gives $X_{\text{CO}_2} = 6 \times 10^{-12}$, while quench at 1100 K would permit X_{CO_2} as low as 1×10^{-12} . Photochemical sources for CO₂ are ignored for previously elaborated reasons.

Shock syntheses of CO₂ are noteworthy for the very low CO₂/CO ratios ($\sim 10^{-4}$) attendant on high equilibration temperatures. By application of the CO argument above, $X_{\text{CO}_2} \simeq 8 \times 10^{-19}$ from this source. Shock waves are thus negligible CO₂ sources. The CO₂ profiles given in Figure 4 therefore reflect only the quench chemistry along the Jovian adiabat.

The acid anhydride CO₂ can be removed by reaction with ammonia at the $\sim 195 \text{ K}$ level to precipitate the salt ammonium carbamate, NH₄COONH₂. Ammonium bicarbonate, NH₄HCO₃, is very slightly more stable, but requires water vapor as a reactant.

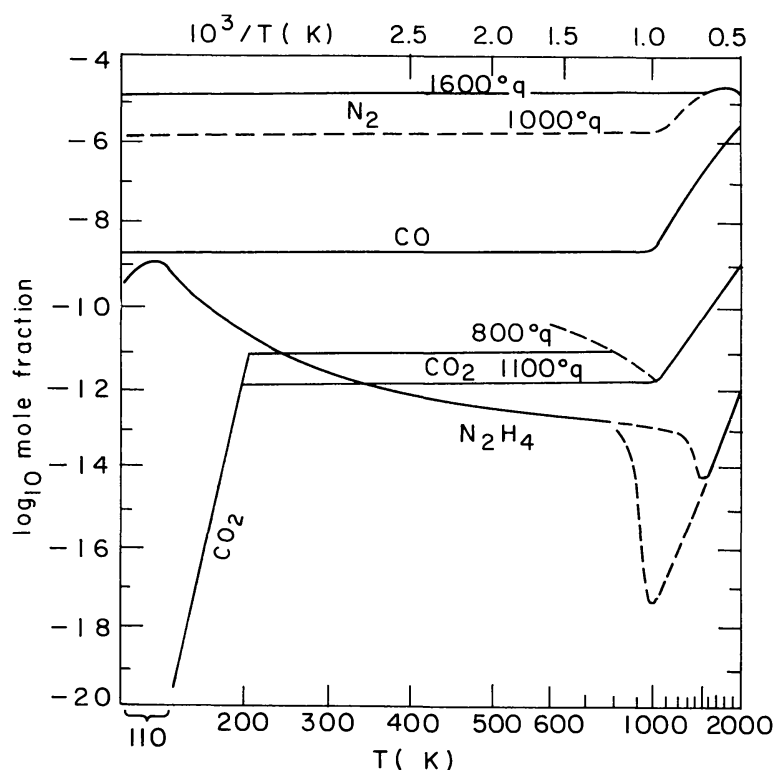


Fig. 4. Vertical distributions of several inorganic tracers. Carbon monoxide, carbon dioxide, and molecular nitrogen are typical high-temperature quench products. The effects of quenching of nitrogen reduction at 1000 K and 1600 K are indicated. Quenching of CO_2 destruction and production at 1100 K along with CO quench is shown with a solid line, while partial reequilibration of C-O species below 1100 K would give a CO_2 mole fraction following the dashed curve. Final CO_2 quench at 800°q is indicated by the CO_2 800 curve. Hydrazine is a predominantly photochemical species which is destroyed by equilibration over a poorly-defined temperature range extending from 800–1200 K at the lower extreme to ~ 2000 K at the upper end, where the equilibrium N_2H_4 abundance again approaches 10^{-12} . CO_2 condenses near 200 K as solid NH_4HCO_3 or $\text{NH}_4\text{COONH}_2$.

It is not clear which species will preferentially nucleate. The observational upper limit on X_{CO_2} is 2×10^{-7} at the cloudtops (Treffers *et al.*, 1978).

N_2

Nitrogen is produced in major amounts by NH_3 photolysis. For the present it will suffice to establish an upper limit on the mole fraction of photochemical N_2 by assuming that 100% of the NH_3 destroyed by UV photolysis is converted into N_2 . This provides a downward N_2 flux of $5 \times 10^{10} \text{ cm}^{-2} \text{ s}^{-1}$, for a mole fraction varying from 5×10^{-9} near the NH_3 cloud base down to 1.5×10^{-11} near the 300 K level.

Molecular nitrogen is also a stable, abundant product at high temperatures. Along the Jovian adiabat, $X_{\text{N}_2} = 2 \times 10^{-6}$ for quench at 1000 K.

We may attempt to estimate the quench temperature directly if we know the rate constant for the major reaction responsible for reducing N_2 , but the rates of the reactions $\text{N}_2 + \text{H}_2 \rightarrow 2\text{NH}$ and $\text{N}_2 + \text{H} \rightarrow \text{NH} + \text{N}$ have not been measured. However, the rate of the reverse reaction $\text{NH} + \text{NH} \rightarrow \text{N}_2 + \text{H}_2$ and its analog

$\text{OH} + \text{OH} \rightarrow \text{O}_2 + \text{H}_2$ have been estimated (Kondratiev, 1972), and the equilibrium constant for the reaction is known. Since the equilibrium constant at a given temperature is simply the ratio of the forward rate to the backward rate, these data suffice to estimate the rate of the reaction $\text{N}_2 + \text{H}_2 \rightarrow 2\text{NH}$. In addition, the closely analogous reaction $\text{NH} + \text{OH} \rightarrow \text{NO} + \text{H}_2$ has been studied, and the reported rate constant are virtually identical to those for $\text{NH} + \text{NH}$ (Kondratiev). This calculation gives a chemical time constant τ_{chem} for reduction of N_2 equal to the dynamic overturn time $\tau_{\text{conv}} = H^2/K$ at the 1600 K level on the Jovian adiabat. However, the equilibrium X_{N_2} at 1600 K is $\sim 2 \times 10^{-5}$, essentially the highest possible N_2 equilibrium abundance along the adiabat.

Prinn and Olaguer (1981) have studied the conversion of N_2 to NH_3 in Jupiter's deep atmosphere. They considered both homogeneous gas phase reactions and heterogeneous iron catalyzed reactions. The former reaction quenched at about the 1700 K level in the atmosphere yielding $X_{\text{N}_2} \sim 10^{-5}$. The iron catalyzed reaction quenched at about the 900 K level yielding X_{N_2} as low as 0.6×10^{-6} . It is important to note that the vertical mixing source of N_2 in the troposphere, with or without heterogeneous catalysis, is several orders of magnitude larger than the photochemical source. The N_2 profiles corresponding to 1000 and 1600 K quench levels for N_2 reduction are illustrated in Figure 4.

N_2H_4

Hydrazine, like N_2 , is a major product of NH_3 photolysis. Advocates of the most hydrazine-rich models give production rates near $10^{10} \text{ cm}^{-2} \text{ s}^{-1}$ and steady-state concentrations near $X_{\text{N}_2\text{H}_4} = 10^{-9}$ in the production region (Prasad and Capone, 1976), corresponding to local saturation (Atreya *et al.*, 1977). At the 300 K level, $X_{\text{N}_2\text{H}_4} \simeq 3 \times 10^{-12}$.

Although N_2H_4 does form at very high temperatures and pressures, its abundance along the Jovian adiabat never gets impressively large: $X_{\text{N}_2\text{H}_4}$ at 1000 K is only 2×10^{-18} , dropping below 10^{-26} at equilibrium at 800 K.

Thermal equilibration of N_2H_4 being mixed downward from the photochemical production region may become important near 800–1200 K, but exact kinetic data are lacking. The profiles given in Figure 4 allow for such a range of quench temperatures.

3.3. TRACERS DIAGNOSTIC OF DEEP CONVECTION

We here briefly summarize the most relevant results of chemical equilibrium studies of the lower atmosphere by Barshay and Lewis (1978) and by Fegley and Lewis (1979) for those moderately volatile but less abundant elements which are useful diagnostic tracers of deep mixing. Barshay and Lewis suggest AsH_3 , GeH_4 , H_3BO_3 , HF , H_2Se , SbH_3 , and GeS as tracers, in addition to the PH_3 and CO already discussed by Prinn and Lewis (1975) and by Prinn and Barshay (1977). Fegley and Lewis delete GeS from this list and suggest AsF_3 , SbS , H_2Te , TlI , and InBr as additions. These species are presented in Figure 5. Depletion of HF at low temperatures is due to condensation of NH_4F and dissolution in the aqueous NH_3 solution clouds. Boric acid vapor condenses primarily as solid HBO_2 , which is also soluble in these clouds. Hydrogen selenide is a

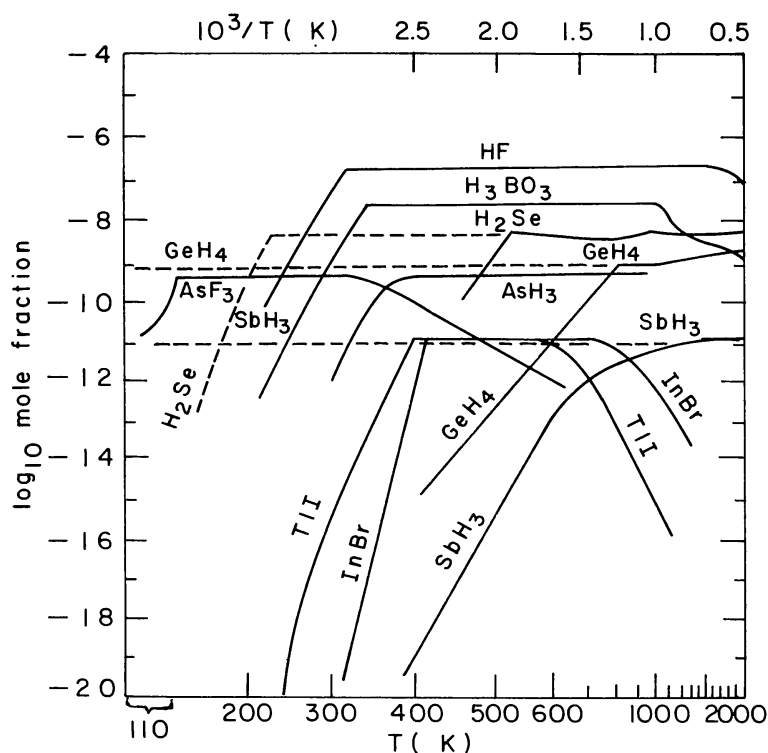


Fig. 5. Vertical distributions of selected moderately volatile tracers of deep mixing. After Barshay and Lewis (1978) and Fegley and Lewis (1979). Arsenic, found mainly as AsH_3 (arsine) over a wide temperature range may later convert to AsF_3 if the (unknown) kinetics are favorable. Germane, GeH_4 , may survive oxidation and precipitation (although depleted $\sim 10 \times$ below the Ge cosmic abundance). Thallium iodide and indium bromide both saturate near 400 K. Most abundant at the NH_4 cloud level are GeH_4 and AsF_3 or AsH_3 , with SbH_3 a poor third. At the ~ 400 K level HF , H_3BO_3 , H_2Se , GeH_4 , and AsF_3 or AsH_3 have abundances greater than 10^{-10} that of H_2 .

plausible product of quenching from temperatures above ~ 500 K. The H_2Se abundance is, however, severely limited by NH_4SeH condensation above the 219 K level (Fegley and Lewis, 1979). Arsine, which is the stable arsenic compound down to ~ 350 K, will be replaced by AsF_3 at lower temperatures if the rates of the interconversion reactions are sufficiently rapid. If 100% conversion of arsenic to AsF_3 occurs, then there may be saturation and condensation of solid AsF_3 near the tropopause.

The detection of GeH_4 on Jupiter by Fink *et al.* (1978) suggests $X_{\text{GeH}_4} \approx 6 \times 10^{-10}$, corresponding to quenching of the destruction of germane at a temperature above 800 K. As previously mentioned, the observed abundances of CO, PH_3 , and GeH_4 are all consistent with quench temperatures near 1000 K.

4. Conclusions

The most succinct summary of the conclusions of this survey can be found in the figures; however, some idea of the typical global-average tropospheric abundances of the species expected to be present at levels above one part per trillion ($x_i = 10^{-12}$) can be had from Table III, which gives our expectations for the atmospheric composition at the 300 K

TABLE III
Mean global atmospheric composition at the 300 K level in Jupiter's troposphere

Species	Mole fraction	Source ^a	Observed?
H ₂	0.88	<i>e</i>	X
He	0.11	<i>e</i>	X
H ₂ O ^c	1×10^{-3}	<i>e</i>	(assumed solar)
CH ₄	5×10^{-4}	<i>e</i>	X
Ne	2×10^{-4}	<i>e</i>	(assumed solar)
NH ₃	1×10^{-4}	<i>e</i>	X
H ₂ S	2×10^{-5}	<i>e</i>	
Ar	6×10^{-6}	<i>e</i>	(assumed solar)
N ₂	$\sim 6 \times 10^{-6}$	<i>q</i>	
PH ₃	4×10^{-7}	<i>q</i>	X
H ₂ Se	$\approx 5 \times 10^{-9}$	<i>q</i>	
Kr	3×10^{-9}	<i>e</i>	(assumed solar)
CO	2×10^{-9}	<i>q</i>	X
HF	2×10^{-9}	<i>e</i>	
H ₃ BO ₃	2×10^{-9}	<i>e</i> (<i>c</i>)	
GeH ₄	$\approx 8 \times 10^{-10}$	<i>q</i>	X
AsF ₃	5×10^{-10}	<i>e</i>	
Xe	3×10^{-10}	<i>e</i>	(assumed solar)
HCN ^b	$\sim 1 \times 10^{-10}$	<i>q, \phi</i>	X
C ₂ H ₆	6×10^{-11}	ϕ	
CH ₃ OH	$\sim 6 \times 10^{-11}$	<i>q</i>	
CO ₂	6×10^{-12}	<i>q</i>	
CH ₃ NH ₂	8×10^{-12}	<i>q</i>	
N ₂ H ₄	3×10^{-12}	ϕ	
CH ₃ SH	3×10^{-12}	<i>e</i>	

^a *e* = equilibrium, *q* = quench, *c* = condensation, ϕ = photolysis.

^b The observed HCN mole fraction is 10^{-9} near the NH₃ clouds.

^c The observed H₂O mole fraction of $\sim 10^{-5}$ refers to the ~ 200 – 260 K region.

level. The processes responsible for providing (or limiting) each gas at that level are given in the table, along with an indication whether that species has yet been detected in the Jovian troposphere. Note that C₂H₆ has been detected only above the tropopause, where its concentration is much higher than at the 300 K level due to local photochemical production.

Table III contains 12 species whose tropospheric abundances are determined by non-equilibrium processes. Nine of these species are primarily produced by the quenching of thermochemical reactions within Jupiter's deep atmosphere. Two other gases (C₂H₆ and N₂H₄) are principally produced by photochemical reactions, although it should be noted that the N₂H₄ abundance given is essentially an upper limit. HCN is produced both photochemically by coupled NH₃–C₂H₂ photochemistry and by quenching of hot gas parcels rapidly transported upward from Jupiter's deep atmosphere. The most abundant chemical tracer in Jupiter's atmosphere is probably N₂ which is due to rapid vertical transport from the lower atmosphere. In addition to PH₃, CO, and GeH₄, which have been observed, other chemical tracers such as SbH₃, SbS, H₂Se,

HF, H₃BO₃, HCl, H₂Te, AsF₃, TlI, and InBr may be potentially valuable indications of atmospheric mixing rates at different levels in Jupiter's atmosphere.

We expect that analytical experiments with sensitivities of $\sim 10^{-8}$ (10 parts per billion) conducted near the 300 K level in Jupiter's atmosphere will add only Ne, H₂S, Ar, and N₂ to the list of already observed species.

Acknowledgments

We are grateful to Ronald G. Prinn, Peter H. Stone, and Stephen S. Barshay for helpful discussions. We thank the NASA Planetary Atmospheres program for support.

References

- Abell, P. I.: 1976, in *Comprehensive Chemical Kinetics*, p. 111.
- Atreya, S. K., Donahue, T. M., and Kuhn, W. R.: 1977, *Icarus* **31**, 348.
- Bar-Nun, A.: 1975, *Icarus* **24**, 86.
- Bar-Nun, A.: 1979, *Icarus* **38**, 180.
- Bar-Nun, A. and Shaviv, A.: 1975, *Icarus* **24**, 197.
- Bar-Nun, A. and Tauber, M. E.: 1972, *Space Life Sci.* **3**, 254.
- Bar-Nun, A., Bar-Nun, N., Bauer, S. H., and Sagan, C.: 1970, *Science* **168**, 470.
- Barshay, S. S. and Lewis, J. S.: 1978, *Icarus* **33**, 593.
- Beer, R.: 1975, *Astrophys. J.* **200**, L167.
- Beer, R. and Taylor, F. W.: 1973, *Astrophys. J.* **179**, 309.
- Beer, R. and Taylor, F. W.: 1978, *Astrophys. J.* **221**, 1100.
- Bjoraker, G., Fink, U., Larson, H. P., and Kunde, V.: 1981, *Bull. Am. Astron. Soc.* **13**, 735.
- Borucki, W. J., Bar-Nun, A., Scarf, F. L., Cook II, A. F., and Hunt, G. E.: 1982, *Icarus* **52**, 492.
- Cook, A. F., II, Duxbury, T. C., and Hunt, G. E.: 1979, *Nature* **280**, 794.
- Drossart, P. and Encrenaz, T.: 1982, *Icarus* **52**, 483.
- Fegley, M. B., Jr. and Lewis, J. S.: 1979, *Icarus* **38**, 166.
- Fegley, M. B., Jr. and Prinn, R. G.: 1983a, preprint.
- Fegley, M. B., Jr. and Prinn, R. G.: 1983b, *Lunar Planet. Sci.* **XIV**, 189.
- Ferris, J. P. and Chen, C. T.: 1975, *Nature* **258**, 587.
- Ferris, J. P. and Morimoto, J. Y.: 1981, *Icarus* **48**, 118.
- Ferris, J. P., Nakagawa, C., and Chen, C. T.: 1977, *COSPAR Life Sciences and Space Research XV*, p. 95.
- Fink, U., Larson, H. P., and Treffers, R. R.: 1978, *Icarus* **34**, 344.
- Flasar, M. and Gierasch, P.: 1977, in A. Vallance-Jones (ed.), *Proceedings: Symposium on Planetary Atmospheres*, Ottawa, p. 85.
- Gann, R. G. and Dubrin, J.: 1967, *J. Chem. Phys.* **47**, 1867.
- Gierasch, P. J.: 1976, *Icarus* **29**, 445.
- Hubbard, W. B.: 1973, *Astrophys. J.* **182**, L35.
- Huffman, R. E., Tanaka, Y., and Larabee, J. C.: 1963, *J. Chem. Phys.* **39**, 910.
- Kaye, J. A. and Strobel, D. F.: 1982, preprint.
- Kerr, J. A.: 1976, in *Comprehensive Chemical Kinetics*, p. 39.
- Khare, B. N. and Sagan, C.: 1971, *Nature* **232**, 577.
- Khare, B. N. and Sagan, C.: 1973, *Icarus* **20**, 311.
- Khare, B. N., Sagan, C., Bandurski, E. L., and Nagy, B.: 1978, *Science* **199**, 1199.
- Kondratiev, V. N.: 1972, *Rate Constants of Gas Phase Reactions*.
- Kuhn, W. R., Atreya, S. K., and Chang, S.: 1977, *Geophys. Res. Letters* **4**, 203.
- Larson, H. P., Fink, U., and Treffers, R. R.: 1976, *Bull. Am. Astron. Soc.* **8**, 476.
- Larson, H. P., Treffers, R. R., and Fink, U.: 1977, *Astrophys. J.* **4**, 972.
- Larson, H. P., Fink, U., and Treffers, R. R.: 1978, *Astrophys. J.* **219**, 1084.
- Lewis, J. S.: 1969a, *Icarus* **10**, 393.

- Lewis, J. S.: 1969b, *Icarus* **10**, 365.
- Lewis, J. S.: 1976, in C. Ponnampereuma (ed.), *The Exobiology of Jupiter*, p. 13.
- Lewis, J. S.: 1980a, *Icarus* **43**, 85.
- Lewis, J. S.: 1980b, *Science* **210**, 1351.
- Lewis, J. S. and Fegley, M. B., Jr.: 1979, *Astrophys. J.* **232**, L135.
- Lewis, J. S., Barshay, S. S., and Noyes, B.: 1978, *Icarus* **37**, 190.
- Lippincott, E. R., Eck, R. V., Dayhoff, M. O., and Sagan, C.: 1967, *Astrophys. J.* **147**, 753.
- Martin, R. W. and Willard, J. E.: 1964, *J. Chem. Phys.* **40**, 3007.
- Miller, S. L.: 1955, *J. Atmos. Chem. Soc.* **77**, 2351.
- Miller, S. L. and Urey, H. C.: 1959, *Science* **130**, 245.
- Munch, G. and Neugebauer, G.: 1971, *Science* **174**, 940.
- Orton, G. S. and Aumann, H. H.: 1977, *Bull. Am. Astron. Soc.* **9**, 478.
- Ponnampereuma, C.: 1976, *Icarus* **29**, 321.
- Ponnampereuma, C. and Molton, P. M.: 1973, *Science* **198**, 1031.
- Prasad, S. S. and Capone, L. A.: 1976, *J. Geophys. Res.* **81**, 5591.
- Prather, M. J., Logan, J. A., and McElroy, M. B.: 1978, *Astrophys. J.* **223**, 1072.
- Prinn, R. G. and Barshay, S. S.: 1977, *Science* **198**, 1031.
- Prinn, R. G. and Lewis, J. S.: 1975, *Science* **190**, 294.
- Prinn, R. G. and Olaguer, E. P.: 1981, *J. Geophys. Res.* **86**, 9895.
- Raulin, F., Bossard, A., Toupance, G., and Ponnampereuma, C.: 1979, *Icarus* **38**, 358.
- Ridgway, S. T.: 1974, *Astrophys. J.* **187**, L147.
- Sagan, C.: 1960, *Astron. J.* **65**, 499.
- Sagan, C. and Khare, B. N.: 1971a, *Astrophys. J.* **168**, 563.
- Sagan, C. and Khare, B. N.: 1971b, *Science* **173**, 417.
- Sagan, C. and Miller, S. L.: 1960, *Astrophys. J.* **65**, 499.
- Sagan, C. and Salpeter, E. E.: 1976, *Astrophys. J. Suppl. Ser.* **32**, 737.
- Scarf, F. L., Gurnett, D. A., and Kurth, W. S.: 1979, *Science* **204**, 991.
- Schnepp, O. and Dressler, K.: 1960, *J. Chem. Phys.* **32**, 1682.
- Steacie, E. W. R.: 1954, *Atomic and Free Radical Reactions*, Reinhold Publ., New York.
- Stone, P. H.: 1976, in T. Gehrels (ed.), *Jupiter*, p. 586.
- Strobel, D. F.: 1969, *J. Atmos. Sci.* **26**, 906.
- Strobel, D. F.: 1973, *J. Atmos. Sci.* **30**, 489.
- Strobel, D. F. and Yung, Y. L.: 1979, *Icarus* **37**, 256.
- Thrush, B. A.: 1965, in G. Porter (ed.), *Progress in Reaction Kinetics* **3**, p. 63.
- Tokunaga, A. T., Beck, S. C., Geballe, T. R., Lacy, J. H., and Serabyn, E.: 1981, *Icarus* **48**, 283.
- Treffers, R. R., Larson, H. P., Fink, U., and Gautier, T. N.: 1978, *Icarus* **34**, 331.
- Weidenschilling, S. J. and Lewis, J. S.: 1973, *Icarus* **20**, 465.
- Woeller, F. and Ponnampereuma, C.: 1969, *Icarus* **10**, 386.