

SOLAR NEBULA CHEMISTRY: ORIGIN OF PLANETARY, SATELLITE, AND COMETARY VOLATILES

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Complex interactions between chemical, physical and dynamical processes in the solar nebula are hypothesized to have played seminal roles in determining the reservoirs of volatile compounds and elements in the planets and their satellites and in comets. These processes include condensation, homogeneous and heterogeneous thermochemical and photochemical reactions, and disequilibrium resulting from fluid transport, condensation, and cooling whenever they occur on time scales shorter than those for the chemical reactions. The ultimate potential starting materials were gases and grains in the pre-nebula interstellar cloud(s). As the nebula was forming the grains may have partially or completely evaporated or decomposed but not necessarily so. Extensive evidence from meteorites and inferences that asteroids are meteorite parent bodies implies that the nebula was extensively physically mixed and chemically reprocessed (but not necessarily chemically and isotopically homogenized) at least out to 4 AU. Possible energy sources for driving nebula chemical reactions include shock waves and photons from lightning discharges, radioactive decay processes, and solar and stellar photons, but we show that all of these are secondary to the thermal energy of the solar nebula itself. The enormous ultraviolet opacity of the gaseous nebula disk (due to H₂O, grains, etc.) caused solar ultraviolet photons to be absorbed only in the very hot inner nebula where rapid thermochemical reactions probably prevented significant photochemical disequilibrium beyond some possible subtle effects on high temperature refractory material. Also, the high dust opacity in the immediate post-nebula solar system probably prevented the high ultraviolet flux from the early Sun being an effective energy input into early planetary atmospheres. Ultraviolet emission from the early Sun would still be remotely observable since the opacity for all photons emitted in directions other than toward the gaseous or dusty disk was probably very small. Surface catalysis was undoubtedly important in the nebula for (thermochemical)

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In Origin and Evolution of Planetary and Satellite Atmospheres
(1989), S. Atreya, J. Pollack, and M. S. Matthews Eds.
University of Arizona Press, Tucson.

organic synthesis. We discuss models for the chemical composition of the gases and grains as functions of space and time in the nebula and the implications of these models for the volatile contents of accreting planets, satellites and comets. The models include the pressure/temperature conditions appropriate to subnebulae around giant planets as well as those appropriate to the solar nebula itself. It is highly probable that as proposed by Lewis and Prinn the major gaseous C and N compounds in the solar nebula were CO and N₂ and that carbonaceous compounds formed from CO by Fischer-Tropsch-type reactions were present in amounts comparable to CO in order to explain recent outer solar system planetary and satellite observations. Vapor-phase hydration of silicates, like the chemical reduction of CO and N₂, was kinetically inhibited in the nebula. Formation of giant planetary satellites in well-mixed subnebulae created by spin-off as proposed by Pollack and Bodenheimer or by a massive impact as suggested by Cameron provides a natural explanation for the occurrence of CH₄-rich satellites like Titan and Triton using the chemistry described by Prinn and Fegley; satellite formation in planetary accretion disks which include nonlinear effects can also explain Titan but accretion-disk-products may be reprocessed in a later-forming spin-off or impact-generated subnebula. Certain volatile ratios (e.g., CO/CH₄, N₂/NH₃, H₂O ice/silicate) in ice-rich bodies are diagnostic of their origin. For example, the observation of CH₄ and NH₃ in Halley implies that at least some of the material in this comet is neither of solar nebula nor interstellar origin but is material condensed in a subnebula of one of the giant planets.

I. INTRODUCTION

A chemist investigating for the first time the distribution of the very volatile atmosphere-forming elements (H, O, C, N, Cl, S etc; He, Ne, Ar, etc.) and their compounds in the solar system would immediately ask why planets, satellites, comets and meteorites were endowed apparently with such different mixtures of these very volatile materials. Despite their often over-emphasized similarities, the volatile element contents of the terrestrial planets Venus, Earth and Mars are significantly different and many of the differences are not attributable simply to (presently recognized) evolutionary processes; the other terrestrial planet Mercury is by comparison almost completely void of volatiles. The gaseous giant planets are all rich in H and He. But the heavier elements (O, C, N, Si, etc.) comprise only a small fraction of the masses of Jupiter and Saturn while they are a large fraction of Uranus and Neptune; and all four planets are enriched in these heavier elements relative to the Sun. The ice-rich satellites of the outer planets differ in uncompressed density (and thus implied ice/rock ratios) and, except for Titan and perhaps Triton, their atmospheres are thin and/or evanescent (e.g. Io) or essentially absent. Where data is available, comets (e.g., Halley) are more rich in CO than CH₄ whereas the converse appears to be true for ice-rich satellites (e.g., Titan, perhaps Triton?). Complex carbonaceous materials are major reservoirs of C, N, and H in carbonaceous chondrites and (by inference from reflection spectra) in many dark asteroids and some outer planetary satellites (e.g., small satellites of Jupiter and Uranus).

These intriguing patterns for volatile distribution are a result of a complex and as yet poorly understood sequence of events which began with the formation of solar system bodies in the primitive solar nebula and was followed by a wide range of both general and specific evolutionary processes on each body (see, e.g., Prinn 1982 for a review). The development of theories concerning the origin of the solar system, and more specifically the advancement of our ideas concerning the chemistry of the volatile elements in the gaseous and dusty solar nebula in which the planets formed, has been guided in large part by observations of the volatile contents of planets, planetary satellites, meteorites and comets. We will emphasize in this Chapter the origin of the volatile compounds formed from the abundant chemically reactive elements H, O, C, and N; the noble gases are discussed in the Chapter by Pepin. By way of an introduction to the chemical theories which we will address in this Chapter, we will first present here a review of some salient facts about chemically active volatiles in solar system objects observed to date.

A. Volatiles in Terrestrial Planets and Chondritic Meteorites

The observed inventories of the important volatiles expressed as CO₂, H₂O and N₂ on the three terrestrial planets which possess atmospheres and in the chondritic meteorites are summarized in Table I. No indigenous volatiles have been observed in Mercury's atmosphere at a pressure greater than 10⁻¹³ bar or on its surface (Lewis and Prinn 1984). The abundances in Table I illustrate that both the chondrites and Venus, Earth and Mars are depleted in C, N, and H₂O relative to solar abundances. Even the volatile-rich CII carbonaceous chondrites have retained only ~ 5 to 10% of the solar abundances of C, N, and H₂O. The similar CO₂ and N₂ depletions for Earth and Venus indicate similar inventories of these volatiles on the two planets. Furthermore, on an absolute (g/g = gram/gram) basis, there is approximately 10 times more carbon than nitrogen on both Earth and Venus. However, Venus is apparently endowed with much less H₂O than the Earth, and Mars is apparently either volatile poor, or has outgassed less efficiently than Venus and Earth, or has lost a substantial portion of its volatile content through atmospheric erosion or escape at an earlier stage of its history.

However, comparisons of the planetary and chondritic volatile inventories are complicated by several factors. The apparently larger depletions for CO₂ and N₂ on the terrestrial planets relative to the chondritic meteorites may simply reflect partitioning of a significant fraction of their C and N inventories into iron cores and/or their silicate interiors. Similarly, the observed presence of CO₂(solid) in the Martian polar caps, and the suspected presence of subsurface water ice on Mars and of CaCO₃ on Venus means that the atmospheric inventories of these volatiles are likely to be underestimates of the planetary inventories (e.g., see Carr 1987; Prinn and Fegley 1987a).

The chondritic meteorites contain a variety of volatile-bearing phases whose occurrence and abundance vary from class to class. Carbon occurs as

TABLE I
Depletions of Important Volatiles in the Chondritic Meteorites and in Venus, Earth and Mars
Relative to Solar Abundances [(g/g Si)/(g/g Si)]^a

Volatile	Chondritic Meteorites ^d				
	Venus ^b	Earth	Mars ^c	C	E (H, L, LL)
CO ₂	3×10^{-5}	3×10^{-5}	2×10^{-8}	$(0.8 - 6) \times 10^{-2}$	1×10^{-3}
H ₂ O	2×10^{-9}	2×10^{-4}	4×10^{-12}	$(0.07 - 10) \times 10^{-2}$	$(0.4 - 2) \times 10^{-3}$
N ₂	1×10^{-5}	2×10^{-5}	5×10^{-9}	$(0.1 - 5) \times 10^{-2}$	$(4 - 6) \times 10^{-4}$ $(0.1 - 1) \times 10^{-2}$

^aSolar abundances from Cameron (1982). The solar abundances of C, N and O (minus 15% of O assumed to be incorporated into rock as MgO + SiO₂) were expressed as CO₂/Si, N₂/Si, and H₂O/Si mass ratios for this normalization. Atmospheric inventories only were considered for Venus and Mars but atmospheric plus oceanic plus crustal inventories were considered for Earth. The abundance data for Venus, Earth and Mars are from Prinn and Fegley (1987a and references therein).

^bBulk composition models V2, E5, and Ma2 from the *Basaltic Volcanism Study Project* (1981b, p. 641) were used to determine Si contents for Venus, Earth and Mars, respectively. The Si contents for the chondritic meteorite classes are from Mason (1979).

^cPresent-day atmospheric inventories of CO₂, H₂O, and N₂ on Mars.
^dThe tabulated values are for C11, CM2, C3 carbonaceous chondrites, EH4, EH5, EL6 enstatite chondrites, and H, L, LL ordinary chondrites. Carbon data: median values from Mason (1979). Nitrogen data: median values from Mason (1979) for the C and H, L, LL chondrites. Data of Grady et al. (1986) for the E chondrites (~100 to ~1000 ppm N by weight). Mason (1979) gives a median value of 260 ppm N for E chondrites corresponding to a depletion factor of 3×10^{-3} . Water data: Mason (1971, 1979), Kolodny et al. (1980), Robert and Epstein (1982) and Yang and Epstein (1983) for the C11, CM2, and C3 chondrites; Yang and Epstein (1983), McNaughton et al. (1981) and Robert et al. (1979) for H, L, LL chondrites; Boato (1954) and Yang and Epstein (1983) for the two EH4 chondrites Indarch and Abee, respectively. The range of water contents (wt. %) and the corresponding depletion factors for the carbonaceous chondrites are: C11 chondrites, $3 - 10\%$, $(0.3 - 1) \times 10^{-1}$; CM2 chondrites, $1 - 16\%$, $(0.8 - 12) \times 10^{-2}$; and C3 chondrites, $0.1 - 2\%$, $(0.7 - 10) \times 10^{-3}$. If the higher values reported by Wiik (cited in Mason 1971) for the water contents of the C11 chondrites are included, the upper limit is ~20% (wt.) corresponding to a depletion factor of $\sim 2 \times 10^{-1}$. However, some of this water is probably terrestrial contamination (see Boato 1954).

graphite, carbides, dissolved C in Fe,Ni alloy, in diamonds, in silicon carbide, disequilibrium organic matter, and carbonates (Mason 1971; Lewis et al. 1987; Bernatowicz et al. 1987). Nitrogen occurs as dissolved N in Fe,Ni alloy, disequilibrium organic matter, nitrides, and possibly as NH_4^+ salts (Mason 1971; Kung and Clayton 1978). However, the major N-carrier(s) in the ordinary chondrites is not well characterized. Finally, hydrogen occurs as water (adsorbed, hydrated in salts and in hydrous silicates) and as organic compounds. Water contents in carbonaceous chondrites may reach 10 wt. % (see Table I; Mason 1971) but are much lower (~ 100 to 1000 ppm by weight) in the ordinary and enstatite chondrites (Robert et al. 1979, 1987a,b; McNaughton et al. 1981; Boato 1954; Yang and Epstein 1983). The hydrogen-bearing phases in these meteorites are apparently a combination of organic matter and trace hydrous phases (e.g., see Yang and Epstein 1983; Nagahara and El Goresy 1984). The stable isotope compositions of H, C, N and O in the chondritic meteorites have recently been reviewed by Pillinger (1984); some implications of the observed D/H ratios will be discussed later.

B. Volatiles in Ice-rich Satellites and Comets

With the exception of Io and Europa, all of the satellites of the outer planets for which we have reliable estimates of mass and radius appear to have low enough densities to conclude that ice must comprise a significant fraction of these satellites. Specifically, the densities of these *ice-rich* satellites range from $\approx 1.9 \text{ g cm}^{-3}$ for Ganymede, Callisto and Titan down to $\approx 1.2 \text{ g cm}^{-3}$ for Mimas, Iapetus and Enceladus (see Burns 1986 for a review). Models for Ganymede, Callisto and Titan suggest that they are 27 to 57, 34 to 58 and 30 to 58% ice, respectively; models for Mimas and Dione suggest they are 45 to 54% ice, and models for Enceladus, Tethys and Iapetus suggest in contrast a 65 to 78% ice composition with the remainder again being rock in each satellite (see Schubert et al. 1986 for a review). For the Uranian satellites and for the Saturnian satellite Rhea, Johnson et al. (1987) have constructed a range of models which imply that Titania is 35 to 53% ice, Oberon 40 to 58% ice and Rhea 53 to 73% ice, with the remainder again being rock in each satellite. We do not know the densities of the Neptunian satellites (Triton, Nereid) or of Pluto and its satellite Charon with sufficient accuracy to deduce useful ice/rock ratios.

In addition to the presence of ice implied from their densities, water ice has been identified spectroscopically on the surfaces of many satellites (Ganymede, Callisto, Rhea, Iapetus, Dione, Tethys, Enceladus, Mimas, Hyperion, Saturn's rings, Titania, Oberon, Umbriel, Ariel, Miranda, Charon), methane ice has been identified on the surfaces of Triton and Pluto, N_2 and CH_4 gas dominate the atmosphere of Titan, and liquid N_2 has been tentatively identified on the surface of Triton (see Burns 1986b; Cruikshank and Apt 1984; Cruikshank et al. 1984; Marcialis et al. 1987). In addition, there are many of the smaller satellites whose densities are not known but whose low

albedos and reflection spectra imply the possible presence of dark carbonaceous material on their surfaces; e.g., Himalia, Elara, Pasiphae, Carme, Sinope, Lysithea, Ananke, Leda, Phoebe, and the rings of Uranus; also Iapetus has a spatially variable albedo suggesting a part water ice and part carbonaceous surface (see Cruikshank 1986).

Earth-based observations of cometary comae have led to identification of a large number of volatile species emanating from comets. Carbon, nitrogen, oxygen, sulfur and hydrogen are seen in molecules (CO, HCN, CH₃CN, H₂O), atoms (C, H, O, S), free radicals (CH, CN, CS, NH, NH₂, OH) and ions (C⁺, CO⁺, CO₂⁺, CH⁺, H₂O⁺, N₂⁺, OH⁺, CN⁺). The number abundances of H, C, N, O, S, Mg, and Fe (relative to Si = 1.0) in recent bright comets are 24.3, 3.73, 1.51, 22.3, 0.55, 1.06 and 0.9, respectively (Delsemme 1982). Except for H (which is depleted by a factor of $\approx 10^3$), these number abundances are not much different from the solar composition values particularly allowing for the factor-of-two uncertainties that accompany some of the cometary values.

Preliminary results from the Giotto mission to Halley suggest nuclear emanation rates for the gases CO, N₂, CH₄ and NH₃ relative to H₂O of 0.05 to 0.2, < 0.01 to 0.1, 0.02 and 0.01 to 0.02, respectively (Balsiger et al. 1986; Eberhardt et al. 1986; Allen et al. 1987). Thus CH₄/CO \approx 0.1 to 0.4 and NH₃/N₂ > 0.1. These abundance estimates for CH₄ and NH₃ are tentative (Allen et al. 1987) but even if they are 2 or 3 times less than estimated, their presence in comets has considerable cosmogonic implications which we will address later. The dust from comet Halley apparently consists of a predominantly *chondritic* core with an *organic* mantle composed mainly of highly unsaturated compounds (Kissel and Krueger 1987).

C. Volatiles in Giant Gaseous Planets

The four giant gaseous planets (Jupiter, Saturn, Uranus and Neptune) range in size from ~ 4 to 10 times the size of the Earth with masses that are ~ 15 to 300 times the Earth's mass (M_{\oplus}). These planets are composed of variable proportions of solar gas and heavy (atomic number > 2) elements, with the former fraction being H₂- and He- dominated and the latter fraction being made up of *icy* (e.g., H₂O, CH₄, NH₃) and *rocky* (e.g., MgO, SiO₂, Fe, etc.) material. The observed radii and mean densities of the four planets show that the gas/(ice + rock) ratio decreases monotonically from Jupiter ($R \sim 6.98 \times 10^4$ km, $\rho \sim 1.33$ g cm⁻³), which is gas rich, to Neptune ($R \sim 2.45 \times 10^4$ km, $\rho \sim 1.67$ g cm⁻³), which is (ice + rock) rich.

More detailed information about the bulk compositions of these four planets, and about the radial distribution of the gaseous and solid components, can be obtained by constructing interior structure models having several compositional zones and by fitting these models to the observed mass, radius and observed J_2 and J_4 gravitational moments. These modeling efforts which have been recently reviewed by Stevenson (1982), yield several important facts.

First, the estimated mass fractions of ice + rock for Jupiter, Saturn, Uranus and Neptune are $\sim 0.05 - 0.09$, $\sim 0.17 - 0.24$, $\sim 0.75 - 0.91$ and $\sim 0.81 - 0.96$, respectively (Pollack 1985). Second, although the *relative* proportion of ice + rock increases from Jupiter to Neptune, the *absolute* abundance of this material is approximately constant (within a factor of 2) while the *absolute* abundance of the solar gas component varies by about a factor of 100. Third, the ice/rock mass ratios for Uranus and Neptune are > 1 (Hubbard 1984a, and references therein). More details of interior modeling efforts are described in the chapter by Hubbard.

Although the solar gas component is H_2 and He dominated, remote sensing observations show that the relative proportions of H_2 to He and of several less abundant gases (e.g., CH_4 , NH_3) to H_2 also vary from planet to planet (Gautier and Owen 1985). In particular, the H_2/He ratio is approximately solar (within the large observational uncertainties) on Uranus, is slightly enhanced over solar on Jupiter, and is enhanced by a factor of ~ 2 (or more) on Saturn (Conrath et al. 1987; Hanel et al. 1986; Gautier and Owen 1985). No accurate data are available for the H_2/He ratio on Neptune. The significantly increased H_2/He ratio on Saturn and the slightly increased H_2/He ratio on Jupiter if real are plausibly explained by an inhomogeneity in the radial distribution of He rather than by the segregation of He from H_2 in the region of the solar nebula where Saturn formed. Also, the CH_4/H_2 ratio for Jupiter and Saturn is slightly enhanced over the solar composition value by ~ 2 to 5 times while much larger enhancements of ~ 20 to 25 times are observed on Uranus and Neptune. Other hydrides (e.g., NH_3 , H_2O , H_2S , etc.) are expected to exhibit similar behavior, but the observations of (or attempts to detect) these gases are complicated by condensation processes, photochemical destruction and vertical mixing in these planetary atmospheres. These topics are discussed at length in several other chapters (see those of Gautier and Owen, Pollack and Bodenheimer, and Hubbard).

II. NEBULA CHEMISTRY

A. Starting Materials: Interstellar Gases and Grains

The abundant volatile elements giving rise to atmospheres must have been present in the dust and gas of the interstellar cloud(s) which collapsed to form our primitive solar nebula. Telescopic observations of dense interstellar clouds indicate the presence of a rich assortment of carbon-, oxygen- and nitrogen-containing compounds in addition to molecular hydrogen which is the probable principal constituent. Knowledge of the dust in these clouds is less definitive but there is tentative evidence that silicates, magnetite, carbonaceous compounds including graphite and ices are all present. The dust thus bears some similarity to the *primitive* material in our present solar system (e.g., carbonaceous chondrites). A detailed review of interstellar clouds is given in the chapter by Irvine and Knacke.

The bulk elemental composition of the specific cloud(s) which collapsed to form our own solar system is inferred largely from data on the composition of the Sun for the volatile elements and of CI1 carbonaceous chondrites for the less volatile ones. A summary of the abundances of the most common elements in the solar system is given in Table II (Cameron 1982).

The collapse of the precursor interstellar cloud into a rotating disk-shaped primitive solar nebula was accompanied by increasing temperatures and densities within the nebula. A central question concerns the extent to which the interstellar dust and gas metamorphosed as it was accreted by the nebula and flowed inward toward the Sun. Extensive evaporation and re-equilibration of the interstellar material is possible to the extent that the material can be transported inwards to sufficiently warm temperatures, chemically reprocessed, and then either accreted locally or transported outwards again. The meteoritic evidence discussed by Niederer and Papanastassiou (1984) and Grossman and Larimer (1974) suggests that extensive chemical reprocessing occurred in at least the inner solar system and we will discuss later tentative evidence for some chemically reprocessed material even in Comet Halley.

B. Thermochemistry, Shock Chemistry, Photochemistry and Radiochemistry

Chemical reprocessing of interstellar material in the solar nebula requires in general a source of energy; either to overcome activation energy barriers or to drive otherwise endothermic reactions such as dissociations. There are several readily recognized sources of energy for chemical reactions in the nebula.

Thermochemistry Using Thermal Energy from Nebular Accretion. During the nebular collapse phase and prior to the formation of an active proto-Sun the major source of energy was undoubtedly conversion of gravitational potential energy to kinetic (thermal) energy. The net energy flux (radiative and convective) through the nebula is given roughly by $\phi_T = sT_e^4$ where T_e is the effective temperature of the nebula and s is Stefan's constant (for illustrative T_e of 100 to 500 K, $sT_e^4 = 5.7$ to $3544 \text{ J m}^{-2}\text{s}^{-1}$). Endothermic chemical reprocessing requiring an energy flux ϕ exceeding ϕ_T would lead to catastrophic

TABLE II
Ratios Relative to H₂ of the 10
Most Abundant Elements in
a Solar-Composition Medium^a

H ₂	1.0	N	1.74×10^{-4}
He	0.135	Mg	7.97×10^{-5}
O	1.38×10^{-3}	Si	7.52×10^{-5}
C	8.35×10^{-4}	Fe	6.77×10^{-5}
Ne	1.95×10^{-4}	S	3.76×10^{-5}

^aTable after Cameron (1982).

local cooling and thus could not be sustained. The availability of thermal energy for driving *thermochemical* reactions is, however, highly temperature dependent since the conversion efficiency varies roughly as the Boltzmann factor $b = \exp(-E/kNT)$ where N is Avogadro's number, E is the activation energy for the reaction of interest, T is the local temperature, and k is Boltzmann's constant (e.g., for $E = 5 \times 10^4$ J/mole, $b = 0.13$ at 3000 K and 2×10^{-9} at 300 K). When b values for all relevant reactions are sufficiently close to unity (i.e., when temperatures are sufficiently high), then the system essentially is in thermochemical equilibrium and there is no net conversion between molecular kinetic (thermal) and molecular internal energy. As the temperature is lowered, thermochemical equilibrium can be maintained provided the system cools at a sufficiently slow rate. Specifically, we need the chemical reaction time $t_{\text{chem}} = -(\text{dln}C/\text{d}t)^{-1}$ to be \leq the cooling time $t_{\text{cool}} = -(\text{dln}T/\text{d}t)^{-1}$ where C is concentration. Once $t_{\text{chem}} > t_{\text{cool}}$, the reaction is quenched essentially and thermochemical equilibrium no longer applies. Since for a reaction with rate $R \propto \exp(-E/kNT)$ the chemical deceleration time in a cooling system $t_{\text{decel}} = -(\text{dln}R/\text{d}t)^{-1} = (kNT/E)t_{\text{cool}} \ll t_{\text{cool}}$, then almost all cooling systems will ultimately reach disequilibrium states as $T \rightarrow 0$. For later discussion, we will assume that the usable thermal energy flux for endothermic thermochemical reactions $\phi \approx b\phi_T$; for thermo-neutral (equilibrium) and exothermic reactions there are of course no net external energy sources required but the activation energy barrier must still be overcome so the same formula can be justified.

Chemistry in Lightning Discharges and Thundershocks. The simultaneous presence of fluid motions and abundant particles in the solar nebula make charge separation (and hence lightning discharges and their accompanying thundershocks) a likely but at the present time speculative phenomenon. In effect, such discharges convert a (very small) fraction ϵ of the convective energy flux into intense electric currents, shock waves and ultraviolet photons all of which are then convertible with high efficiency into chemical potential energy through the breaking of chemical bonds. For Earth and Jupiter the lightning energy flux ϕ is approximately 4×10^{-7} and 4×10^{-5} , respectively, of the net flux in moist convective regions (Borucki et al. 1984); that is $\phi = \epsilon sT_e^4$ where $\epsilon \approx 4 \times 10^{-7}$ to 4×10^{-5} . It is arguable whether similar ϵ values apply in the nebula where the convection is largely dry but, if it does apply, then $\phi = (2.3 \text{ to } 1418) \times 10^{-5} \text{ J m}^{-2}\text{s}^{-1}$ for nebular $T_e = 100$ to 500 K and $\epsilon = 4 \times 10^{-6}$. The temperatures attained in lightning are several thousand Kelvin (and hence the Boltzmann factors $b \rightarrow 1$) so that the number of chemical bonds broken per unit area per unit time $\phi_B \rightarrow \phi/D$ where D is a representative bond energy. However, a good deal of subsequent recombination occurs during cooling prior to quenching so the net ϕ_B is less than ϕ/D (e.g., on the Earth the net $\phi_B \approx 0.1 \times \phi/D$ using $D = 5 \times 10^5$ J/mole appropriate to O_2).

Photochemistry Driven by the Proto-Sun: Opacity Dilemmas. In the present-day solar system, ultraviolet light from the Sun provides a potent disequilibrium mechanism in planetary atmospheres. The present-day flux F of the photochemically important Lyman- α radiation at 1 AU is not large (3.5×10^{11} photon $\text{cm}^{-2} \text{s}^{-1}$; 5.7×10^{-3} J $\text{m}^{-2} \text{s}^{-1}$), but the early Sun may have emitted a flux some 10^3 to 10^4 times greater than the present Sun (see, e.g., Zahnle and Walker 1982 for a comprehensive review). It has recently been conjectured that enhanced ultraviolet radiation from the proto-Sun served as an important disequilibrium mechanism for nebula gases (Yung et al. 1987a), and (presumably after dissipation of the nebula) as both a disequilibrium process and an energy source for hydrodynamic escape in evolving protoplanetary atmospheres (Zahnle and Walker 1982). Are these latter conjectures plausible?

First, it is arguable whether the proto-Sun was a powerful source of ultraviolet radiation while the dense *gaseous* nebula was present; current theories and observations do not enable definitive conclusions. To assess the viability of protosolar-driven photochemistry in the gaseous nebula, it is additionally important to determine the *ultraviolet* opacity of the nebula itself. In particular, if the opacity is very large the protosolar photons will be absorbed wholly in the very hot ($T \geq 2500$ K) relatively dense inner nebula where large thermochemical reaction rates involving abundant thermally produced radicals and atoms overwhelm or negate the dissociative effects of the ultraviolet photons. The solar ultraviolet photons then effectively become another source of heating to be added to the dominant source (namely conversion of the kinetic energy of infalling material to thermal energy). We note parenthetically that this situation in the gaseous inner nebula would be very different from that in the present-day terrestrial thermosphere where solar ultraviolet photons are the dominant source of energy for dissociation, where molecular diffusion, gravitational stratification and selective escape are important processes, and where pressures are much lower (and recombination reactions therefore much slower).

To calculate the minimum ultraviolet opacity we will deliberately use one of the lightest mass nebula models, specifically that of Hayashi (1981). The vertical optical depth (τ_z measured from midplane to outer surface of nebula at radius $r = r_1$) and radial optical depth (τ_r measured between radii r_1 and r_2) are:

$$\tau_z(r_1) = \frac{1}{2} (\Sigma_{\text{gas}} \sigma_{\text{gas}} + \Sigma_{\text{dust}} \sigma_{\text{dust}}) \quad (1)$$

$$\tau_r(r_1, r_2) = \int_{r_1}^{r_2} (\rho_{\text{gas}} \sigma_{\text{gas}} + \rho_{\text{dust}} \sigma_{\text{dust}}) dr. \quad (2)$$

We use the Hayashi (1981) expressions for vertical column mass densities for

gas and dust (Σ_{gas} , Σ_{dust}) and midplane gas and dust mass density (ρ_{gas} , ρ_{dust}). For the Lyman- α wavelength (≈ 122 nm), the minimum value of the gas absorption cross section σ_{gas} is given by considering the absorption cross section due to H_2O alone (1.59×10^{-17} cm^2 molecule $^{-1}$; Kley 1984). For a nebular H_2O molar mixing ratio of 10^{-3} and nebular mean molecular weight of 2.3, we thus have $\sigma_{\text{gas}} = 1.59 \times 10^{-17} \times 6 \times 10^{23} \times 10^{-3}/2.3 = 4.1 \times 10^3$ cm^2 g^{-1} . For the dust, we have $\sigma_{\text{dust}} \approx 3/(4aD)$ provided the particle radius $a \gg 122$ nm. Specifically for $a = 10^{-4}$ cm and particle density $D = 4.4$ g cm^{-3} (i.e., silicate plus metal), $\sigma_{\text{dust}} \approx 1.7 \times 10^3$ cm^2g^{-1} . Thus since $\sigma_{\text{dust}} \approx 0.4 \sigma_{\text{gas}}$ and also $\Sigma_{\text{dust}} \approx 0.01 \Sigma_{\text{gas}}$ (Hayashi 1981), we can ignore the small additional ultraviolet opacity due to the dust (this is reasonable unless the dust has a much smaller scale height than the gas (e.g., 250 times smaller) in which case the dust and gas opacities in the central plane could be comparable). Hence we obtain:

$$\begin{aligned} \tau_z(r_1) &\approx \frac{1}{2} \times 1.7 \times 10^3 \left(\frac{r_1}{1 \text{ AU}} \right)^{-3/2} \times 4.1 \times 10^3 \\ &= 1.7 \times 10^7 (r_1 = 0.35 \text{ AU}) \end{aligned} \quad (3)$$

$$\begin{aligned} \tau_r(r_1, r_2) &\approx 1.4 \times 10^{-9} \times 4.1 \times 10^3 \times 1.5 \times 10^{13} \\ &\times \left[\left(\frac{r_1}{1 \text{ AU}} \right)^{-7/4} - \left(\frac{r_2}{1 \text{ AU}} \right)^{-7/4} \right] / 1.75 \\ &= 2.6 \times 10^8 (r_1 = 0.35 \text{ AU}, r_2 = 1 \text{ AU}). \end{aligned} \quad (4)$$

These massive optical depths correspond to decreases in photochemically important photon fluxes ϕ from their midplane values at 0.35 AU due to absorption alone (i.e., not even including the $1/r^2$ geometric term) by 7 million and 110 million orders of magnitude, respectively. For photons beginning at the surface of the proto-Sun (i.e., $r_1 \rightarrow 0$), the τ_z and τ_r values are several orders of magnitude greater than their values computed above at 0.35 AU (we have not presented precise values because the Hayashi (1981) ρ and Σ expressions are strictly derived only for $r_1 \geq 0.35$ AU and because H_2O begins to be thermally dissociated to OH and H for $T \geq 2500$ K). It is almost academic to add that consideration of the more massive Cameron (1978) nebula would increase these numbers by more than another factor of 10. Thus, while the gaseous nebula was present, any protosolar-driven photochemistry must have been confined to the very hot gas near the proto-Sun where its ability to induce chemical disequilibrium must have been small with surviving relicts, if any, restricted to high-temperature refractory material.

After the nebula gases and fine dust were dissipated (in a T-Tauri phase), the young Sun would then be initially irradiating a vast but thin disk of orbiting objects (boulder size to planet size?). High collision rates in this disk would have provided a potent source of dust (Greenberg et al. 1978a) which

would not have abated until the planets as we know them today had largely accreted and collision rates had dropped dramatically: a process which probably took several 100 Myr (Safronov and Ruzmaikina 1985a). This is the very time during which the Sun was its most luminous in the ultraviolet (Zahnle and Walker 1982). Thus, to assess the viability of solar-ultraviolet driven photochemistry and hydrodynamic escape in early planetary atmospheres, we need to determine the ultraviolet opacity of the gas-free but very dusty, post-nebula disk. The radial optical depth τ_r can be related to the total mass $M(r)$ of dust inside radius r by

$$\begin{aligned}\tau_r &= \frac{M\sigma_{\text{dust}}}{2\pi r h_{\text{dust}}} \\ &\approx \frac{3M}{8\pi r h_{\text{dust}} a D}\end{aligned}\quad (5)$$

where h_{dust} is the vertical scale height of the dust.

For an optical depth $\tau_r \geq 4 \ln 10 = 9.2$, a solar ultraviolet flux 10^4 times its present value will be reduced to \leq present value. From Eq. (5) this is achieved provided

$$\begin{aligned}M(r) &\geq 77 \times r h_{\text{dust}} a D \\ &= 3.2 \times 10^{20} \text{ g } (r = 1 \text{ AU}) \\ &= 5.3 \times 10^{-8} M_{\oplus} (r = 1 \text{ AU})\end{aligned}\quad (6)$$

where we have used $h_{\text{dust}} \approx$ Earth radius = 6380 km, $a = 10^{-4}$ cm, $D = 4.4$ g cm $^{-3}$, and $r = 1.5 \times 10^{13}$ cm to obtain the numerical value. This is an extremely small value indeed. To place it in perspective, the numerical multi-body collision/accretion calculations of Greenberg et al. (1978a) resulted typically in about 1% of the total initial mass of colliding bodies being processed into unresolved (sub-31-m diameter) *dust* in 25,000 yr. This translates into a *dust* production rate inside 1 AU of 2.3×10^{21} g yr $^{-1}$ or 3.8×10^{-7} M_{\oplus} yr $^{-1}$. Given these massive production rates, it is difficult to argue that the $M(r)$ value required by Eq. (6) was not easily achieved while the terrestrial planets were accreting and collisions were common in the solar system. An important theoretical problem yet to be addressed is the precise duration of this dusty *high-opacity* epoch in the solar system and how the duration of this epoch compared to the duration of the enhanced ultraviolet emission from the young Sun. The latter problem is coincidentally common to Wetherill's (1981b) explanation for ^{36}Ar in terrestrial atmospheres.

As a postscript to this topic, it should be emphasized that the above opacity arguments refer to solar photons emitted in the direction of the (equatorial) nebula disk. Solar photons emitted in other (e.g., polar) directions may

suffer little or no absorption and escape the protosolar system. Hence the fact that ultraviolet emission is observed from T-Tauri stars is not an argument in favor of low-opacity conditions and extensive solar-driven photochemical disequilibrium in the nebula disk.

Photochemistry Driven by Stellar Photons. The maximum energy flux in interstellar photons with $90 \text{ nm} < \text{wavelength} < 200 \text{ nm}$ occurs in transparent parts of our Galaxy and is about $7 \times 10^{-7} \text{ J m}^{-2} \text{ s}^{-1}$ (see, e.g., Duley and Williams 1984). Assuming a similar flux was applicable 4.6 Gyr ago, the energy flux for driving photochemistry in the outer skin of the solar nebula disk $\phi \leq 7 \times 10^{-7} \text{ J m}^{-2} \text{ s}^{-1}$ with the actual value depending on the opacity of interstellar space in the vicinity of the solar nebula. The interstellar flux is thus very small but it impinges the chemically perturbable (low-temperature) parts of the nebula. Hence it does not suffer from the same solar nebula opacity dilemmas which accompany solar-driven photochemistry and it may have been larger in the past than today. Specifically, the above ϕ value corresponds to a 90 to 200 nm photon flux of $\leq 5 \times 10^7 \text{ photon cm}^{-2} \text{ s}^{-1}$. In the inner nebula H_2O will be a major absorber of these photons (as already noted in the previous section). At 1 AU there are about $2.2 \times 10^{23} \text{ H}_2\text{O molecule cm}^{-2}$ on either side of midplane in the Hayashi (1981) model so that over the 10^5 to 10^6 yr lifetime of the nebula ≤ 0.07 to 0.7% of this H_2O will be dissociated by the above photon flux. Thus the interstellar flux would have had to have been at least 10^2 to 10^3 times greater than present in order to be important in nebula chemistry. In the cold outer nebula (e.g., $T < 150 \text{ K}$), the stellar ultraviolet photons will mainly be absorbed by ice/rock grains and CO gas (H_2O is essentially totally condensed and we do not expect CH_4 in the solar nebula). Thus the H_2O photochemistry discussed by Yung et al. (1987b) could only have proceeded in the inner nebula and would require greatly enhanced interstellar ultraviolet fluxes over present-day values. Whatever photochemistry proceeds will also need to compete with shock chemistry and with the general inward transport and thermal reprocessing of material during the solar accretion phase.

Radiochemistry Driven by ^{26}Al . The short-lived radionuclide ^{26}Al was apparently present in dust particles in the early solar nebula with an average mass mixing ratio f relative to $\text{H}_2 + \text{He}$ of $\approx 2 \times 10^{-9}$ (Lee et al. 1976). Consolmagno and Jorjipii (1978) have noted that the 1.83 MeV γ photons and 1.16 MeV positrons (or the 1.02 MeV γ photons produced on their annihilation by electrons) which result from ^{26}Al decay were important sources of ionization in the solar nebula. Specifically, we can show that the power produced per unit area of the nebula disk by ^{26}Al decay (i.e., the energy flux available for radiochemistry) is

$$\begin{aligned}
\phi &\approx j f \Sigma_{\text{gas}} d/26 \\
&= 1.2 \times 10^{-9} \left(\frac{r}{1 \text{ AU}} \right)^{-3/2} \text{ J m}^{-2} \text{ s}^{-1} \\
&= 1.2 \times 10^{-9} \text{ J m}^{-2} \text{ s}^{-1} \quad (r = 1 \text{ AU}) \tag{7}
\end{aligned}$$

where $j = 2.97 \times 10^{-14} \text{ s}^{-1}$ is the ^{26}Al decay rate constant, $d = 3 \times 10^{11} \text{ J/mole}$ is the average available ^{26}Al decay energy, and we have again used the Hayashi (1981) expression for Σ_{gas} . Evidently ϕ for radiochemistry is very small; indeed for ionization reactions even lightning may have been a more important (albeit spatially inhomogeneous) source of energy than ^{26}Al in the nebula.

C. Synopsis

To determine what types of chemistry will dominate in the nebula it is instructive to compare the *usable* energy fluxes ϕ available for chemical reactions to the net flux $\phi_T = sT_e^4$. Specifically for representative $T = 600 \text{ K}$, $r = 1 \text{ AU}$, $E = 5 \times 10^4 \text{ J/mole}$, $\epsilon = 4 \times 10^{-6}$ and $T_e = 300 \text{ K}$ we have:

$$\phi(\text{thermochemistry})/\phi_T \approx \exp(-E/kNT) = 4 \times 10^{-5} \tag{8}$$

$$\phi(\text{thunder - shock chemistry})/\phi_T \approx \epsilon = 4 \times 10^{-6} \tag{9}$$

$$\phi(\text{solar - driven photochemistry})/\phi_T \approx 10^4 \times F \exp(-\tau_r)/\phi_T \approx 0 \tag{10}$$

$$\phi(\text{stellar - driven photochemistry})/\phi_T \approx 10^{-9} \tag{11}$$

$$\phi(\text{radiochemistry})/\phi_T \approx 3 \times 10^{-12} \tag{12}$$

Clearly thermochemistry is the expected dominant chemical process at $r = 1 \text{ AU}$ except for reactions with very large activation energies where shock chemistry (lightning) could be comparable. Solar photons and radioactivity are totally negligible at 1 AU. Stellar photons are not important in the inner nebula ($r \leq 1 \text{ AU}$) but may be quite important in the cold, outer portions of the nebula ($r \geq 10 \text{ AU}$). Specifically, for a low $T_e = 100 \text{ K}$ the value of ϕ/ϕ_T for stellar photochemistry increases to 10^{-7} (i.e., approaching thunder-shock chemistry and much greater than thermochemistry).

As we move closer to the Sun than 1 AU, thermochemistry becomes more and more dominant (e.g., at 1500 K, $\phi(\text{thermochemistry})/\phi_T = 0.018$ for the E value used in Eq. (8), while lightning becomes successively more important farther from the Sun (e.g., at 150 K, $\phi(\text{thermochemistry})/\phi_T = 4 \times 10^{-18}$ for the same E value while $\phi(\text{thunder-shock chemistry})/\phi_T$ remains at 4×10^{-6}). As a check, we note that if we apply Eqs. (8) through (12) to the present-day Earth atmosphere ($T_e = 255 \text{ K}$, $T = 300 \text{ K}$, and most important relatively small τ_r value), we do predict correctly that solar-driven pho-

tochemistry is the dominant (abiotic) present-day atmospheric chemical process. Note also that when these equations are applied to specific chemical reactions the E value for that specific reaction must be used.

The fact that thermochemistry appears to have been the dominant type of chemistry overall in the solar nebula places important constraints on chemical reprocessing of cold interstellar material in the nebula. In particular, the cold material will need to be transported inwards to temperatures and pressures at which reactions can proceed within the lifetime of the nebula (10^5 to 10^6 yr). These temperatures and pressures are reached by approaching the proto-Sun in the solar nebula or approaching a giant protoplanet in a protoplanetary subnebula or atmosphere. This means that a discussion of nebula chemistry can only proceed in tandem with a discussion of nebula dynamics.

III. INTERPLAY BETWEEN NEBULA CHEMISTRY, DYNAMICS AND STRUCTURE

Advances in our understanding of nebula chemistry are coupled in several important ways to advances in our knowledge of nebula dynamics and evolution. The generally accepted evolutionary picture (see, e.g., Cassen et al. 1985; chapter by Boss et al.; Morfill et al. 1985) has the original interstellar cloud collapsing inwards with material of successively higher angular momentum accreting as time progresses thus forming a growing, rapidly rotating *accretion disk*. Mass inflow through the disk into the proto-Sun then continued until the proto-Sun ignited. Extensive chemical, petrographic and isotopic evidence from meteorites and inferences that asteroids are meteorite parent bodies suggest that the solar nebular accretion disk was extensively physically mixed (but not necessarily chemically and isotopically homogenized) out to at least 4 AU from the proto-Sun (Wilkening 1977; Niederer and Papanastassiou 1984; Grossman and Larimer 1974). The giant planets accreted in the nebula perhaps with their own accretion disks but we argue here that the probable site of formation of their regular satellites was in later-forming well-mixed subnebulae *spun off* during contraction of these initially very hot planets toward their present dimensions (chapter by Pollack and Bodenheimer) or *impact-generated* subnebulae formed by a massive collision (Cameron 1975). A simplified physical picture of the nebula is shown in Fig. 1.

It seems probable that an intense T-Tauri solar wind provided an important mode for the newly ignited proto-Sun to radiate away energy and that this intense wind first blew away the thinnest part of the nebular disk (over the protosolar poles) and also decelerated the inward gas flow in the protosolar equatorial plane; ultimately this wind then swept away all the remaining unaccreted gases and fine dust in the nebula. The time span from initial cloud collapse to proto-Sun ignition and nebular blow off was about 10^5 to 10^6 yr (Cameron 1985a).

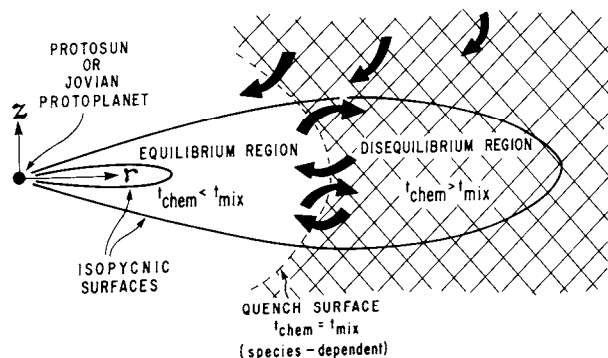


Fig. 1. Schematic illustrating the occurrence of a quench surface separating thermochemical equilibrium and transport-induced-disequilibrium regions in the solar nebula or a well-mixed protoplanetary subnebula. See text for details.

After the gaseous nebula was dissipated, the surviving bodies (ranging in size from giant gaseous protoplanets down to m-sized objects and perhaps smaller) began an evolutionary period of several 100 Myr duration characterized by high collision frequencies, accompanying accretion, fragmentation and degassing, evolution of terrestrial bodies, and further growth of the giant planets (see chapter by Greenberg). These processes proceeded in a largely gas-free but dust-rich (due to dust production in collisions) solar system environment.

Thermochemistry in both the solar nebula and protoplanetary subnebulae depended in two important ways on the pressure/temperature conditions in these nebulae. This is illustrated first in Figs. 2 and 3 where it is seen that the P, T profile for a representative solar nebula model (Lewis and Prinn 1980; Barshay 1981) implies that, in *thermochemical equilibrium*, CO and N_2 are much more abundant than CH_4 and NH_3 in the warm inner parts of the nebula. In contrast, CO is always less abundant than CH_4 and N_2 is at most comparable in abundance to NH_3 in the much higher-pressure (at a given T) protoplanetary subnebulae (Prinn and Fegley 1981). We should add that most solid/vapor and solid/solid transition temperatures in thermochemical equilibrium show much less pressure dependence than the above gas/gas transitions and thus they are much less sensitive to the choice of nebula model.

The nebula P, T profiles affect thermochemistry in a second important way. Because reaction rates generally increase rapidly with temperature and because the presence and abundance of efficient solid catalysts (e.g., Fe, Fe_xC particles) is temperature dependent, then the rates of the $CO \rightarrow CH_4$ and $N_2 \rightarrow NH_3$ reactions at the CO/CH_4 and N_2/NH_3 boundaries are much greater in the planetary subnebulae than in the solar nebula. As a result the $CO \rightarrow CH_4$ and $N_2 \rightarrow NH_3$ conversions are kinetically inhibited in the nebula (Lewis and Prinn 1980) but *not* in the subnebulae (Prinn and Fegley 1981a).

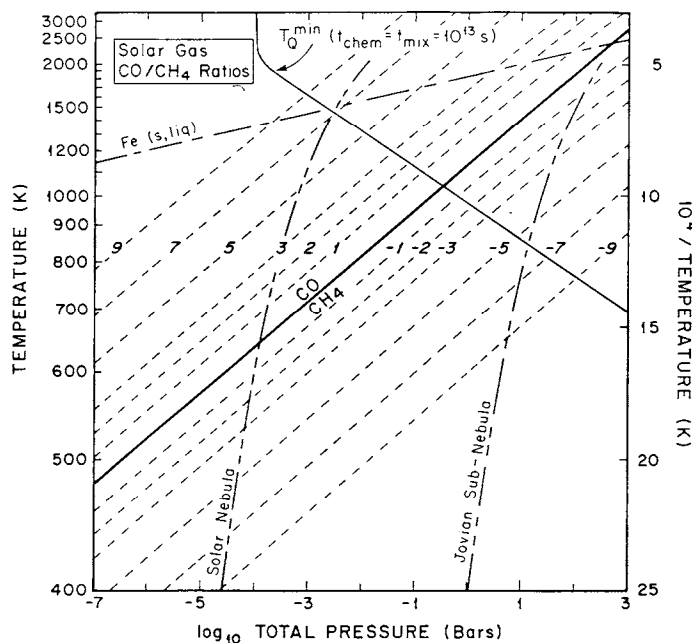


Fig. 2. Calculated ratios of CO/CH₄ at thermochemical equilibrium in a solar composition gas. The solid line labeled CO - CH₄ is the boundary where the abundances of the two gases are equal; CO is more abundant to the left and CH₄ is more abundant to the right. The dotted contours labeled 9, 7, 5, . . . -5, -7, -9 are constant log₁₀ CO/CH₄ contours. The line labeled Fe(s, liq) is the Fe condensation line; Fe(s, liq) is stable below this line. Two P, T profiles for an illustrative solar nebula model (Lewis and Prinn 1980; Barshay 1981) and an illustrative subnebula model (Prinn and Fegley 1981a) are also shown. The solid line labeled T_0^{\min} illustrates the minimum quench temperatures for homogeneous gas-phase conversion of CO to CH₄ assuming that the CO chemical lifetime (t_{chem}) = the maximum nebular mixing time (t_{mix}) of 10^{13} s (i.e., the nebular gases are mixed once during the nebula's lifetime). Shorter mixing times (i.e., more frequent mixing) result in higher quench temperatures. See Fig. 7 for details of Fe-catalyzed heterogeneous CO \rightarrow CH₄ conversion in the solar nebula.

Thermochemistry in the nebula potentially is profoundly influenced by nebula dynamics. Current models for the solar nebula accretion disk (see, e.g., Morfill et al. 1985) indicate that outward diffusive mixing is opposed by the advective inward flow. It is therefore difficult in these models for nebula material which might have been chemically processed in the hot inner nebula to diffuse outward (Stevenson 1987b). This conclusion is, however, at odds apparently with the observational evidence for extensive inner nebula processing and mixing contained in chondritic meteorites (see also Cabot et al. [1987b] for a discussion of other problems in current models). Perhaps the solution lies in the fact that the quadratically nonlinear momentum equation is replaced by a linear diffusive momentum equation in current accretion disk

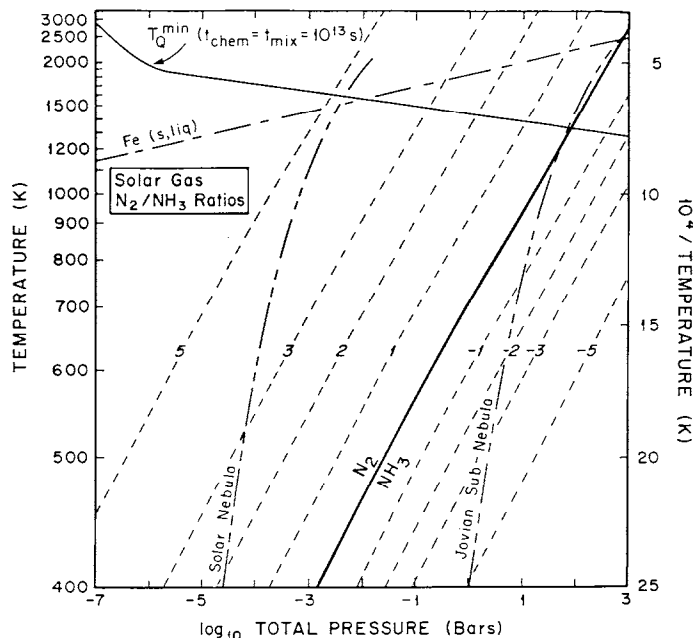


Fig. 3. As in Fig. 2 but for calculated ratios of N_2/NH_3 at thermochemical equilibrium in a solar composition gas. In this case, the line labeled T_Q^{min} illustrates the minimum quench temperatures for homogeneous gas-phase conversion of N_2 to NH_3 .

models thus precluding in particular nonlinear counter-gradient momentum fluxes. These nonlinear fluxes are expected and when included in the models enable the shear to be maintained in an accretion disk in which diffusive mixing is strong enough to overcome the negative effect of the mean inward flow on outward trace constituent mixing (Prinn 1988).

Dynamics is also important in understanding the chemistry of subnebulae around the giant protoplanets. Prinn and Fegley (1981a) proposed a model for the chemistry in a convective circumplanetary subnebula involving inward mixing of accreted solar material (rich in CO and N_2), thermochemical conversion of the CO and N_2 to CH_4 and NH_3 , and outward mixing of this processed material to form satellites rich in CH_4 and NH_3 . If one assumes that the Prinn and Fegley (1981) subnebula is an accretion disk (its precise nature was in fact unspecified), then the efficiency for outward mixing in accretion disks which include nonlinear effects makes it probable that the above processed material could be mixed outward to form CH_4 -rich satellites. Thus an accretion disk subnebula model may explain Titan. As mentioned earlier, it is, however, probable that the subnebulae in which outer planetary regular satellites formed were not accretion disks but later-occurring highly convective subnebulae spun off by the giant protoplanets as they contracted toward their