

PRESENT STATE AND CHEMICAL EVOLUTION OF THE ATMOSPHERES OF TITAN, TRITON AND PLUTO

J. I. LUNINE

University of Arizona

S. K. ATREYA

University of Michigan
and

J. B. POLLACK

NASA Ames Research Center

Titan, Triton and Pluto are lunar-sized solid bodies which have substantial atmospheres. The atmosphere of Saturn's satellite Titan has been well characterized by the Voyager 1 flyby; it is mostly molecular nitrogen with an admixture of methane, a surface pressure of 1.5 bars and a surface temperature of 95 K. The atmosphere of Neptune's satellite Triton is inferred from the spectroscopic presence of surface methane and, possibly, nitrogen. Temperatures at Triton's distance from the Sun are substantially lower than at Titan's and hence a thinner atmosphere is expected. Pluto's atmosphere is poorly characterized but spectroscopically identified methane exists partitioned to some unquantified extent between a surface and atmosphere. Preliminary studies of Pluto's satellite Charon show no evidence of methane. The fundamental driving force in the long-term evolution of Titan's atmosphere is the photolysis of methane in the stratosphere to form higher hydrocarbons and aerosols. The current rate of photolysis, together with the inferred undersaturation of methane in the lower troposphere, suggests a reservoir of methane mixed with higher hydrocarbons. This "ethane-methane ocean" serves as both the source and sink of photolysis, and contains a mass of nitrogen comparable to the atmospheric abundance. In the absence of outgassing or external resupply, the ocean composition evolves toward more ethane rich as

methane is photolyzed over geologic time. The atmosphere responds to the change in ocean composition with a corresponding change in gaseous composition and spatially averaged cloud composition. The resulting change in the atmospheric thermal structure, and hence climate, is an evolutionary problem which taxes our present understanding of the checks and balances of infrared opacity and incident sunlight. The outstanding problem in the earliest evolution of Titan concerns the origin of atmospheric nitrogen: was it introduced into Titan as molecular nitrogen or ammonia? Measurement of the argon-to-nitrogen ratio in the present atmosphere is a diagnostic test of the competing hypotheses: a large argon abundance suggests molecular nitrogen, while a small abundance favors ammonia. Titan has an atmosphere in contrast to the Galilean satellites because temperatures were low enough in its region of formation to incorporate ammonia into hydrates and methane into clathrates. In the region of Jupiter, methane clathrate was not stable. The absence of ammonia-derived nitrogen, however, is not so easy to explain: perhaps ammonia hydrate was not stable in the Jovian nebula, nitrogen was removed by magnetospheric processes, or the absence of methane prevented a greenhouse environment from being present at the appropriate time to build up a molecular nitrogen atmosphere. Similar speculations on the atmospheres of Triton and Pluto must await the Voyager-Neptune flyby in 1989 and development of advanced Earth-based observational tools for observing the outer solar system.

I. INTRODUCTION

Overview

Three lunar-sized objects in the outer solar system are known or strongly suspected to have atmospheres of mass sufficient to affect surface processes in a measurable way. Saturn's largest satellite Titan is encased in a nitrogen-rich atmosphere with a surface density five times that of the Earth's nitrogen-rich envelope, and a secondary methane component which plays the role of condensable. The outermost planet, Pluto, has an atmosphere which contains at least methane at a partial pressure of perhaps one-fiftieth the total pressure of the Martian atmosphere. Neptune's large satellite Triton has methane and possibly nitrogen present as condensed volatiles on its surface; estimates of the surface atmospheric pressure range over orders of magnitude from microbars to one-tenth of a bar (one bar \sim one atmosphere = 760 torr).

Since the first of these atmospheres was positively identified 44 yr ago (Kuiper 1944), their relationship to the envelopes surrounding the terrestrial planets has been pondered. The work of Urey, his students and scientific descendants in establishing cosmochemistry (the study of the relationship of the chemical composition of planets and their satellites to the origin of the solar system) as a *bona fide* field of study sharpened the questions (Urey 1952; Lewis 1971; Stevenson 1985). The era of exploration of the outer solar system by spacecraft and advanced groundbased techniques provides the basis for making the questions more specific and numerous. Fundamentally, however,

we wish to understand *the evolution of the atmospheres of Titan, Triton and Pluto to their present state, the processes during formation of these bodies which initiated their atmospheres, and the characteristics of the atmospheres which are diagnostic of the particular processes by which these objects formed.*

In this chapter we attempt to synthesize the most recent work on the present state and evolution of the atmospheres of Titan, Triton and Pluto, and present in a balanced fashion current ideas on the formation of these objects and their parent systems. Notice that dealing with Titan, Triton and Pluto as a set of objects requires artful rhetoric at times, because the first two objects are satellites of major planets, the last itself a planet with a satellite, Charon. Study of Titan's atmosphere presumably teaches us something about how satellites form around giant planets, because Titan's very regular orbital characteristics strongly suggest an origin associated with the formation of Saturn. Neither Triton nor Pluto have orbits which are sufficiently "regular" (low eccentricity and inclination) that they can be typed so readily. Triton may have formed in place about Neptune, or been captured; Pluto might have been a satellite of one of the outer planets to start with, but no compelling model of its evolution to a solar orbit is available. Pluto's Charon may or may not have been captured. Compounding our difficulty is that we have much more detailed information on Titan than we do on the other objects, because of the Voyager-Saturn encounters in 1980 and 1981. However, the Voyager 2 flyby of Neptune's system in 1989 will provide us with comparable information on Triton.

The difficulties cited above should not be considered a rationale for abandoning comparative studies of the atmospheres of these three objects. The location of Titan, Triton and Pluto in the outer solar system, with consequently low temperatures, affords us study of atmospheres with compositions distinctly different from those of the terrestrial planets. Hypotheses involving steady-state processes and evolution of Titan's atmosphere can be tested on Triton's atmosphere after the 1989 Voyager encounter. Finally, the knowledge acquired of the atmospheres of Titan and Triton will provide us with better notions of what processes and constituents to look for in Pluto's atmosphere, and how to look for them.

In pondering the origin and evolution of atmospheres, we cannot ignore the surfaces and interiors of the bodies in question. Unfortunately, our knowledge of the interior of Titan, based upon bulk density, is rudimentary. For Triton and Pluto, it is essentially nonexistent. The state of our understanding of the surfaces of these bodies is ironically, the reverse: Titan's ubiquitous haze prevents any observation of the surface, whereas Triton's and Pluto's surfaces have to the best of our understanding, been detected by groundbased studies. As we discuss below, our conceptions of the nature of Titan's surface based on inferences from its atmospheric properties are of crucial importance in modeling the evolution and origin of the atmosphere itself.

Organization

We begin this chapter with a subsection containing questions which can be addressed by study of the cryogenic atmospheres of Titan, Triton and Pluto. While not complete, these questions serve as a guide to the types of inquiries which the current state of our knowledge allows. Section II summarizes current understanding of physical processes operating on the atmospheres and surfaces of Titan, Triton and Pluto, to provide a foundation for the discussions of origin and evolution which make up the bulk of the chapter. By necessity, details of the observations and associated controversies are omitted; we emphasize processes. We recommend the excellent review chapters by Hunten et al. (1984), and Cruikshank and Brown (1986), as well as Chapter 7 of Atreya (1986), for more details on the observations. A review chapter by Morrison et al. (1986) contains a brief analysis of issues of the evolution of Titan's atmosphere based upon the available data. Section II also discusses inferred inventories of volatiles based on our understanding of the atmospheres and surfaces. (In this chapter, the term "volatile" is used to denote any material capable of having a substantial vapor pressure under temperature conditions obtained in the outer solar system; anything more volatile than ammonia is included.)

Section III considers atmospheric evolution inferred from physical processes identified as operating in the present-day environment. These include photochemistry and radiation-driven chemistry, atmospheric escape, and surface-atmosphere coupling. An attempt is made to use these processes to "run the clock back" and tie the present-day state to models of the origin and early evolution of Titan, in particular. Section IV considers models for the origin and early evolution of Titan, Triton and Pluto with emphasis on their atmospheres. This section overlaps with the chapters by Coradini et al., and Prinn and Fegley, but is placed in the context of the evolution studies of Sec. III. Section V discusses the relevance of outer solar-system atmospheres to those of the terrestrial planets, in terms of composition and modes of formation. The chapter concludes with a summary of the major points.

Atmospheres of Titan, Triton and Pluto: Questions

Of primary interest is the relationship of the chemical composition of the atmospheres of Titan, Triton and Pluto to that of the gaseous reservoirs (nebulae) out of which they formed. What is the origin of nitrogen in Titan's atmosphere? More specifically, is it primordial, i.e., derived from a gas containing molecular nitrogen, or was it produced by chemical processing of ammonia? How much carbon monoxide was introduced into Titan and its early atmosphere? Was methane brought into Titan as frozen condensate or entrapped in clathrate? The noble gas abundances in Titan's atmosphere, as yet only weakly constrained, contain some of the information needed to answer these questions. Similar questions can be asked for Triton and Pluto,

although with less assurance that they are relevant to the poorly determined atmospheric compositions.

A related set of questions arises regarding the physical processes operating during the origin and evolution of these atmospheres. Was Titan formed in an optically thick gaseous nebula or a relatively gas-free environment? What was the primary process responsible for conversion of ammonia to nitrogen: photolysis or shock heating? How hot could a massive primordial atmosphere around Titan have been, and how long did it exist? Was a massive primordial atmosphere lost by extreme ultraviolet (EUV) radiation, a T-Tauri wind or shock heating due to impacts? Why does Titan have an atmosphere while Ganymede and Callisto do not? Could most of Titan's atmosphere have been added by impact of volatile-rich comets after accretion? Were Triton's volatiles extruded onto the surface during a heating episode associated with capture by Neptune? What is the relationship between the atmospheres of Titan, Triton and Pluto and those of the terrestrial planets?

Finally, a set of questions regarding the later evolution of Titan's atmosphere to the present state can be framed. What processes control the overall thermal structure of the present Titan atmosphere? Is it stable against perturbations by volcanic extrusion of volatiles or cometary impacts? Is there a surface liquid hydrocarbon layer (i.e., an ethane-methane ocean)? What is the response of the atmosphere to secular changes in such an ocean due to photolysis of methane? Are there qualitative differences between the evolution of Titan's atmosphere in contact with an ocean as opposed to a solid surface with little or no methane? What is the effect of a large chemical reservoir such as an ocean on the abundance of deuterated species in the atmosphere, and on the atmospheric noble gas ratios? Can the total surface and atmosphere volatile abundance be deduced from an ethane ocean model and our understanding of methane photolysis? For Triton, what is the effect of seasonal variation of insolation on the present-day atmosphere? Is the response of the atmosphere to Triton's seasons, as observed by ground- and space-based observatories, diagnostic of the total volatile abundance on the surface? Is the origin of methane on Pluto related to that of methane on Triton and Titan?

In the remainder of the chapter we address these questions in the context of our current knowledge of Titan, Triton and Pluto.

II. CURRENT UNDERSTANDING OF PHYSICAL PROCESSES IN THE ATMOSPHERES AND SURFACES OF TITAN, TRITON AND PLUTO

Titan

Atmospheric Properties. The most detailed description of Titan's atmosphere based upon the Voyager observations is that of Hunten et al. (1984); significant work has occurred subsequent to the writing of that chapter primarily in the area of thermal structure. The information that we cite in this

subsection is derived from the reviews of Hunten et al. (1984), Morrison et al. (1986) and Atreya (1986), unless otherwise noted.

Titan's atmosphere is predominantly molecular nitrogen (N_2), with a surface pressure of 1.5 bars. The air temperature at the surface is 94.5 ± 0.4 K, and drops to 71 K at the tropopause level of ~ 45 km, 0.1 bar (see subsection on thermal structure, below). This is a conservative lower bound because of opacity effects in the 540 cm^{-1} region of the Voyager Infrared Interferometer Spectrometer (IRIS) data used to determine this value. An upper bound derived from the tropopause temperature and the radio occultation profile is ~ 102 K (Lellouch et al. 1987). The Voyager radio-occultation experiment, when combined with the temperature measurements of the IRIS experiment, yields a range of atmospheric mean molecular weights which center on 28 AMU. That nitrogen and not carbon monoxide is the dominant gas was determined by Voyager Ultraviolet Spectrometer (UVS) observations of ions of atomic and molecular nitrogen in the upper atmosphere. Atmospheric constituents of different molecular weight are also allowed, so long as they balance in such a way as to yield a mean value near 28 amu. Neon has not been detected; its abundance in the upper atmosphere can be no more than 1%. The upper limit of 6% for argon in the upper atmosphere may still allow for greater amounts in the lower atmosphere; obviously its maximum abundance can be played off against the abundance of methane in the lower atmosphere to yield an appropriate mean molecular weight:

$$\begin{aligned} 28 &= 16 x_{\text{CH}_4} + 28 x_{\text{N}_2} + 36 x_{\text{Ar}}; \\ x_{\text{CH}_4} + x_{\text{N}_2} + x_{\text{Ar}} &= 1. \end{aligned} \quad (1)$$

Here x_y is the mole fraction of component y . Setting the maximum methane abundance near the surface to be its saturated value (but see below) permits up to 25% argon near the surface.

The methane abundance is uncertain, and yet most telling about the atmospheric thermal structure and possible surface states. The maximum physically permissible methane mixing ratio as a function of temperature is given by the saturation vapor pressure (supersaturation may locally permit higher abundances, but, averaged globally and over time, the abundance is expected to be less than its saturated value). Using the vapor pressure relations from Brown and Ziegler (1979) we find the vapor pressure for pure methane over its liquid at 95 K to be 0.19 bars, or 13% mole fraction at the surface. However, the radio occultation temperature profile in the lowermost atmosphere is consistent with a dry adiabat in pure nitrogen gas. Allowing methane condensation at 95 K would drop the adiabatic temperature gradient by a factor of 2 to its moist value. Moreover, variations in mean molecular weight due to methane condensation affect the derivation of temperature from the density determined by the radio occultation results, in such a way as to produce super-adiabatic temperature gradients near the surface. Detailed analyses of these

constraints have been conducted by Lindal et al. (1983), Eshleman et al. (1983) and Flasar (1983). The argument of Eshleman et al. is that methane condensation cannot occur anywhere that the Voyager-derived temperature gradient exceeds the moist pseudo-adiabat (a moist adiabat in which the condensate is assumed to drop out). They derived an upper limit to methane abundance of 3% at the surface, with condensation occurring above 15 km. Flasar (1983) imposed the constraint that the molecular weight variation due to methane condensation not result in a moist superadiabatic temperature profile, when applied to the T/m data from the radio occultation results. His analysis permits a surface methane abundance of 0.07, or a pressure of 0.11 bars, with condensation beginning at ~ 3 km above the surface. At the tropopause the methane mixing ratio is limited to 1 to 2% by condensation, consistent with the stratospheric value based on IRIS data. These results set constraints on the atmospheric thermal structure and surface models.

The presence of condensable methane in the troposphere forces consideration of cloud formation, which affects incoming solar and outgoing thermal infrared radiation. The issue of the amount of condensate, morphology of cloud and size of the particles is far from being resolved, because no currently available observational technique is very sensitive to the presence of tropospheric condensate. Recent determinations of limits on cloud optical thickness include Pope and Tomasko (1986) and Toon et al. (1988), which serve as constraints on models of cloud thickness morphology and microphysics. We defer a discussion of cloud models to the subsection on thermal structure of Titan's atmosphere.

Other significant constituents include molecular hydrogen (H_2), at $\sim 2 \times 10^{-3}$ mixing ratio, and hydrocarbons including ethane (C_2H_6), propane (C_3H_8) and acetylene (or ethyne; C_2H_2), in order of abundance. These range from 20 down to 2 parts per million (ppm) in the stratosphere, and are highly oversaturated at the tropopause. A suite of other hydrocarbons and nitriles are present in the stratosphere in varying abundances. Finally, carbon monoxide (CO) has been detected from the Earth at a level of 60 to 150 ppm, and carbon dioxide (CO_2) at 1.5 parts per billion (ppb).

This array of chemical components in Titan's atmosphere carries critical information on current atmospheric processes, surface composition, and weakly constrains models for the origin and evolution of the atmosphere. The essential key to applying the compositional constraints to surface models and evolution lies in the inferred photochemical cycles.

Inferred Photochemical Cycles and Atmospheric Escape. In the present atmosphere of Titan, constituents with different combinations of C and H (such as hydrocarbons CH_4 , C_2H_2 , C_2H_6 , C_2H_4 , C_3H_4 , C_3H_8 and C_4H_2), C and N (C_2N_2), C, N and H (HCN, HC_3N) and C and O (CO and CO_2) are present. CO and CO_2 could be either indigenous to Titan, or they could have an extraplanetary source. The C-H, C-N-H compounds and hydrogen are all

produced as a result of chemical processes operative in the present atmosphere. Although the solar ultraviolet-driven chemistry (photochemistry) plays the dominant role, the precipitation of charged particles may be important at high latitudes, especially when Titan is within the magnetosphere of Saturn. The following discussion on the photochemistry of methane illustrates the manner in which the various C-H, C-N-H and H compounds are formed on Titan. The most extensive photochemical scheme is that of Yung et al. (1984 and references therein).

For the most part, the hydrocarbons on Titan are produced in a manner similar to Jupiter, with one major difference: the Jovian H_2 is replaced by N_2 . This results in the production of C-N-H molecules. The CH_4 photochemical scheme, shown in Fig. 1, however, applies to Titan insofar as the production of major hydrocarbon species is concerned. The photodissociation of CH_4 occurs following the absorption of solar photons with wavelengths between 1000 and 1600 Å. For all practical purposes, however, Lyman-alpha photons at 1216 Å account for the bulk (90%) of CH_4 photolysis rate due to the large solar flux at that wavelength. Since the mole fraction of CH_4 is 2% at the tropopause of Titan, the optical depth in CH_4 at Lyman-alpha would be approximately 7×10^6 , implying that most of the photolysis would occur several hundred kilometers above the tropopause. The direct photolysis of CH_4 yields a diurnally averaged column-integrated rate of $1.2 \times 10^9 \text{ cm}^{-2} \text{ s}^{-1}$. The catalytic photolysis (see reaction R18 later), however, could result in a

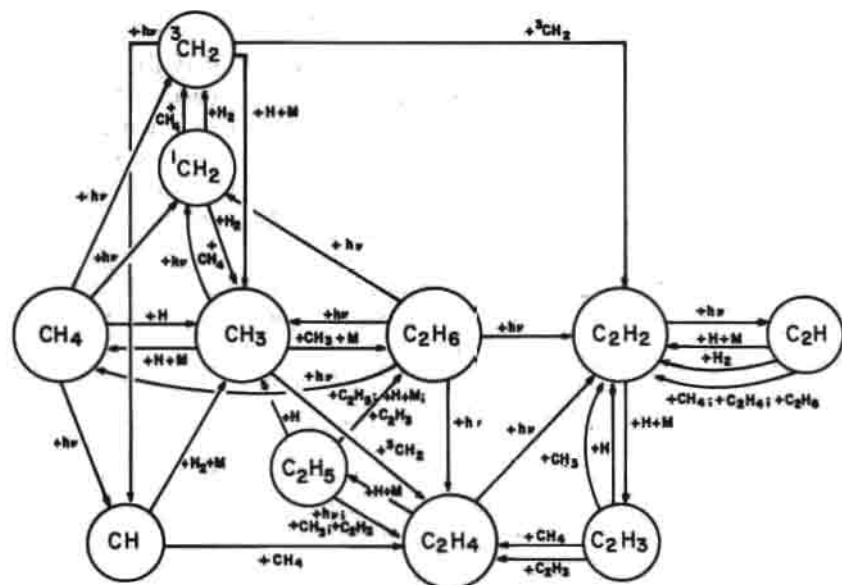
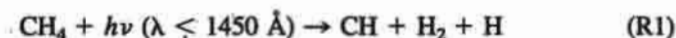
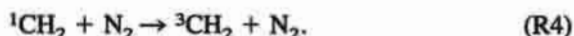


Fig. 1. Photochemistry of methane on the major planets and Titan (figure from Atreya and Romani 1985).

rate 3 times greater (Yung et al. 1984). The photodissociation of CH_4 yields $^1\text{CH}_2$, $^3\text{CH}_2$, $^3\text{CH}_2$ and CH^a (note the conspicuous absence of CH_3 , as it is kinetically disallowed), i.e.



followed by

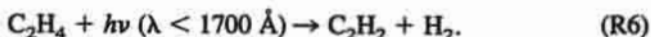


Unlike Jupiter, $^1\text{CH}_2$ is rapidly quenched by N_2 to $^3\text{CH}_2$ (reaction R4).

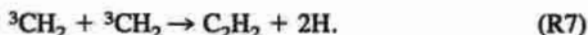
CH radicals react with CH_4 yielding C_2H_4 . The latter is photolyzed below 1700 \AA to yield C_2H_2 , i.e.



followed by



The most likely fate of the $^3\text{CH}_2$ is the conversion to C_2H_2 by the self-reaction



Further reaction of $^3\text{CH}_2$ with C_2H_2 can result in the formation of C_3H_4 (methylacetylene or allene):



or

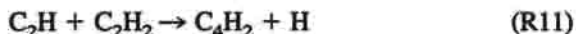


Allene has not yet been detected on Titan.

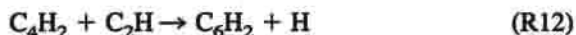
The acetylene produced in the upper atmosphere is transported to the lower atmosphere. It is photolyzed in the stratosphere (at least partially catalytically), and condenses at the tropopause temperature (Yung et al. 1984). The photolysis of C_2H_2 leads to the formation of diacetylene, C_4H_2 , and

^aThe reader is referred to Yung et al. (1984) for the best currently available data on rate constants, many of which are simply estimates.

possibly higher order polyacetylenes ($C_{2n}H_2$, where $n = 3, 4, 5 \dots$) in the following manner (Allen et al. 1980; Romani and Atreya 1986, 1988; Pollack et al. 1987a; Glicker and Okabe 1987):



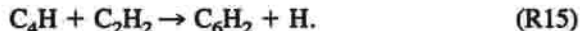
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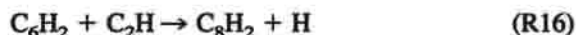
or



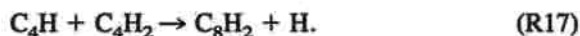
followed by



C_8H_2 may be formed on reaction of C_6H_2 with C_2H or on reaction of C_4H with C_4H_2 , i.e.



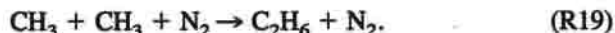
or



At the appropriate proportion of CH_4 , the reaction of C_2H with CH_4 is favored, and it leads up to the formation of C_2H_6 , i.e.



followed by



(It has been suggested [W.R. Thompson, personal communication, 1987] that reactions of CN with the hydrocarbons may be even faster than those of C_2H , resulting in the formation of complex nitriles and other com-

pounds. The abundance of CN and the rate constants and kinetics of the CN reactions at the appropriate atmospheric conditions are poorly known, however.)

As with C_2H_2 , the loss of C_2H_6 is by downward transport, followed by photolysis and condensation (Yung et al. 1984). In the subsequent chemistry, propane, butane and other heavier hydrocarbons may be formed, as follows:



C_2H_5 , C_3H_5 , C_3H_6 , C_3H_7 etc. are formed in the hydrogen-addition reactions of, respectively, C_2H_4 , C_3H_4 , C_3H_5 , C_3H_6 , etc.

Some recycling of CH_4 occurs on reaction of CH_3 with atomic hydrogen, and partially by surface chemistry following the precipitation of the condensible hydrocarbons. The rate of conversion of methane to higher hydrocarbons and the resulting accumulated thickness of material at the surface from Yung et al. (1984) is given in Table I. The values of thickness assume, for simplicity, that the present rate of photolysis was maintained over the age of the

TABLE I
Downward Flux of Products of Methane
and Carbon Monoxide Photolysis
and Accumulated Depth Over the Age
of the Solar System

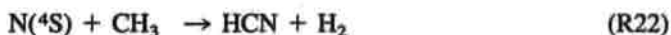
Species	Flux ^a	Depth ^b
C_2H_6	5.8×10^9	0.6
C_2H_2	1.2×10^9	0.1
C_3H_8	1.4×10^8	0.02
CH_3C_2H	5.7×10^7	0.006
HCN	2.0×10^8	0.02
HC_3N	1.7×10^7	0.002
C_2N_2	6.0×10^6	0.001
CO_2	3×10^5	2×10^{-5}

^aFlux in $cm^{-2}s^{-1}$ normalized to the surface, from Yung et al. (1984). Discrepancies between their model stratospheric abundance and Voyager IRIS results lead to a factor of 5 uncertainty in flux for propane, a factor of 2 for acetylene and hydrogen cyanide, and less than a factor of 2 for ethane. The model does not include production of aerosols. Loss of methane by photochemistry is $1.5 \times 10^{10} cm^{-2} s^{-1}$ (Yung et al. 1984).

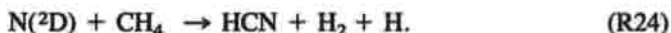
^bDepth is given in km for densities of pure substances from Raulin (1985).

solar system. It should also be remembered that they are based upon a model which does not determine the abundance of hydrocarbons converted to the aerosol particles observed in the upper stratosphere of Titan. The results of Pope and Tomasko (1986) indicate that one-fifth of the photolyzed methane is converted to aerosols in the stratosphere (if their mass production rates refer to the surface which is not explicitly stated). A crucial conclusion of our understanding of photochemistry on Titan is that in the absence of resupply of methane, photolysis alone would irreversibly convert all of Titan's methane to heavier hydrocarbons in a time scale ~ 10 Myr.

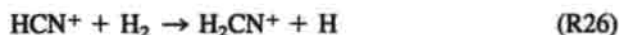
The CH_4 photochemistry just discussed is modified due to the presence of large quantities of N_2 on Titan. Being inert, N_2 by itself does not participate directly in the chemistry. However, N_2 dissociates into $\text{N}(^2\text{D})$ and $\text{N}(^4\text{S})$ by the action of solar ultraviolet radiation below 1000 \AA , magnetospheric electrons and galactic cosmic rays. The globally averaged production rate of $\text{N}(^2\text{D})$ and (^4S) , $1.8 \times 10^9 \text{ cm}^{-2}\text{s}^{-1}$ (Strobel and Shemansky 1982), by the magnetospheric electrons is by far the largest. It is, respectively, a factor of 3 and 10 greater than that due to the ultraviolet radiation and the cosmic rays. The reactions of $\text{N}(^2\text{D})$ and $\text{N}(^4\text{S})$ with CH_4 , $^3\text{CH}_2$ and CH_3 lead to the production of HCN as follows:



and



The photolysis of HCN gives CN, which produces C_2N_2 in a self reaction, cyanoacetylene (HC_3N) on reaction with C_2H_2 and ethyl cyanide ($\text{C}_2\text{H}_3\text{CN}$) on reaction with C_2H_4 . Formation of polymers is also likely as a result of reactions between CN and other hydrocarbons. The complete chemical scheme involving the above-mentioned reactions in an N_2 - CH_4 atmosphere is depicted in Fig. 2. It is important to recognize that a relatively significant source of HCN lies in the ionosphere of Titan (Atreya 1986). The magnetospheric electrons, as well as the solar EUV photons produce N_2^+ and N^+ ions, following their action on the atmospheric N_2 . N_2^+ charge exchanges readily with N, producing N^+ ions. The reaction between N^+ and the upper atmospheric CH_4 gives rise to HCN^+ ions, among other products. HCN^+ reacts with H_2 to give H_2CN^+ . The latter is removed by dissociative recombination, yielding HCN in the following manner (Atreya 1986):



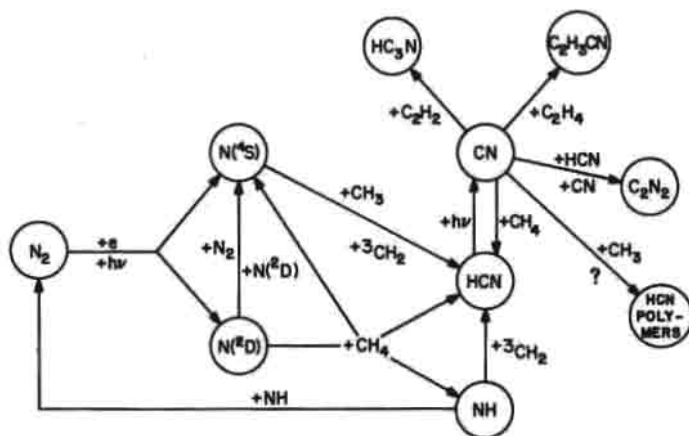


Fig. 2. Photo- and electro-chemistry of methane in the presence of nitrogen (figure from Arey 1986).

The above-mentioned ionospheric scheme provides a significant source of HCN at ionospheric altitudes. It is also consistent with the results of a Voyager plasma experiment which showed the presence of mass 28 ions in Titan's magnetic tail (Hartle et al. 1982). These ions are presumably N_2^+ or H_2CN^+ of ionospheric origin picked up by Saturn's rotating magnetosphere.

The photolysis of methane produces large quantities of H and H_2 . In fact, the limiting flux of H_2 at the homopause of Titan $(3.8 \pm 2) \times 10^{10} \text{ cm}^{-2} \text{ s}^{-1}$ is comparable to the photodecomposition rate of CH_4 (direct as well as catalytic) discussed earlier in this chapter. The limiting flux, ϕ_l is given by

$$\phi_l = b f_i / H_a (1 - m/m_a) \quad (2)$$

where f_i is the constituent mixing ratio, H_a is the atmospheric scale height, b_l is the binary collision parameter, m is the mass of the escaping atom, and m_a is the mass of a nitrogen molecule. b_l can be further expressed in terms of the molecular diffusion coefficient (D_l) and the atmospheric number density n as follows:

$$b_l = n D_l \quad (3)$$

Also $b_l = AT^a$ where $A = 2.8$ and $a = 0.740$ for an H_2 - N_2 system and $A = 4.87$ and $a = 0.698$ for an H - N_2 system (cgs units).

At the critical level of Titan, the thermal velocities of H and H_2 are, respectively, 1.8 and 1.3 km s^{-1} . The critical level signifies the height at which the mean free path of the escaping constituent becomes equal to the scale height—thus collisions become rare. This level for Titan is at a radius of

4175 km where the atmospheric density is $9.3 \times 10^6 \text{ cm}^{-3}$, and the escape velocity is 1.7 km s^{-1} . Thus, escape of both H and H_2 from the exosphere of Titan is assured. The presence of H and H_2 in the present atmosphere of Titan implies continuous supply of their source CH_4 .

The primary loss process for nitrogen is formation of atomic nitrogen with a kinetic energy of 0.33 eV or larger, sufficient to escape Titan. Strobel and Shemansky (1982) calculated that 40% of the N atoms produced from molecular nitrogen escape. From the disk-averaged intensity of the molecular nitrogen Rydberg bands, they concluded that 3×10^{26} nitrogen atoms per second are supplied to the magnetosphere, equivalent to loss of 10% of the present abundance of atmospheric nitrogen over the age of the solar system (Hunten et al. 1984).

Finally, the atmospheric CO and CO_2 can be explained if there is an extraplanetary source of an oxygen-bearing constituent. An ideal candidate is water which quickly dissociates to yield OH. The latter in turn reacts with CH_4 photolysis products CH_2 , CH_3 and C_2H_2 to eventually produce CO, and CO_2 (Samuelson et al. 1983). The CO_2 condenses out and falls to the surface, with an accumulated yield of a cm thickness over the age of the solar system, assuming the present CO abundance and water influx rate. The rings of Saturn and the carbonaceous chondritic meteorites are well suited for supplying water to the atmosphere of Titan. Another possibility for the presence of CO is that it was captured in a clathrate-hydrate directly from the solar nebula. W. R. Thompson and C. Sagan (personal communication, 1987) surmise that CO may have been produced by shock impact of comets on a surface containing CH_4 and H_2O . Such a mechanism involves a number of uncertainties including the physical state of the surface and size spectrum of impactors which have yet to be quantified. The implications of various evolutionary models for the present abundances of CO and CO_2 are discussed in Sec IV.

Photochemistry and charged-particle chemistry of methane most probably are responsible for the production of the orange haze which uniformly covers the disk of Titan. A suite of laboratory studies have established that a variety of materials, ranging from C_2 hydrocarbons to complex polymers, are produced when methane and nitrogen are subjected to irradiation or an electric discharge (Bar-Nun and Podolak 1979; see also other work referenced in Hunten et al. 1984). More recent work has established that some of these products approximately match the optical constants of the Titan aerosols over a wide range of frequencies (Khare et al. 1984, and references therein). Laboratory experiments do not provide the yield of aerosols relative to simpler hydrocarbons because they cannot simulate condensation in the tropopause region. Photochemical models incorporate condensation but cannot calculate the yield of complex polymeric aerosols (Yung et al. 1984, and references therein).

Observational studies of the aerosols, including the use of Voyager images through 1984, are reviewed in Hunten et al. (1984). Of interest to us here

are both the effect of hazes on the thermal structure and the fraction of methane converted to haze vs simpler hydrocarbons and nitriles. The former issue is discussed in the thermal structure subsection. The latter has no firm answer; the most recent estimate of aerosol mass production rate by Pope and Tomasko (1986) is $\sim 8 \times 10^{-14} \text{ g cm}^{-2} \text{ s}^{-1}$, or one-fifth the mass-loss rate of methane. This corresponds to a 0.1 km thick layer of compacted aerosol on the surface if the production rate is integrated over the age of the solar system. Although the photochemical models are constrained to reproduce the column abundances of hydrocarbons in the stratosphere observed by the Voyager IRIS experiment, sufficient uncertainty exists in our understanding of both the aerosols and simpler hydrocarbons that one cannot definitely rule out a model in which most of the products of methane photolysis reaching the surface are complex aerosols. The nominal models would predict, however, that most of the material is in the form of ethane, acetylene and propane. The composition of the material raining down is the primary determinant of surface properties.

Thermal Balance of the Atmosphere. Titan absorbs about 73% of the solar energy incident at the top of its atmosphere (Neff et al. 1985). Thus, it radiates to space at an effective temperature of about 83 K. The temperature profile of Titan's atmosphere is quite different from isothermal because of absorbing haze particles in its stratosphere, and tropospheric gases which absorb in the infrared. Figure 3 illustrates the temperature profile, from Lindal et al. (1983). Hunten (1978) demonstrated the conceptual simplicity of Titan's thermal structure by constructing a temperature profile of the troposphere and stratosphere using sound physical arguments. His temperature profile, truncated at the 1.5 bar level, bears a remarkable resemblance to that derived two years later from the Voyager flyby.

According to Fig. 3, the temperature at Titan's surface is elevated by about 10° above the satellite's effective temperature, due to a modest greenhouse effect (Samuelson 1983). The temperature lapse rate, as discussed above, is close to a dry adiabat in the bottom 3.5 km of the atmosphere. At higher altitudes, a shallower lapse rate occurs, with the temperature achieving a minimum value of about 70 K near an altitude of 40 km. This temperature minimum limits the mixing ratio of methane in the stratosphere to about 2%. Temperatures steadily increase with increasing altitude above the cold trap, attaining a value of 170 K above an altitude of 150 km. This highly elevated asymptotic temperature is believed to be the result of the efficient absorption of sunlight and the inefficient re-emission of thermal energy by haze particles, submicron in size, which populate the lower several hundred kilometers of the stratosphere (Danielson et al. 1973).

Figure 3 also plots the methane mixing ratio along the temperature profile, at which condensation of methane in equilibrium with nitrogen would occur. Clearly, cloud formation is extensive, in the absence of gross supersaturation effects, for methane mixing ratios in excess of 2%. The substantial

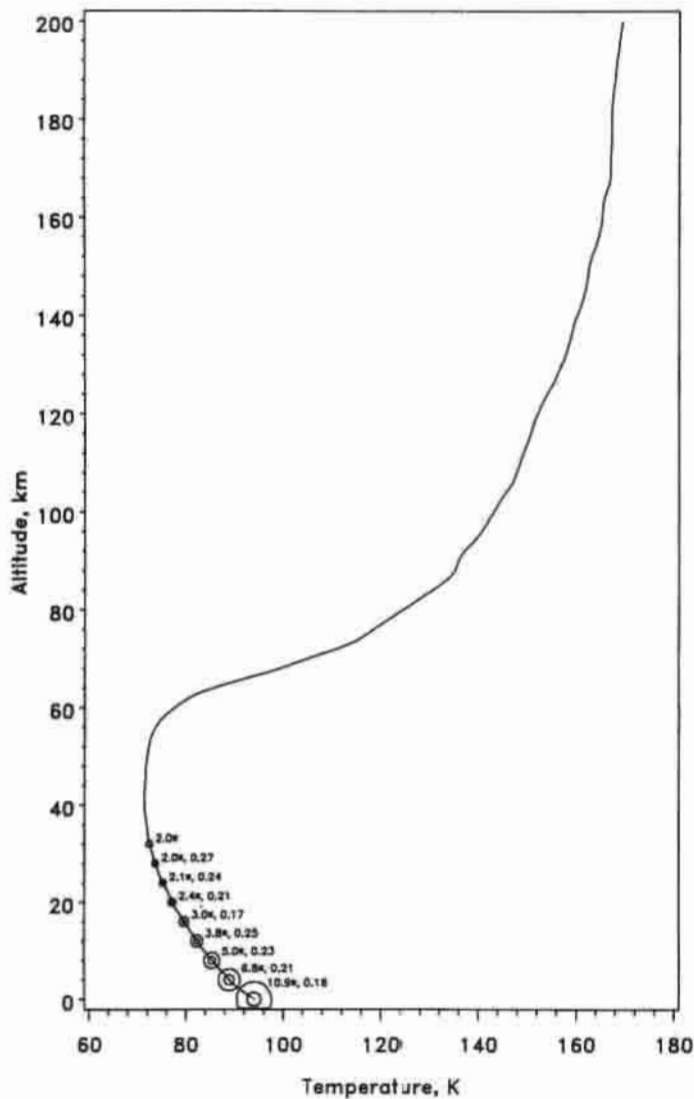


Fig. 3. Saturation equilibrium gas-phase percentages of CH_4 ($X_{M,s}$) and N_2 mole fractions in the condensate (X_N) are given along the altitude-temperature curve for Titan. Outer circle represents uncertainty in $X_{M,s}$ based on thermodynamic data and is assumed proportional to $X_{M,s}$; inner circle represents uncertainty in X_N and is assumed proportional to X_N . Open inner circle represents liquid condensate; filled represents solid. First condensate (base of cloud deck) occurs at the altitude where $X_{M,s}$ equals the surface mole fraction of gaseous methane. Temperature profile is from Lindal et al. (1983); thermodynamic values were calculated by W. R. Thompson who supplied this figure.

solubility of nitrogen in methane implies that cloud particles contain between 15 and 27% nitrogen, and the altitude of condensation is lower than would be obtained assuming pure methane condensate. The results shown here are those of W. R. Thompson (personal communication), who kindly supplied this figure. Kouvaris and Flasar (1985) report similar results. The uncertainties in the figure reflect our incomplete understanding of the thermodynamics of this system at low temperature, as discussed in Thompson (1985).

The surface temperature is determined by a balance between the amount of solar visible and atmospheric thermal radiation absorbed and the amount of thermal radiation emitted, as first described by Samuelson (1983). What follows is a detailed description of the thermal model results of McKay et al. (1988a) based upon very recent determinations of collision-induced gas absorption coefficients and constraints of the Voyager IRIS data. Figure 4 illustrates the variation of the net solar flux as a function of altitude in Titan's atmosphere (McKay et al. 1988a). It has been normalized to have a value at the top of Titan's atmosphere equal to the fraction of the incident sunlight absorbed by Titan. The calculations were performed assuming a haze model constrained to match the satellite's observed geometric albedo spectrum and to be in a steady state between production and sedimentation. For this calculation, the scattering effects of a methane cloud layer were neglected. The amount of sunlight reaching the ground is on the order of 10% under these

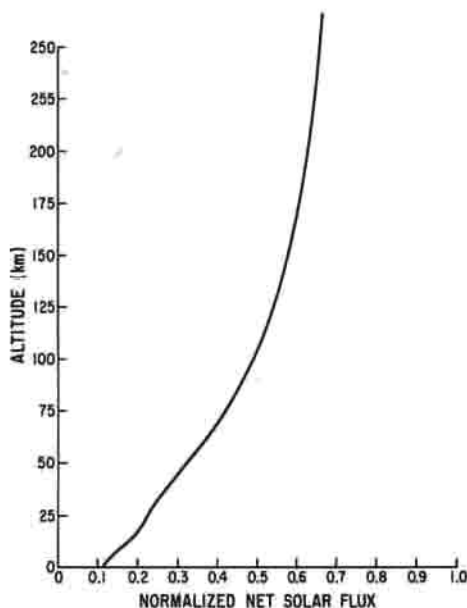


Fig. 4. Net solar flux vs altitude on Titan, normalized as described in text (figure from McKay et al. 1988a).

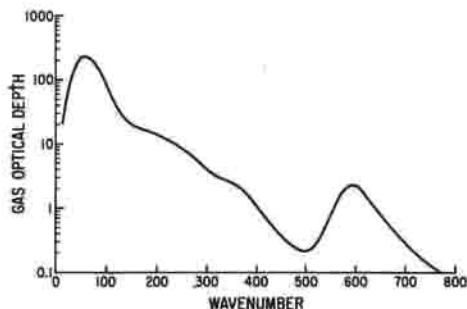


Fig. 5. Infrared optical depth at Titan's surface vs wavelength, due to collisional gas opacity, as calculated in McKay et al. (1988a).

assumptions. Absorption of sunlight by the stratospheric haze in the near ultraviolet and blue, and absorption by gaseous methane in the near infrared act to limit severely the amount of sunlight reaching the surface.

Figure 5 plots the pressure-induced gas opacity of Titan's atmosphere as a function of wavenumber in the thermal infrared (McKay et al. 1988a). At wavenumbers shortward of about 150 cm^{-1} , the pressure-induced transitions of nitrogen make the atmosphere very opaque; the pressure-induced transitions of methane (in collisions with nitrogen) dominate the region from 150 to 500 cm^{-1} ; those of molecular hydrogen are a key between about 500 and 650 cm^{-1} , and the permitted transitions of ethane, acetylene and HCN cause localized elevated opacities between about 650 and 900 cm^{-1} . Thus, the surface is warmed by tropospheric radiation at wavenumbers shortward of 650 cm^{-1} and stratospheric radiation from photochemically produced gases at higher wavenumbers. The surface also receives thermal radiation from the stratospheric haze particles near the 500 cm^{-1} window.

The amount of greenhouse warming of the surface is limited by the window near 500 cm^{-1} . Within this window, the surface can radiate fairly freely to space, while receiving only a small compensation from atmospheric radiation. The pressure-induced transitions of nitrogen, methane and hydrogen play the key role in generating the small but important amount of warming which does occur. Radiation by gases and particles in the hot stratosphere also makes an important contribution to the greenhouse warming.

By way of contrast, a methane cloud can at best have a neutral effect on the greenhouse warming and at worst a cooling effect (McKay et al. 1988a). This is because the clouds reduce the amount of sunlight reaching the surface, while their effect in the infrared is limited since they mostly scatter rather than absorb thermal radiation near the 500 cm^{-1} window. This conclusion, reached by McKay et al. (1988a), rests upon significant improvements in the absorption coefficients of pressure-induced gas opacity, calculations of both solar and thermal fluxes, and application of available constraints to define the

values of free parameters. It differs from earlier modeling results of Thompson and Sagan (1984) and Samuelson (1985). It should be noted that McKay et al. (1988a) find a somewhat better fit to the IRIS data if some cloud infrared opacity is added. The constraint that at least a few percent of the incident sunlight reach the surface demands that the clouds be either (1) limited in vertical extent due to a small methane mixing ratio, (2) confined to very large particle sizes or (3) broken in areal coverage (Samuelson 1985). The second possibility is intriguing, since for methane mixing ratios greater than a few percent, the large amount of condensate and lack of condensation nuclei tend to favor formation of raindrops rather than smaller, suspended cloud particles (Toon et al. 1988).

Our understanding of the present state of Titan's thermal structure is crucial to the construction of believable models of the evolution of Titan's atmosphere in response to the photochemical cycle (Sec. III). We can summarize our current understanding of how the observed temperature profile is established as follows:

1. Most sunlight is absorbed before reaching the ground, the blue and ultraviolet by stratospheric haze, the near infrared by methane. Absorption of sunlight by the haze establishes the warm stratosphere.
2. The dominant thermal infrared opacity source is collision-induced absorption, largely by nitrogen-methane collisions. The balance between the 5 to 15% sunlight reaching the ground and the thermal infrared repeatedly absorbed and re-emitted on its way up establishes to first order the tropospheric temperature profile.
3. Clouds play a small, perhaps negligible, role in affecting the heat balance at the surface.

Surface Models. In this section, we show that the model of Titan's surface most consistent with Voyager data is a liquid hydrocarbon ocean with substantial quantities of methane. Difficulties with other surface models are discussed.

The surface of Titan cannot be probed directly except by microwave radio emission and radar. Prior to the Voyager encounter, lack of information on the atmospheric composition hindered models of the surface. Lewis (1971) proposed a surface composed of methane clathrate hydrate and ice, based upon the equilibrium vapor pressure of methane over clathrate at 127 K, the reported spectroscopic abundance of methane on Titan, and reported radio brightness temperatures. The measured surface temperature of 95 K corresponds to a maximum methane pressure over clathrate hydrate of $\sim 2 \times 10^{-6}$ bars (Lunine and Stevenson 1985a, and references therein), four orders of magnitude less than the minimum methane surface pressure deduced from the lower-stratospheric mixing ratio of methane of 2%. The predicted maximum

vapor pressure of nitrogen over the clathrate is three orders of magnitude lower than Titan's surface pressure. If clathrate is present at the surface of Titan, it is not in thermodynamic equilibrium with the atmosphere; rather, it would be a surface layer of limited thickness determined by the inefficient diffusion of gas molecules through water ice. Good thermodynamic contact requires either that fissures and cracks in the ice penetrate to the submicron level, which is unlikely, or that a regolith be present which is stirred by impacts. Impact causes formation of a regolith as deep as a kilometer (Hartmann 1973), which consists of a wide range of particle sizes (Kawakami et al. 1983); only the upper 100 meters is likely to be stirred sufficiently to be in occasional contact with the gas. A 100-m thick layer of clathrate hydrate can accommodate an equivalent thickness of 15 m of methane and nitrogen, 10 to 100 times less than the total hydrocarbon rainout estimated above, and equivalent to at most 0.1 of the mass of atmospheric nitrogen, or 1 to 10 times the mass of atmospheric methane. (The Voyager determination of Titan's density [Hunten et al. 1984] confirmed that water ice comprises half the mass of the satellite, and so must certainly be a major component of at least the near-surface layers of the satellite.)

A more satisfactory way to infer the nature of the surface is to require consistency with the Voyager determinations of atmospheric composition and thermal structure, and demand that the photolytic destruction of methane be balanced over geologic time by a supply of methane. This approach was considered by Flasar (1983), and in detail by Lunine et al. (1983) and Lunine (1985a). The assertions which go into the models are as follows:

1. Methane is present in the atmosphere but at mixing ratios below saturation near the surface. The near-surface temperature gradient is consistent with a nitrogen dry adiabat.

2. Methane is photolyzed in the stratosphere to form higher hydrocarbons, with minimal recycling. The maximum allowed methane in the atmosphere (7% at the surface) would be depleted in 40 Myr in the absence of resupply. The *primary* products of methane photolysis are ethane, acetylene and propane. Ethane and propane are liquid, and acetylene solid, at Titan's surface temperature of 95 K.

The surface state consistent with these constraints is a liquid hydrocarbon layer containing dissolved methane: a so-called ethane-methane ocean. The properties of such a layer which are consistent with the constraints can be summarized as follows:

- a. Gaseous methane is in vapor equilibrium with the ocean. Because the ocean is only partially composed of methane, the amount of methane in the atmosphere is below the saturated value for a pure liquid methane surface. Since other hydrocarbons contained in the ocean have vapor pressures orders of magnitude lower than methane at 95 K, the amount of condensable vapor in the lowermost troposphere is too small to alter the temperature gradient from its dry adiabatic value by a measurable amount. If the ocean were pure meth-

ane, the near-surface temperature gradient would be significantly smaller than the dry adiabatic value.

b. The mole fraction of methane in the ocean can be estimated if the atmospheric abundance is known. This relationship is illustrated in Fig. 6a. (All figures assume ethane as the liquid heavy hydrocarbon component. The thermodynamic properties of propane are sufficiently similar that the two can be considered identical.) For a methane mole fraction in the atmosphere of 7%, the fraction of methane in the ocean is 60%. For 2% methane in the troposphere, the ocean fraction is 0.15.

c. The depth of the ocean can be calculated from the depth of the ethane layer deposited over the age of the solar system, and augmenting this with enough methane to produce the ocean composition calculated in paragraph b.

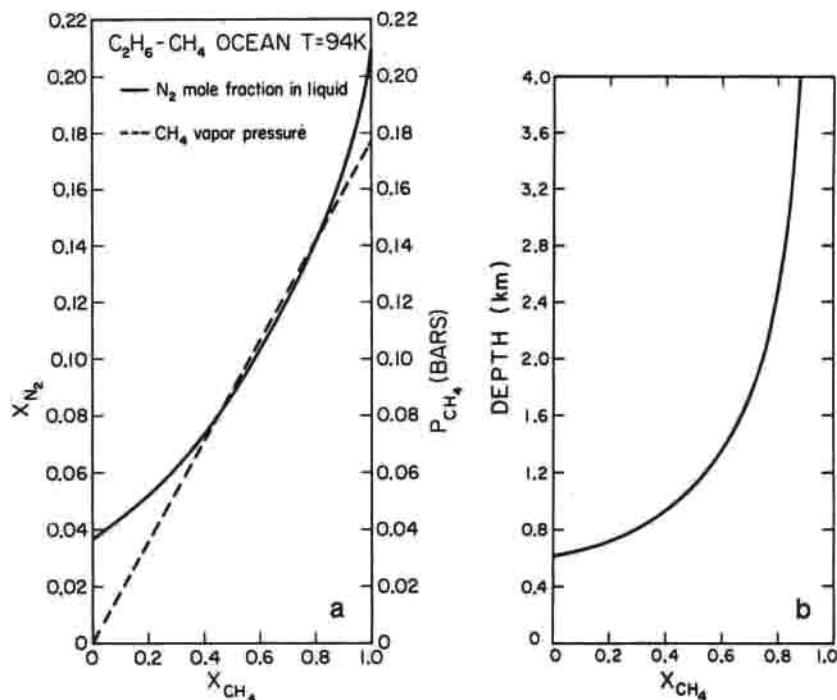


Fig. 6. (a) Partial pressure of methane (bars) at base of atmosphere and mole fraction of molecular nitrogen dissolved in methane-ethane liquid as a function of liquid composition, at 94 K. The abscissa is mole fraction of methane relative to total methane-plus-ethane component. To convert right-hand scale to gaseous methane mole fraction divide by 1.5 bars. The mole fraction of molecular nitrogen dissolved in the liquid is overestimated by as much as 30% for the methane-rich end of the figure, due to the assumption of an ideal solution (see, e.g., Thompson 1985). (b) Ocean depth in km as a function of methane mole fraction in ocean, assuming remainder of ocean is ethane produced photochemically over the age of the solar system at the rate given in Table I (figure based on Lunine 1985a).

The ocean depth is given as a function of composition in Fig. 6b. The mass of methane available in the ocean reservoir for photolysis is then determined immediately. For the 60% methane ocean, enough methane is available in the ocean to supply photolysis for 2.5 Gyr beyond the present day; for the 15% case, the ocean methane will last 0.4 Gyr.

Several additional details of the surface state emerge from this model and the constraints given above:

d. Nitrogen is soluble in both methane and ethane. The mole fraction of the ocean which is composed of nitrogen is given in Fig. 6a, as a function of oceanic methane mole fraction for an atmospheric nitrogen pressure of 1.5 bars. The dissolved amount is comparable to the atmospheric mass of nitrogen.

e. Other hydrocarbons produced by methane photolysis either dissolve in the ocean or sink to the bottom, depending upon their solubility in liquid ethane-methane. Acetylene is predicted to sink to the base as a sediment of roughly 100-m thickness, based on Table I. All precipitated hydrocarbons and aerosols are predicted to sink, unless they exhibit substantial porosity. Carbon dioxide is predicted to be soluble; as much as 10^7 times its atmospheric abundance may be dissolved (Raulin 1985). The solubility of noble gases in liquid hydrocarbons will be discussed in the context of origin models, in Sec. IV.

Lunine and Stevenson (1985b) and Lunine (1985b) consider further implications of the presence of an ocean on the present-day surface and atmosphere, including the possibility of erosion of crater and tectonic water ice topography by an ocean. At least 100 m of water ice vertical topography may be eroded by the hydrocarbon liquid. Thompson (1985) examined the thermodynamics of nitrogen-hydrocarbon systems in more detail, and confirmed the conclusions of the earlier work. The methane-nitrogen cloud structure of the middle and upper troposphere is unchanged by the ethane ocean arguments, because the very small amount of ethane-methane mist produced in the lower troposphere hardly affects the altitude profile of methane mixing ratio. Such a mist, however, if ubiquitous in the lower few km, must be constrained in morphology and particle size by the insolation arguments reviewed in the subsection on thermal structure.

Few tests of the ethane-methane ocean hypothesis are available. Muhleman et al. (1984) measured the brightness temperature of Titan at cm wavelengths to determine a "disk emissivity" of 0.82 ± 0.05 . When compared with microwave emissivities of smooth ice (0.87) and liquid ethane (0.91) given in their abstract, the result argues against an ethane ocean at the two standard deviation level. Efforts to detect a radar return from Titan at Goldstone are proceeding. An additional constraint comes from Sagan and Dermott (1982) who argue that the present nonzero free eccentricity of Titan would be destroyed by tidal friction in a surface liquid layer less than a few hundred meters deep. It is not clear how to apply such tidal friction calculations to a km-deep ethane ocean on a satellite for which the amplitude of

topography due to cratering is likely to be of order a km (by analogy with Ganymede and Callisto).

Stevenson and Potter (1986) have used the symmetry of northern and southern hemisphere brightness temperatures from Voyager IRIS data at 540 cm^{-1} to argue for dewpoint condensation of methane and molecular nitrogen at polar latitudes. If their model is correct, it requires the methane mole fraction in the lower troposphere to be between 4 and 8%. This would better constrain the composition of a global hydrocarbon ocean, and predict substantial variation in surface composition with latitude. The validity of the model is sensitive to uncertainties in the opacity in the 540 cm^{-1} region, which could be higher than assumed (McKay et al. 1988a) and so imply that the symmetry in brightness temperature is atmospheric and not surface in origin.

Alternative models in which the surface is covered largely by solid aerosol or polyacetylenes require that the following assumptions be made:

1. The photochemical models are wrong; most of the products of methane photolysis are acetylene or the complex polymers believed to comprise the aerosols. The alternative, that a significant flux of high-energy particles reaches the surface to convert *most* of the liquid hydrocarbons to solid polymers, is not plausible based on the results of Sagan and Thompson (1984).

2. The absence of liquid methane on the surface implies that methane is resupplied by cometary impact or outgassing over the age of the solar system.

The latter constraint requires some fine tuning of the resupply source, since the atmospheric methane is within a factor of 1.5 to 5 of saturation near the surface. Either we are looking at Titan at a special time, when the surface methane has dried up and the atmospheric methane is within 10 Myr of being depleted, or the resupply mechanism is such that it just avoids saturating the atmosphere with methane.

Figure 7 illustrates the interpretations of Voyager data and our understanding of present-day processes on Titan which lead either to the hydrocarbon ocean model or to the solid polymeric surface case. A clean water ice or water-ammonia hydrate surface requires very recent global resurfacing and is not considered here. The two extreme models have rather different implications for the steady-state evolution of Titan's atmosphere, as we discuss in Sec. III. Figure 8 presents in outline form our current understanding of Titan's atmosphere and surface.

Inferred Volatile Inventory of Titan's Surface. From the hydrocarbon ocean model and an assumed rate of photolysis constant over the age of the solar system, it is possible to estimate the mass of volatiles present on the surface and in the atmosphere of Titan. In Table II, we display the results for a present-day ocean containing 25% methane. From Fig. 6, the same quantities can be estimated for other methane mole fractions in the present-day ocean. Two results are of particular importance: (1) the mass of nitrogen in the ocean is comparable to that in the atmosphere, while the amount of methane in the

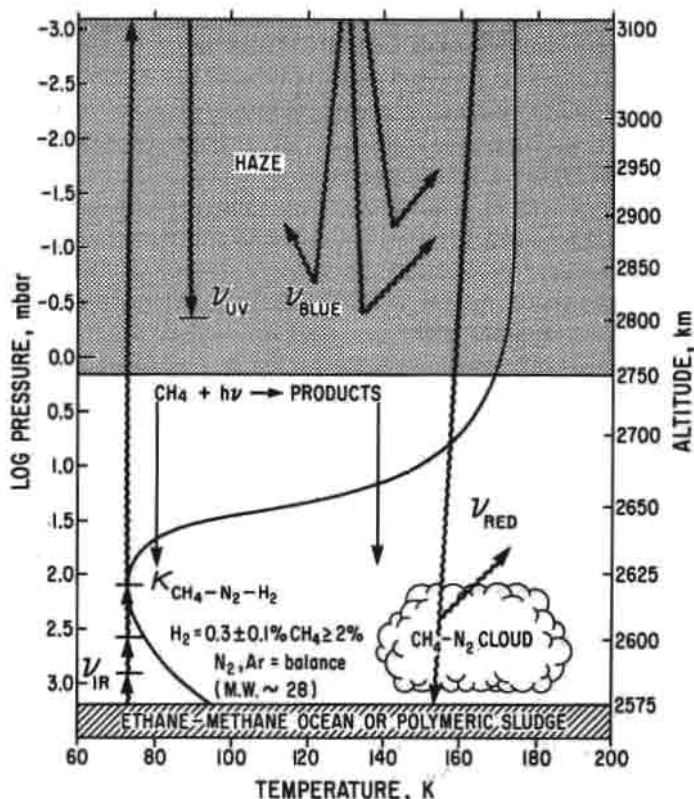


Fig. 8. The atmosphere and surface of Titan based upon Voyager data and inferred physical processes, as discussed in text. Base figure adapted from Thompson and Sagan (1984), with permission. Altitude scale is set for a surface radius of 2575 km.

TABLE II
Approximate Inventory of Volatiles on Titan's Surface*

	CH_4 (g)	N_2 (g)
Atmosphere	3×10^{20}	9×10^{21}
Dissolved in ocean	1×10^{22}	3×10^{21}
In ocean and sediment as higher hydrocarbons	6×10^{22}	
Total ocean + atmosphere	7×10^{22}	1×10^{22}

*Adapted from Lunine (1985b) with modifications from Lunine and Stevenson (1987), for an ocean model with 25% methane.

variations of the visible and infrared flux (Lebofsky et al. 1982; Morrison et al. 1982). For a cosine distribution of infrared radiation around the satellite, i.e., local radiative equilibrium (asteroid model), the radius is 1750 ± 250 km.; if thermalized sunlight is instead reradiated uniformly over the surface (thick atmosphere model) the radius is 2500 km. The smaller radius yields a density as high as 6 g cm^{-3} ; the larger radius gives 2 g cm^{-3} . Unless Alden's mass is a gross overestimate, Triton is as large as Titan. The corresponding albedos in the two cases are 0.4 and 0.2, respectively. The brightness variation of Triton in the V filter as a function of orbital phase seen by Franz (1981) in 1977 has been challenged recently: Lark et al. (1987) found no variation at 8900 \AA in 1987. Possible explanations include temporal changes on Triton, effects due to choice of filter, and spurious results caused by variations in Neptune's brightness (Franz used the planet as his standard).

The mass of the Pluto-Charon double planet system is well established, being $1.48 \times 10^{25} \text{ g}$ (Harrington and Christy 1981). The ratio of masses and the radii are less well constrained. Although observations prior to the mutual eclipses of Pluto and Charon suggested densities < 1 , the eclipse results establish that the mean density of the system is 1.99 g cm^{-3} , with Pluto's radius being 1123 km, 1.9 times that of Charon (Tholen and Buie 1987). Corresponding blue geometric albedos are 0.51 and 0.37, respectively.

The albedo variation on Pluto may be complex. Marcialis (1988) analyzed photoelectric lightcurves taken over 30 yr and fitted the data with two spots of low albedo, colocated in latitude but on opposite sides of the planet. He also proposed high-albedo polar caps to explain the secular dimming of Pluto with time since 1930. An alternative explanation for the secular dimming is progressive sublimation of bright frosts (Stern et al. 1988).

Additional support for the presence of polar caps comes from an analysis by Sykes et al. (1987) of IRAS pointed observations. Constraining the overall albedos and radii of Pluto and Charon from the eclipse data reported by Tholen et al. (1987), various surface models were tested for consistency with the observed fluxes at 60 and $100 \mu\text{m}$. The albedo of Charon was assumed uniform. The best fit involves a Pluto model with polar caps of high albedo (0.3 to 0.8) and low emissivity (0.1 to 0.4), and a low albedo, high emissivity equatorial region. Satisfactory fitting to the IRAS data requires that the temperature decrease with increasing latitude up to the polar caps which are isothermal; completely isothermal models are ruled out. Assuming the polar caps are composed of methane, a maximum methane vapor column abundance of 920 centimeter-amagats (cm-am) is derived.

Analysis of the same IRAS data set by Aumann and Walker (1987) yields a completely isothermal surface for Pluto, in contradiction to the work of Sykes et al. (1987). It has not yet been possible to identify the source of the inconsistency between the two analyses. It should be pointed out that Sykes, et al. used a more sophisticated modeling approach, however. A third IRAS analysis by Tedesco et al. (1987) uses poorer-quality survey-mode data at a

single wavelength and should be considered superseded by the pointed observations.

Species Detected Spectroscopically. Information on the volatile components of Triton's and Pluto's surfaces come from near infrared spectroscopy; the visible region has added some information on nonvolatile components. Triton shows methane absorption bands in the near infrared indicative of a condensed phase, generally thought to be fine-grained methane frost (Cruikshank and Apt 1984). An additional spectroscopic feature at about 2.15 μm was tentatively identified in 1984 as being an overtone of pressure-induced absorption in nitrogen (Cruikshank et al. 1984). For plausible surface temperatures (see below), the vapor pressure of gaseous nitrogen is too low to produce the feature; hence a long (meter) path length absorption in condensed nitrogen is required. Because of the required long path length, the feature was ascribed to liquid nitrogen. More recent spectroscopy has either failed to see the liquid nitrogen feature (Rieke et al. 1985) or observed a shape different from laboratory liquid nitrogen (Cruikshank et al. 1987). Moreover, while the spectroscopic data from the early 1980s show substantial variability with orbital phase, suggesting that a nonuniform distribution of volatiles was seen, in the most recent data the effect is apparently masked, and the absorption bands are characteristic of either extremely small grains (microns) or a highly dilute solution of liquid methane (Cruikshank et al. 1987). Both condensed nitrogen and methane would produce significant atmospheres; however, absorption due to gas has not been seen in the infrared data. Spectroscopic data also hint at the presence of fine-grained water frost. Triton's reddish color suggests a component on the surface analogous to the aerosols produced on Titan from photolysis of methane (Cruikshank and Brown 1986).

The near-infrared spectrum of Pluto is dominated by absorption bands most closely resembling those produced by methane ice (Cruikshank and Brown 1986). Shortward of 1 μm , the interpretation of spectral features is more ambiguous. Buie and Fink (1987) find an upper limit column abundance of methane, if all of the absorption is due to gas, of 940 to 1460 cm-am, variable with orbital phase. The variation implies a frost-plus-gas model to be more physically sensible; the best-fit case yields a gaseous abundance of 540 cm-am which is consistent with the IRAS analysis of Sykes et al (1987). There is no evidence for additional spectroscopically active components. Pluto is also reddish, suggesting that methane is being converted to higher hydrocarbons by sunlight or charged particles. A recent experiment separated the infrared signatures of Pluto and Charon, indicating the absence of methane and tentative presence of water ice on Charon's surface (Marcialis et al. 1987).

Although carbon monoxide has not been detected on Triton or Pluto, its signature could be hidden in the 2.3 μm band of methane. It should be possible to ratio the strengths of two methane bands to determine the amount of

additional absorption due to carbon monoxide at 2.3 μm , but to date the data are not of sufficiently high quality, nor the laboratory methane analogs sufficiently good matches to the methane features, to be able to derive CO abundance in this fashion.

Surface Models: Physical State of Volatiles and Seasonal Modulations. To understand the nature of the surfaces of Triton and Pluto requires (1) that the spectroscopic data be well characterized, (2) that the thermodynamic properties of the volatiles be understood, and (3) that seasonal modulation of insolation be taken into account. Triton is in a retrograde orbit inclined to the spin axis of Neptune, which is inclined relative to its solar orbit. Harris (1984) determined that the pole of rotation of Triton is probably inclined only about 1° relative to its orbit plane, and that the subsolar latitude of Triton undergoes extreme excursions to $\pm 50^\circ$ latitude every 600 yr or less, with smaller higher frequency oscillations in between (see figure in Cruikshank and Brown 1986). Trafton (1984) used Harris' results to show that the net deposition of sunlight was greatest at Triton's equator, that volatiles such as methane would tend to migrate toward the poles over geologic time, and that seasonal movement of volatiles from pole to pole by sublimation would occur.

The temperature at the subsolar point of Triton if there is no major surface volatile component is given by

$$T = 72 * [(1 - A) / e]^{0.25} \quad (4)$$

where A = albedo and e = emissivity. For unity emissivity and an albedo of 0.4, Eq. (4) yields a subsolar temperature of 63 K. When a material of sufficient volatility is present on the surface, a significant amount of insolation goes into sublimation; that energy is released upon condensation elsewhere on the body. In effect, the solar energy is redistributed areally by volatile transport; since vapor pressure is an exponential function of inverse temperature, materials are either completely *involatile* or *volatile* in regard to redistribution of solar heat. The ratio of energy going into sublimation to that going into heating is

$$f_{\text{sub}} = \frac{L P_s}{\sigma T^4} \sqrt{\frac{\mu}{2\pi R_g T}} \quad (5)$$

where L = latent heat of sublimation, P_s = vapor pressure, μ = molecular weight, R_g = universal gas constant and σ = Stephan-Boltzman constant. For methane at 60 K, f_{sub} is 5000; for nitrogen, it is higher by three orders of magnitude. Clearly these materials must alter the temperature distribution on Triton, and by doing so determine the physical states under which they can exist. Trafton (1984) showed that over the age of the solar system the net

amount of methane transferred from the equator to the poles could exceed the mass of Triton. Thus, solid (as opposed to liquids that would flow) volatiles are confined to the polar caps. The temperatures of the polar caps, which determine the maximum atmospheric pressure in equilibrium with the surface volatiles (the vapor pressure) are equal to each other due to volatile transport. From Trafton's formulation of the polar-cap temperatures as a function of subsolar point and cap extent, we derive

$$T_{pc} = 67.2 [(1 - A)/e]^{0.25} \quad (6)$$

for the epoch of the Voyager flyby (mid-1989), when the subsolar latitude will be 47.6° and assuming for concreteness a polar-cap colatitude of 30° . Figure 9

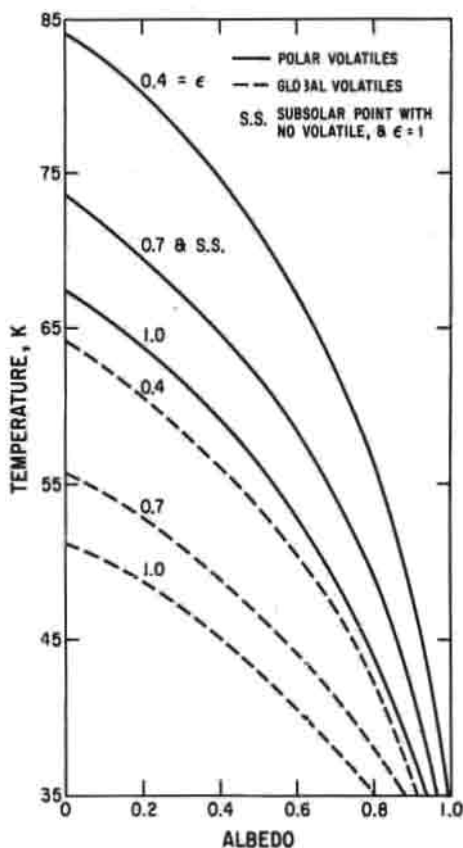


Fig. 9. Surface temperature vs albedo for two different distributions of surface volatiles, and for various emissivities. Polar refers to methane or nitrogen confined to polar caps, and global to uniformly distributed volatiles. SS refers to the temperature at the subsolar point of a non-volatile surface with unity emissivity.

plots temperature as a function of albedo and emissivity for this case. Also shown is the temperature for a liquid volatile, which is assumed to cover uniformly the surface:

$$T_{\text{eq}} = 51. [(1 - A)/e]^{0.25}.$$

The proper assignment of emissivity for Triton's surface is difficult. A value for methane ice of 0.4 was favored by Trafton (1984), based on Trafton and Stern's (1983) comparison of the gas abundance of methane on Pluto with a calculated surface temperature. This approach is now questionable, since it was based upon an upper limit for gaseous methane on Pluto by Fink et al. (1980), substantially higher than the most recent determination of Buie and Fink (1987). However, Sykes et al. (1987) find a best fit to IRAS data of Pluto by including methane polar caps with thermal emissivity < 0.4 . Finally, an emissivity significantly < 1 is suggested for liquid nitrogen by the work of Jones (1970). Clearly, determination of the emissivity of condensed nonpolar species is a high priority for laboratory work. Also uncertain is Triton's albedo, since the polar-cap value is likely to be higher than the global average. A global ocean model radiates over 4π steradians (Eq. 7); hence the correct albedo to choose from the radiometric observations is the lower one of 0.2.

Given the temperature range of Fig. 9, nitrogen and methane are most plausibly present in the solid state on Triton's surface, according to the work of Lunine and Stevenson (1985*d*). They assessed a number of surface models in terms of the available thermodynamic and spectroscopic constraints. The primary thermodynamic constraint is the freezing point of nitrogen, 63 K, which is lowered by only one degree through addition of methane. The only cosmochemically abundant material capable of lowering the nitrogen freezing point substantially is neon, which is not expected to be present in significant quantities as discussed in Sec. IV. Figure 9 shows that temperatures on Triton are below 62 K if liquid nitrogen is assumed to be present in a global ocean; hence such a model is thermodynamically inconsistent. If the nitrogen is confined to lakes near the poles, temperatures above 62 K are possible.

The primary spectroscopic constraint is that the $2.3 \mu\text{m}$ methane absorption band be narrow enough that the $2.16 \mu\text{m}$ nitrogen feature is visible. Lunine and Stevenson (1985*d*) concluded that for a saturated mole fraction of methane in liquid nitrogen ($\sim 20\%$), the wing of the methane band could obscure completely the nitrogen feature. This was confirmed experimentally by Piscitelli et al. (1987), who observed the nitrogen feature disappear when the methane mole fraction dissolved in a liquid nitrogen solution reached 1% of the saturated value. Lunine and Stevenson asserted that avoiding methane saturation in liquid nitrogen on Triton would be difficult.

The preferred model for Triton's surface has nitrogen and methane in solid form, perhaps in solid solution, but more probably as a disequilibrium assemblage. The presence of pure nitrogen atop methane or a methane-nitro-

gen mixture is ensured by seasonal transport and the much higher vapor pressure of nitrogen compared to methane. Lunine and Stevenson estimate that a m-deep layer of nitrogen can be sublimed and deposited elsewhere on a seasonal time scale of 100 yr. The high path length required in the nitrogen solid by the near-infrared observations requires large crystal sizes, on the order of tens of cm, which is plausible only if significant grain metamorphism occurs. A surface temperature below but near the triple point substantially aids this process (Clark et al. 1983). Liquid nitrogen cannot be ruled out absolutely; Cruikshank et al. (1987) assert that the methane absorptions seen in the latest Triton data are well fit by very small amounts of methane dissolved in liquid nitrogen. The same may be true for methane in solid nitrogen, which, however, has not been synthesized for laboratory infrared spectra.

Finally, one can assess the likelihood of a thick, greenhouse atmosphere for Triton, using pressure-induced gas opacities shown to be important on Titan. The low effective temperature of Triton compared to that of Titan limits the vapor pressures which can be raised from the surface, and significant infrared optical depths can be maintained only for a very thick atmosphere (surface temperatures greater than 75 to 80 K). Whether the lack of photometric and spectroscopic variability in recent observations of Triton indicates obscuration by haze in a substantial atmosphere is an issue which will remain open until the Voyager 2 encounter in 1989.

Pluto's rotation axis is highly inclined to the ecliptic (Cruikshank and Brown 1986), and its high orbital eccentricity brings it closer to the Sun than Neptune. Trafton and Stern (1983) examined the dynamics of a methane atmosphere in equilibrium with surface frosts. Because of methane's volatility, Pluto's atmosphere would be expected to be globally uniform in temperature, at least in its near perihelion state. The range of possible temperatures on Pluto near perihelion is the same as that for Triton (for a given assumed model of surface coverage of volatiles). Aphelion temperatures are as much as 20% less than perihelion temperatures (Trafton 1980). Stern et al. (1988) examine the orbitally driven sublimation and freezeout of methane in more detail, and conclude that the process is essential for maintaining bright methane (non-radiation-darkened) on Pluto's surface. The secular dimming of Pluto toward aphelion, in this model, is due to sublimation of methane frosts, in contrast to the fixed-cap model of Marcialis (1988). Their model predicts a lower limit to the atmosphere of Pluto of 16 to 45 cm-am, consistent with data analyses cited above.

Role of Photochemical and Cosmic-Ray Chemistry on Triton and Pluto. In the above-mentioned ranges of temperature, both Triton and Pluto can maintain large column abundances of CH_4 for photolysis. The column abundance of an ideal, isothermal gas in hydrostatic equilibrium is given by $N = P/mg$, where m = mass of gas per molecule, P is pressure and g surface gravity. For a nominal surface gravity of 100 cm s^{-2} , methane column abun-

dances range from $3 \times 10^{18} \text{ cm}^{-2}$ for $P = 8 \times 10^{-9}$ bar (corresponding to a surface temperature of 40 K if the methane vapor is in equilibrium with surface frost), to $9 \times 10^{23} \text{ cm}^{-2}$, for a vapor pressure of 2.5×10^{-3} bar (corresponding to a surface temperature of 70 K). Since only $6 \times 10^{16} \text{ cm}^{-2}$ of CH_4 is required for unit optical depth (where most of the photolysis occurs), it follows that the photolysis regions on Triton and Pluto would lie at least several scale heights above the surface. In the presence of large amounts of N_2 as the background gas, one might then expect the photochemistry on Pluto and Triton to bear some resemblance to that on Titan. The major uncertainty in such a comparison is ignorance of the temperature structure of the atmospheres of Triton and Pluto. Until this issue can be resolved (by the Voyager flyby of Triton in 1989), detailed models of altitude regimes of photolysis and alterations in chemistry due to transport of products vertically can be constructed for neither Triton nor Pluto.

It should be recognized that at the distance of Triton and the perihelion of Pluto's orbit, the solar flux is reduced by a factor of 1000 relative to its value at 1 AU, or by a factor of 10 compared to that at Titan's orbit. This would result in a correspondingly lower production rate of the photolysis products. Since the densities of the products go roughly as the square root of the production rates, they would be lower by about a factor of 3 compared to Titan, all other things being equal. As solar ultraviolet dissociation declines, the charged particle dissociation and ionization of the atmospheric constituents could become more significant. Depending upon the atmospheric composition, pressure and the nature of the magnetic field (intrinsic or induced), galactic cosmic rays with energies greater than 1 GeV, subrelativistic solar-wind protons with energies in the 10 to 100 MeV range, and occasionally solar relativistic protons with energies greater than 10 GeV would interact with Pluto and Triton producing some of the same constituents as in the photochemical processes discussed above. A likelihood also exists for the production of many more complex species, and of polymerization all the way down to the surface (Delitsky and Thompson 1987). Because of the low temperatures prevalent on Triton and Pluto, many of the species produced subsequent to the charged particle induced chemistry are subject to condensation in the form of atmospheric aerosols.

Strazzulla et al. (1984) have measured the cross sections of energetic protons for polymerization on hydrocarbons of relevance to the surfaces of Pluto and Triton. Although the flux of solar cosmic rays at the orbits of Pluto and Triton is not known, a rough estimate may be made by taking the value at 1 AU and assuming a $1/r^2$ dependence in the worst case. Slower variation in flux is indicated by the Pioneer measurements at Jupiter's orbit. McDonald et al. (1974) give for maximum solar activity a flux of $10^{10} \text{ cm}^{-2}\text{yr}^{-1}$ for protons with energies ≥ 20 MeV, and incident energy spectrum that varies as $E^{-\gamma}$, where $3 \leq \gamma \leq 6$. Assuming a surface of methane ice, CH_4 -vapor pressure of 0.025 mbar (corresponding to a 55 K surface) and McDonald et

al.'s energy spectrum with $\gamma = 3$, Strazzulla et al. (1984) calculate that the time constant for polymerizing 50% of the original methane on Pluto would be expected to be 100 Myr at a depth of 0.5 cm, 1 Gyr at a depth of 2.2 cm and 4.6 Gyr at a depth of 5 cm. For Triton, they assumed a monolayer of CH_4 adsorbed on the surface, and calculated polymerization to a depth of 0.1 μm . It is important to recognize that Strazzulla's estimates could easily change by orders of magnitude if a different energy spectrum, e.g., with $\gamma = 6$, and a different flux variation with distance were assumed. Their results should therefore be regarded as tentative. Despite the possibility of polymerization at the surface, it is virtually certain that the surfaces of Triton and Pluto would be continually renewed by seasonal oscillations in the rates of condensation and evaporation, and by gardening. Survival at the surface of some products of Triton's energetic chemistry seem likely, because of the satellite's reddish appearance (Piscitelli et al. 1987).

As for Triton's interaction with Neptune's magnetosphere, it seems at this time to be of little consequence. Unlike Titan, the nitrogen chemistry at Triton is not likely to be controlled by the magnetospheric particles (Atreya 1986). This conclusion is based on the fact that the IUE observations give an "upper limit" of 200 R for Lyman-alpha emission from Neptune (J. T. Clark, personal communication, 1986, 1987). Almost all of this intensity can be explained by conventional means: resonance scattering, backscattering of interplanetary/interstellar hydrogen, with perhaps a small contribution from a possible electroglow. Charged-particle input from a magnetosphere is not required. Galactic cosmic rays as well as interplanetary electrons are expected to play an important role in Triton's atmospheric and surface chemistry.

Stability of Methane on Triton and Pluto. Trafton (1980) considered the hydrodynamic escape (blowoff) of methane from Pluto. He argued that if the average thermal energy per molecule is comparable to the gravitational potential energy at the exobase, then free escape of the molecules can occur. The essential condition is that

$$\lambda = GMm/RkT = 1.5 \text{ at the exobase} \quad (8)$$

where G = gravitational constant, M = mass of Pluto, m = mass of methane molecule, k = Boltzmann's constant, T = temperature, R is radial distance from Pluto's center. At Pluto's surface, for the parameters given earlier, $\lambda = 25$ at $T = 50$ K. An atmosphere supplied by methane sublimation at the surface and supported hydrostatically would extend up to altitudes at which $\lambda = 1$. Trafton showed that for temperatures in excess of 47 K, the blowoff flux would be $> 2 \times 10^{13} \text{ cm}^{-2}\text{s}^{-1}$ (referred to the surface), enough to vaporize a mass of methane equal to the mass of Pluto. The result suggested that a heavier gas, e.g. nitrogen, is present in the atmosphere of Pluto to limit the escape of methane which must diffuse to the exobase.

Hunten and Watson (1982) applied the analytic scheme of Watson et al. (1981) to calculate a more realistic escape flux accounting for energy transport in the atmosphere. Escape at the exobase is driven by solar EUV heating, which is absorbed many scale heights above the surface. The efficiency of escape of gas is primarily limited by the conduction of heat from the level of absorption of ultraviolet to the region where the bulk of the atmosphere is located. The energy limited escape flux is then determined by allowing the temperature minimum to equal 0. Using this model, Hunten and Watson (1982) calculated an escape flux for methane on Pluto of $4 \times 10^{10} \text{ cm}^{-2} \text{ s}^{-1}$ referred to the surface, implying that the amount of methane lost over the age of the solar system is less than 0.5% of the mass of Pluto, i.e., equivalent to a layer 8 km deep. Although this is a large quantity of methane, it is much smaller than the maximum amount of methane which could have been incorporated in Pluto based on cosmochemical models (see Sec. V), which in terms of mass fraction is in the range of 5 to 15%.

The absence of methane on Charon (Marcialis et al. 1987) combined with its smaller mass, suggests that hydrodynamic escape may have depleted that object of its methane. Application of the Watson et al. (1981) formalism supports that conclusion (Trafton et al. 1988).

Because Triton's mass is probably substantially greater than that of Pluto, the same conclusion holds more strongly for that satellite. Other loss processes for methane such as tidal stripping by Neptune have not been demonstrated to be important. It appears that, as for Titan, the dominant loss of methane on Triton is photochemical. On Pluto, energy-limited escape may indeed dominate over photolysis as the primary sink of methane, but it is not rapid enough at present to require invoking a heavier secondary gas to maintain methane on Pluto. The role of enhanced EUV flux from the early Sun in atmospheric escape is discussed in Sec. V.

III. EVOLUTION OF TITAN'S ATMOSPHERE DRIVEN BY PHOTOCHEMISTRY

We have laid the foundation for discussing the primary processes operating at present which drive the evolution of the atmosphere of Titan. The coupling of the irreversible photochemical conversion of methane with the thermal structure of the troposphere is achieved through the postulated existence of an ethane-methane-nitrogen ocean. In this section we explore the interactions between these systems, and describe how the results of such models test our understanding of the present Titan atmosphere, as well as constrain models for its formation and early evolution. Couplings in the absence of a massive ocean are also discussed. We further consider the effect of a massive ocean and the photochemical cycle on the atmospheric D to H ratio. Finally, we describe the additional information on Triton and Pluto required for similar modeling of those bodies.

Coupled Evolution of Titan's Ocean and Atmosphere

Figure 10 illustrates the conceptual coupling between the photochemical cycle, atmospheric thermal structure and hydrocarbon ocean described in Lunine and Stevenson (1985*b*). The model is a closed box for nitrogen, which is partitioned between ocean and atmosphere but does not escape. The loss of methane is entirely photochemical. To first order, two methane molecules derived by evaporation from the ocean are photolyzed to form one molecule of ethane, which condenses and falls back to the ocean. The primary correction to this scheme is the production of acetylene and aerosols, decreasing the ethane production rate by a factor of perhaps 10 to 30%. Hydrogen escapes from the system, with the consequence that the process is irreversible. As a function of time, then, assuming no resupply of methane by outgassing or cometary impact, the ocean (1) becomes more ethane rich, and (2) decreases in number of molecules (volume).

The effects of these changes on the atmosphere are determined by the thermodynamic properties of the ocean. Since the ethane-methane liquid system is nearly ideal in the sense of Raoult's law (Lunine et al. 1983), the partial pressure of methane in the atmosphere is proportional to the mole fraction of

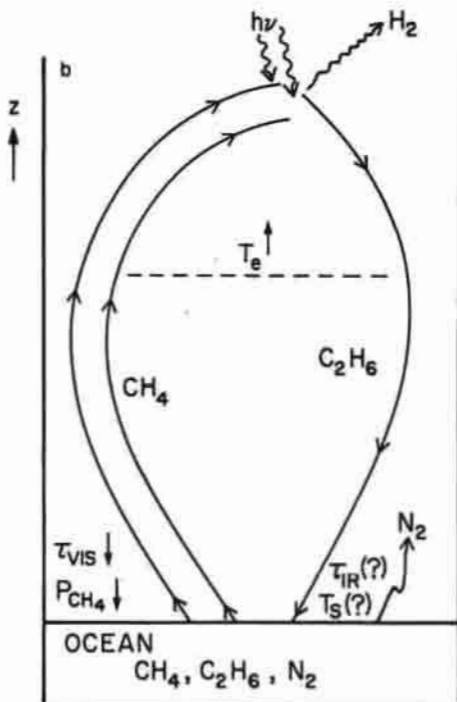


Fig. 10. Illustration of the physical processes which couple the atmospheric thermal structure to the evolution of the ocean, as described in the text.

methane in the ocean; hence at a fixed temperature, the amount of atmospheric methane decreases as the ocean becomes more ethane rich. The nitrogen dissolved in the ocean tends to outgas to the atmosphere with time, both because its solubility decreases for increasing ethane mole fraction (Fig. 6) and because the ocean is decreasing in volume.

The atmospheric thermal structure is determined largely by the amount of sunlight reaching the surface and the infrared opacity contributed by pressure-induced absorption in gaseous nitrogen, hydrogen and methane. The decreasing methane pressure determined by ocean evolution decreases the infrared opacity and tends to lower the surface temperature. The increasing nitrogen pressure has the opposite effect. Which effect dominates depends upon the relative contributions of the two gases to the infrared opacity, and the relative rates at which the gas pressures change with changing ocean composition. In addition, the decrease in methane mole fraction in the ocean increases the altitude at which methane cloud formation occurs, which probably acts to increase the amount of solar flux reaching the ground. Finally, the change in the thermal structure of the troposphere changes the mole fraction of methane admitted to the stratosphere, which under some conditions could alter the photolysis rates and composition of products.

Analytic Model of Climate Evolution. The rather complex couplings cited above were explored in a preliminary way by Lunine and Stevenson (1985b). An analytic representation for the change in Titan's tropospheric climate with ocean evolution illustrates the interplay between the various physical processes. The infrared optical depth at Titan's surface due to pressure-induced gas opacity, suitably averaged over frequency, is

$$\tau = \left(P_N^2 \frac{\alpha_{NN}}{2} + P_N P_H \alpha_{NH} + P_N P_C \alpha_{NC} \right) \frac{1}{\eta^2 k T m g} \quad (9)$$

where α_{xy} = absorption coefficient for collision of molecule x with molecule y , in $\text{cm}^{-1} \text{ amagat}^{-2}$, P_x is partial pressure of molecule x , η = Loschmidt's number, m is mass of primary atmospheric molecule, g is the surface gravitational acceleration, k is Boltzmann's constant and T is temperature. We exclude other collisional combinations such as methane-methane because their contribution is negligible.

We wish to find the change in surface temperature with time, or equivalently, with decreasing ocean methane mole fraction x_C , since the methane conversion rate is assumed constant with time. We use the grey atmosphere solution to the equation of radiative transfer in the Eddington limit, i.e.,

$$T = T_e (0.5 + 0.75 \tau)^{0.25} \quad (10)$$

where T_e is an "effective" temperature which is tied to the amount of solar flux reaching Titan's lower troposphere. To make further progress, we must

(a) find expressions for the change in nitrogen, methane and hydrogen pressures with ocean composition and temperature, and (b) decide on the relative importance, and temperature dependences of, absorption due to collisions between various pairs of molecules.

The methane pressure follows Raoult's law:

$$P_C = x_C e_C \quad (11)$$

where e_C is the saturation vapor pressure of methane at the surface temperature T (deviations from Eq. [10] for methane can be as large as 40% in pressure; W.R. Thompson, personal communication). The solubility of nitrogen in methane and ethane is given by Henry's law (Lunine and Stevenson 1985b):

$$P_N = K x_N \quad (12)$$

where K is the Henry's law constant and x_N is the mole fraction of nitrogen in the ocean. We evaluate this constant for a mixed ethane-methane liquid, and conserve the total amount of nitrogen in ocean and atmosphere:

$$M_N = 4 \pi R_T^2 P_N / g + 28 P_N M_o / K \mu_o \quad (13)$$

where M_N is the total amount of nitrogen in the atmosphere and ocean, M_o is the mass of ethane and methane in the ocean, R and g are the radius and surface gravity of Titan and μ_o is the ocean mean molecular weight. This expression is strictly valid for dilute nitrogen solutions only ($K \gg P_N$).

The effect of the ocean on the hydrogen partial pressure has not been explored. Two reasonable limiting cases are (1) constant atmospheric mixing ratio of hydrogen and nitrogen (implying similar thermodynamic interactions with the ocean) and (2) constant partial pressure of hydrogen (no interaction of hydrogen with the ocean).

We first assume that collisions between nitrogen molecules dominate the infrared opacity. In this case, the dependence on methane and hydrogen pressure disappears, and optical depth goes as the square of the nitrogen pressure in Eq. (9). Evaluating Eqs. (9) through (13) yields the result that the optical depth increases as methane mole fraction decreases, i.e., surface temperatures were colder in the past. The physical argument is that as the ocean becomes more ethane rich and decreases in volume, nitrogen comes out of solution to increase the atmospheric pressure and hence infrared optical depth. Figure 11 summarizes the quantitative results of such a model. Two curves are shown, one for the solubility of N_2 constant with temperature as considered above, and the other for a solubility which decreases with increasing temperature. Work by Thompson (1985) suggests that the latter is more reasonable. The dashed lines are temperature boundaries for the freezing out of the ocean.

Recent work by Dagg et al. (1984,1986) and Courtin (1988) confirms

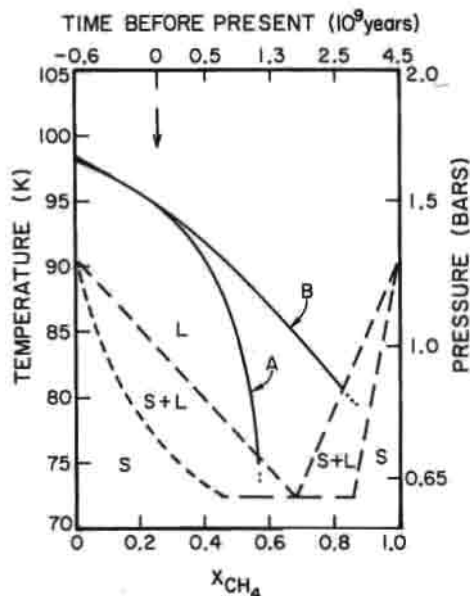


Fig. 11. Evolution of a simplified Titan ocean-atmosphere system, plotted as surface temperature vs mole fraction of methane in ocean, for a present-day ocean containing 25% methane. The sole atmospheric opacity source in this model is nitrogen-nitrogen molecular collisions; as discussed in the text more detailed atmosphere models yield different results. Curve A assumes a temperature-dependent solubility of nitrogen in the ocean; curve B assumes temperature independence. Two auxiliary scales are plotted: atmospheric pressure in bars corresponding to temperature, and time before present corresponding to ocean methane mole fraction assuming constant photolysis rate. Dotted lines are ethane-methane solid-liquid phase diagram from Moran (1959), with L = all liquid, $S + L$ = coexisting liquid and solid and S = all solid (figure from Lunine and Stevenson 1985b).

what was suspected for several years (Courtin 1982), that the dominant gas opacity in Titan's atmosphere is contributed by collisions between nitrogen and methane, and nitrogen and hydrogen molecules. Although the absorption coefficients for the various collision pairs differ only by a factor of several below 100 cm^{-1} (and hence the much larger mole fraction of nitrogen would result in its opacity dominating), the nitrogen-nitrogen collisional opacity drops rapidly to zero for higher frequencies. The higher multipole processes leading to methane and hydrogen absorption provide substantial opacity out to 400 wavenumbers. Since the peak of Titan's Planck function is at ~ 200 wavenumbers for the present surface temperature, and opacity averaging schemes tend to weight this or higher frequencies (Mihalas 1978), clearly for the present conceptual model the appropriate choice of opacity is that due to nitrogen-methane and nitrogen-hydrogen collisions. Thompson (1985) has discussed possible effects of including the nitrogen-methane collisions.

Lunine (1988) considered the evolution of Titan's atmosphere for these two sources of opacity, using the grey atmosphere formalism described above, and absorption coefficients calculated as in Courtin (1988). The coefficients were frequency averaged using a Rosseland-mean scheme. Hence, the nitrogen-hydrogen and nitrogen-methane cases had to be considered separately. The two alternative assumptions for the behavior of the hydrogen vapor pressure lead to an optical depth in Eq. (9) either (1) proportional to the square of the nitrogen pressure, or (2) linearly proportional to the nitrogen pressure. Case (1) is formally identical to the results in Fig. 11; for case (2), the evolution is in the same direction but more gradual. If the nitrogen-methane opacity dominates, Eq. (9) becomes more complex because the nitrogen and methane vapor pressures change in opposite directions with ocean evolution. The methane pressure dominates, and the sense of the evolution is toward warmer temperatures in the past.

The frequency-averaged absorption coefficient for nitrogen-hydrogen was significantly larger than for nitrogen-methane, and on this basis one would argue that Titan's surface was colder in the past. However, as Lunine (1988) points out, the averaging technique probably underestimates the methane contribution, and a non-grey scheme may be required to determine the evolution of the surface for both opacity sources.

The analysis presented shows that the present state of Titan's troposphere, and the evolution of its thermal structure, must be understood in the context of the surface physical state and composition. Additional effects, not included above, are the change in stratospheric thermal balance due to changing tropospheric temperatures (and hence changing methane mole fraction admitted to the stratosphere), the increase in solar luminosity over geologic time, and changes in cloud deck thickness and opacity. To first order, the effects of cloud infrared and visible opacity tend to cancel each other out (McKay et al. 1988a). However, the play-off between methane vapor pressure and cloud infrared optical depth is complex, and includes changes in altitude of the lifting condensation level, higher cloud density for larger temperatures, possible change in cloud particle size distribution for different cloud densities, and possible changes in cloud morphology and areal homogeneity for large changes in surface temperature. These may alter the rough balance between the visible and infrared optical depths due to clouds, and hence contribute to the evolution of the thermal structure.

The surface-atmosphere coupling presented here does not work if an ocean containing large quantities of exchangeable methane and nitrogen is not present. The solid polymer model decouples the atmosphere from any steady-state interaction with the surface. Sporadic resupply of atmospheric methane by volcanic or impact sources would perturb the atmospheric thermal balance, but analysis of such effects is rendered difficult by their stochastic nature.

Clearly, then, observational evidence for or against the presence of a hydrocarbon ocean carries implications both for the long-term photochemical

cycle on Titan *and* long-term climate evolution. Our understanding of this satellite's evolution will increase enormously when such evidence can be obtained.

Effect of Photochemical Cycle on D/H Ratio. Recent observations of deuterated methane in the reflection spectrum of Titan near the 1.6- μm region lead to a D/H ratio in the atmosphere of $1.65^{+1.65}_{-0.8} \times 10^{-4}$, 8 times higher than the value derived for Jupiter and Saturn (and generally assumed to be primordial) and comparable to the value found on Uranus (de Bergh et al. 1987a) and on the Earth. It is compatible with an analysis of Voyager IRIS data of Titan (Kim and Caldwell 1982). Pinto et al. (1986) explored the effects of a hydrocarbon ocean, and the photochemical cycle, on the deuterated methane abundance relative to total atmospheric methane. Fractionation into the ocean by vapor-pressure differences turns out to be negligible, since the deuterated methane molecule turns out to have a nearly identical vapor pressure to that of normal methane (the result of a fortuitous cancellation between inter- and intra- molecular effects on the vapor pressure). Other solubility effects lead to at most an atmospheric deuterium enhancement of 1.3.

Also considered was the possible photochemical partitioning of deuterium in methane. The slightly higher binding energy of deuterium in methane compared to normal hydrogen results in preferential dissociation of CH_4 . The deuterated methane enhancement factor is then dependent upon the ratio of the amount of methane photolyzed to the total available methane reservoir, i.e., ocean composition. For a 25% methane ocean, Pinto et al. (1986) find $\text{CH}_3\text{D}/\text{CH}_4 = 1.7$. Thus, at most a factor of 2 enrichment in deuterated atmospheric methane may be caused by surface and atmospheric photochemical process. The remainder may be a signature of the original materials out of which Titan was assembled; a discussion of the source of this deuterium-rich material is given in Sec. IV.

Evolution of Surfaces of Triton and Pluto

At present we have no information on the abundance of methane and nitrogen on the surfaces of Triton and Pluto. Establishment by Voyager 2 of the areal coverage of volatile material on Triton, and the atmospheric pressures of methane and nitrogen, would aid in understanding how much volatile material is present. The seasonal transport of volatiles on Triton amounts to meters thickness; Earth-based observations as solstice is approached in the next 20 yr could establish whether volatiles become depleted from the summer hemisphere. The photochemical processing of methane on Triton and Pluto also puts constraints on the amount of surface methane; since the photolysis rate is down by a factor of 10 from Titan to Triton, the depth of processed organics is 10s to 100s of meters on the latter body. Clearly the sort of modeling presented in this section must await the results of the Voyager flyby of

Triton in 1989; for Pluto improved groundbased techniques will remain the primary tool for some time to come.

IV. ORIGIN AND EARLY EVOLUTION OF THE ATMOSPHERES OF TITAN, TRITON AND PLUTO

As with any atmosphere, the atmospheres of Titan, Triton and Pluto contain information on the environments within which these bodies formed and underwent early evolution driven by atmospheric escape, enhanced EUV radiation from the Sun, bombardment by debris and internal processes. In this section we examine these processes and identify their chemical signatures in the present atmospheres. Of greatest interest are the origin of nitrogen and methane on Titan and Triton, for which noble gas abundances may be diagnostic, and the implications of the deuterium abundance in the atmosphere of Titan for its environment of formation. The role of nebular chemistry in the formation of atmospheres is contained in the Chapter by Prinn and Fegley; some of the discussion below overlaps with material in that chapter.

Regular satellites such as Titan undoubtedly originated in a nebula of gas and dust that surrounded their parent outer planets during the latter's early history. The origins of Triton and Pluto are much less clear. Given the large inclination of Triton's orbital plane to Neptune's equatorial plane, it is possible alternatively to consider Triton to be a regular satellite formed in a nebula around Neptune, with this system subsequently severely disturbed by a passing large planetesimal; or to suppose that it was formed in the solar nebula and later captured by Neptune. The latter hypothesis is advocated by McKinnon (1984); earlier capture hypotheses are reviewed by Cruikshank and Brown (1986).

Pluto/Charon represents a fully tidally evolved system (Burns 1986a) and hence no information on the mechanism of producing this double planet system is available from the orbit of Charon. Although a number of hypotheses for ejection of Pluto from orbit around Neptune have been advanced, some involving Triton, they all suffer from significant problems when compared to the present state (Burns 1986a). Burns advocates the view that Triton, Pluto and Charon were leftover planetesimals; Triton was captured by gas drag into Neptune orbit while Pluto-Charon remained in solar orbit because their 3:2 resonance with Neptune prevented close encounters with the outermost giant planet.

The rest of this section is organized to provide an overview of the formation and early evolution of satellite atmospheres first (focusing necessarily on Titan) from models of the nebula, through condensation and accretion of planetesimals, to processes affecting post-accretional evolution of the primordial Titan atmosphere. Following this, the two competing scenarios for the origin of nitrogen in Titan's atmosphere are discussed in terms of diagnostic

observations. The issue of the total surface abundance of methane is then considered. We close with an assessment of the significance of the deuterium abundance in Titan's atmosphere, and the relationship of the origin of Titan's volatiles to those on Triton.

An Overview of the Formation and Early Evolution of Titan's Atmosphere: Nebula Models. The giant planets formed from the gaseous and solid components of the primordial solar nebula, a flattened disk of material derived from a collapsing molecular cloud fragment in association with the formation of the Sun. Solid-body accretion processes operating in the solar nebula led to the creation of progressively larger-sized planetesimals that served as the source material for the cores of the giant planets (see, e.g., Pollack 1985). Extensive treatments of nebula models are available in the chapters by Coradini et al., Morfill et al. and Pollack and Bodenheimer. Briefly, the solar nebula underwent perhaps four major stages of evolution. First was a growth phase dominated by the accretion of material from the collapsing molecular cloud fragment. By the end of this stage the solar nebula may have been quite massive, perhaps several tenths of a solar mass. The next stage was marked by turbulence and consequent outward transfer of angular momentum and inward transfer of nebular mass (Lynden-Bell and Pringle 1974). Following this, grain formation would have increased the nebular opacity to the extent that thermal convection would have been dominant in some regions. Planetesimal formation would have reduced the grain opacity and, in the final stage, gas and small grains were eliminated from the solar system by a strong wind emanating from the Sun. Based on the properties of T-Tauri stars, the formation and dissipation of the nebula took place in 10 Myr (see discussion in Lissauer 1987).

The radial temperature profile in such a nebula is complicated by the variation in opacity due to grain formation (Ruden and Lin 1986), and does not follow a simple power law. However, the general trend defined by planet composition (Lewis 1974a) is maintained in sophisticated numerical models. The same type of physics as pertained to the solar nebula controlled the qualitative behavior and evolution of satellite-forming accretion disks around giant planets. However, there are a number of key differences between the two, detailed in Stevenson et al. (1986). Primary among them is that pressures in the satellite-forming nebulae were 5 to 8 orders of magnitude larger than the pressures in the outer solar nebula. As a consequence the satellite-nebulae of Jupiter and Saturn, at least, were optically thick throughout and may have had temperature profiles inversely proportional to radial distance from the planet at some point during their evolution (Lunine and Stevenson 1982a). Temperatures were higher in the inner regions of these disks than in the surrounding solar nebula. Satellite accretion disks also evolved much faster than the solar nebula, with dynamic time scales of perhaps 10^2 to 10^4 yr.

Planetesimal Composition. The composition of the building blocks of satellites is determined by a combination of the temperature and oxidation state of the nebula from which they formed, and also possibly by an inheritance of small amounts of solid material from earlier times. At temperatures expected in the outer solar nebula during most of its history, and in a nebula around Saturn, both water ice and rock-forming materials would have been entirely in the condensed state. The relative proportions of these two key ingredients depends strongly on the partitioning of elemental oxygen (O) among various chemical species (Lewis and Prinn 1980; Prinn and Fegley 1981a; Johnson et al. 1987; Pollack and Bodenheimer, personal communication). In particular, about 15% of the O available in the solar nebula would have gone into oxides of the rock component. The remainder would have been partitioned between CO and water. CO can be a potent sink for O since the solar abundance of C is 60% that of O. Thus, the relative proportion of rock and water in planetesimals depends primarily on the oxidation state and molecular speciation of C in the solar and giant planet nebulae.

As quantified in detail by Lewis and Prinn (1980) and Prinn and Fegley (1981a), methane is the thermodynamically favored form of C at the temperatures characterizing the outer solar nebula. However, kinetic factors may prevent this equilibrium from being realized. If there is effective exchange of material between the inner and outer parts of a nebula, CO derived from the warmer regions, where reactions proceeded rapidly, may not have been converted to methane in the outer regions before remixing to warmer regions occurs (or even within the lifetime of the nebula). A similar conclusion holds for gas derived from the molecular cloud, which is dominated by CO (see chapter by Irvine et al.). A giant planet (protosatellite) nebula, with hydrogen pressures orders of magnitude higher than in the solar nebula, *would* be dominated by methane (Prinn and Fegley 1981a). The oxidation state of nitrogen tends to follow the same direction as carbon (see chapter by Prinn and Fegley).

Because the oxidation state of carbon so strongly controls the abundance of water, and because CO is too volatile to form a pure condensate, the densities of the satellites are diagnostic of the oxidation state of the nebulae from which they formed. First, suppose that methane was the dominant form of C in the outer solar nebula. In that case, the rock to water-ice ratio in planetesimals would have been approximately 40/60 by mass. Conversely, if CO were the dominant C species, this ratio would have equalled about 75/25. The mass ratios derived from large satellites of the outer solar system provide an *upper bound* on this ratio for nebula planetesimals, since it is possible to lose water by vaporization during accretion (see below). (On the other hand, the rock-to-ice ratio of planetesimals formed in a satellite-nebula around Saturn might have been altered by preferential dissolution of water in the Saturnian atmosphere, and loss of rock to the core.) The observed density of Titan implies a mass ratio of 55/45, suggesting either (a) some CO in the nebula, or

(b) a CH_4 -rich nebula with loss of water during Titan's accretion. Interestingly, the Uranian satellites' densities fall within the same rock-to-ice range (Johnson et al. 1987); since they are not large enough to lose significant quantities of water during accretion (see below), they probably formed from a gas containing significant quantities of CO. This gas could have been the solar nebula (Johnson et al. 1987) or a disk of material spun out from Uranus after a giant impact, in which CO was produced from shock heating (Stevenson 1984b). Until we learn Triton's density from the Voyager flyby, we cannot say anything about the oxidation state of its formation region.

Condensation of planetesimals is a powerful fractionation process which largely determines the bulk composition of the assembled body. Incorporation of a gaseous molecular species into solids is accomplished by (a) direct condensation, (b) clathration and (c) physical adsorption. Considering elements more volatile than water ice, temperature profiles for nebulae around giant planets (Prinn and Fegley 1981a; Lunine and Stevenson 1982a; Pollack and Consolmagno 1984) allow for direct condensation of ammonia hydrates and methane ice in the Saturnian nebula. In the solar nebula, the T - P profile also may allow for condensation of carbon dioxide if it comprises as much as 1% of the total carbon. Direct condensation of molecular nitrogen, argon and carbon monoxide are unlikely in the solar nebula, and certainly very implausible at Saturn's distance from the Sun.

Clathrate formation involves a structural alteration in water ice to accommodate more volatile species in voids, or cages. Application of the thermodynamics of clathrate formation to astrophysical environments and a review of earlier work is presented in Lunine and Stevenson (1985a). As with condensation, clathrate formation requires a threshold partial pressure of volatile gases as a function of temperature. Once water ice is induced to form clathrate, all gases present in the surrounding nebula will be incorporated to varying degrees, largely determined by their volatility. The total volatile-to-ice ratio in clathrate is 1 to 6. Essentially all of the condensed ice can be converted to clathrate, excluding that which formed ammonia hydrates (Lewis 1972a; Lunine and Stevenson 1985a), so long as good physical contact exists between the gas and ice. This requires frequent collisions between planetesimals to expose fresh ice to the gas, plausible in a nebula around Saturn but perhaps less so in the solar nebula, where orbital times are longer.

The chemical partitioning of gases into clathrate has important consequences for the proportions of nitrogen, carbon and noble gas species incorporated into satellites. Figure 12 illustrates the fractionation. The left panel shows that methane much more readily incorporates in clathrate than does nitrogen, as shown by experimental data. As confirmed by recent data on CO clathrate (Davidson et al. 1987), CO is predicted by Lunine and Stevenson to incorporate more readily than nitrogen but less so than methane. This figure makes the generous assumption that all of the nitrogen is molecular; it thus yields the maximum amount of nitrogen incorporated in the clathrate. As an

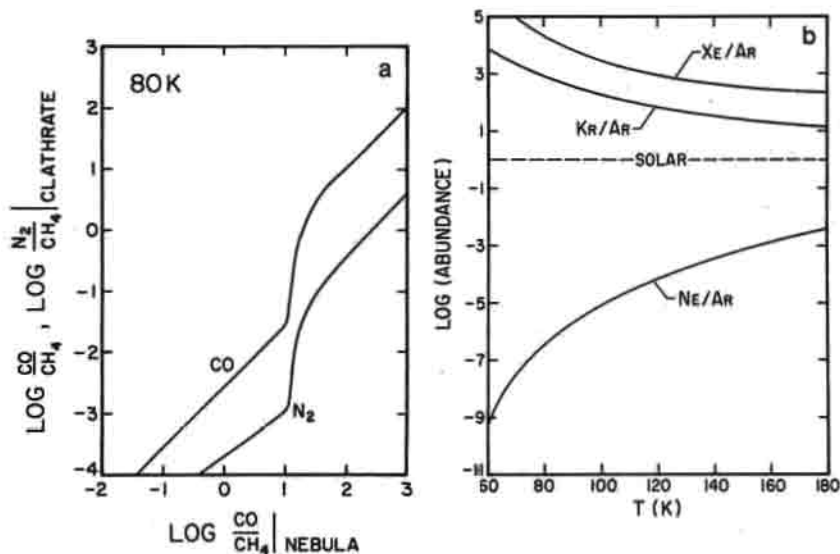


Fig. 12. (a) Ratio of CO and N₂ to CH₄ incorporated in clathrate as a function of CO-to-CH₄ ratio in a solar-composition nebula, at 80 K. All nitrogen is assumed to be in the form of N₂; total carbon-to-oxygen ratio in H₂O + CO + CH₄ is solar. (b) Noble gas abundance ratios in CH₄-dominated clathrate relative to abundance ratios in solar composition gas, as a function of temperature (figure from Lunine and Stevenson 1985a).

illustrative example, assume the nitrogen-to-methane ratio in the present Titan surface-atmosphere system is primordial and equals the ratio of nitrogen to methane incorporated in clathrate (see discussion of the origin of nitrogen below). This ratio is ~ 0.1 to 1 (Table II). Selecting a value of unity for concreteness, and reading across Fig. 12a from the ordinate value $\log \text{N}_2/\text{CH}_4 = 0$ shows that such a value in the clathrate requires a CO-to-CH₄ ratio in the nebular gas of ~ 500 . Physically, the methane ratio in the nebula gas must be small, so that methane does not overwhelm nitrogen and occupy almost all of the cage sites. We also see from the figure that the CO-to-N₂ ratio in the clathrate is 10; for the example cited, CO is the dominant molecule in the clathrate (because the methane nebular abundance is so small), and by the starting assumption in this example, should dominate the present Titan atmosphere (see discussion of CO photolysis later in this section). Note that the CO-dominated nebula required in this example produces a Titan which is too rock rich.

Alternatively, if we assume the CO-to-CH₄ ratio in the nebula was less than unity, as seems to be required by Titan's density, we find that the nitrogen-to-methane ratio in the clathrate is $< 10^{-3}$, and an additional source of nitrogen to supply the present-day atmosphere is required. As discussed below, the likely source is ammonia, brought into Titan in the frozen chemical

compounds ammonia monohydrate, ammonia dihydrate, or pure condensed ammonia.

One additional piece of information not contained in Fig. 12 is that nitrogen and argon partition into clathrate with roughly equal ease. Thus argon becomes a major indicator of the origin of nitrogen in Titan, as discussed below.

Physical adsorption, in which volatile molecules stick directly to ice grain surfaces, produces a similar chemical partitioning effect. However, the amount of area available for adsorption is limited, and hence the amount of volatile material which can be incorporated in the ice is much less than the maximum which can be incorporated in clathrate. Amorphous ice grains have a much higher specific adsorption area (Mayer and Pletzer 1986), and if volumetric contact between ice and gas is inhibited, adsorption could be more important than clathration.

Accretion of Large Satellites. Accretion of a satellite provides the initial source of energy for creation of a primordial atmosphere. Although a wide range of accretion models have been explored, which differ in the manner in which energy is deposited in the subsurface, surface or gaseous envelope of a protosatellite, accretional energy input is an important process only for satellites as large or larger than Rhea and Titania. Above this mass threshold, enough heating is generated to melt and/or vaporize volatiles (see the extended discussion in Stevenson et al. 1986). For bodies the size of the Galilean satellites and Titan, accretional heating quickly raises a substantial atmosphere, that overwhelms the ambient hydrogen envelope from the surrounding nebula (Lunine and Stevenson 1982). This atmosphere is sufficiently thick that planetesimals deposit their energy largely in the envelope; hence even if accretion starts off gas free, it conforms to the gaseous scenarios during the later stages. If Triton is as massive as Titan, then the same considerations apply; Pluto's reported mass makes accretional heating a marginal process for raising a massive primordial atmosphere (although methane would be volatilized to some extent).

No models for the accretion of Titan have been published, except for the thesis of Lunine (1985a) which assumes the planetesimals to be largely rock, methane clathrate hydrate and ammonia hydrate. To some extent the results apply to ammonia-poor planetesimals as well. The heating during accretion is sufficient to devolatilize the clathrate and release most of the methane into the primordial atmosphere. The only methane intact after accretion is buried in the innermost 5 to 20% of the mass of Titan (Lunine and Stevenson 1987). Ammonia and water form a massive envelope together with the methane and any other volatiles previously clathrated. The ammonia and water are in vapor pressure equilibrium with a surface ammonia-water "magma" ocean. Some of the atmosphere escapes back into the nebula by a hydrodynamic flow which taps part of the energy of planetesimal infall (Stevenson et al. 1986); the net

effect is to increase the rock-to-ice ratio of Titan relative to that of the original planetesimals.

The final state is shown in Fig. 13. The primordial atmosphere consists of up to several hundred bars of methane, and up to 200 bars of ammonia and water. The mass of the primordial atmosphere due to gaseous accretion is 10^3 times larger than the present atmosphere.

Escape of Primordial Atmosphere. Energy sources available for escape include solar EUV radiation, T-Tauri wind, and post-accretion impact. (The primordial atmosphere does not adiabatically expand away, or "uncork", as the surrounding nebula is dissipated, because many of the processes occurring during accretion were thermodynamically irreversible.) Enhanced EUV from the Sun can drive atmospheric escape at the energy-limited rate described by Watson et al. (1981) and Hunten et al. (1987). Analysis of pre-main-sequence stars by International Ultraviolet Explorer (IUE) satellite indicates that before the Sun reached the stellar main sequence at an age of 50 Myr, its flux shortward of 2000 \AA may have been up to 10,000 times greater than the present value (Zahnle and Walker 1982; Canuto et al. 1982). Lunine (1985a) applied the atmospheric escape model of Watson et al. (1981) (discussed in Sec. II in the context of the present atmosphere of Pluto) to the primordial Titan atmosphere. For an EUV flux 100 times the present-day, the escape flux is $10^{15} \text{ g yr}^{-1}$, insufficient to permit the primordial atmosphere to escape within the age of the solar system. EUV fluxes greater than this were not considered as the model formalism breaks down; whether higher fluxes persisted sufficiently long to remove the primordial atmosphere remains unclear.

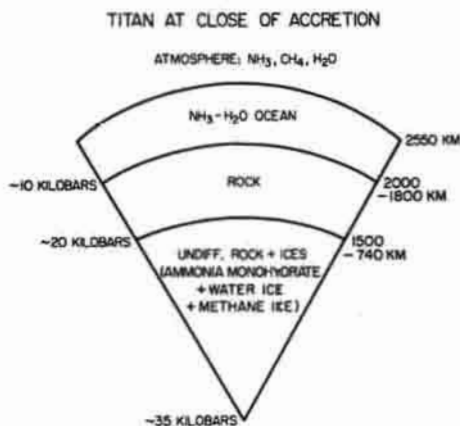


Fig. 13. Schematic model of the interior structure and atmospheric composition of Titan immediately after accretion. Radii are indicated on the right side of the figure; approximate pressure on the left (figure from Lunine and Stevenson 1987).

Loss of a massive Titan atmosphere by T-Tauri wind from the Sun (or an analogous process at Saturn) has never been quantified. Uncertainties include the coupling of the wind to the atmosphere (is it direct or through the Saturnian nebula?), and the timing and duration of the wind.

Impact of solar orbiting debris represents a potentially large source of energy for escape. This loss process is qualitatively different from hydrodynamical escape at the exobase level powered by EUV. It involves accelerating air in the lower atmosphere to escape velocity by shock waves accompanying the impactor during descent and after it hits the surface. The impact process and net loss of solid target debris have been considered by O'Keefe and Ahrens (1982c); atmospheric loss for the case of Mars has been considered by Watkins (1983; see also Lewis and Prinn 1984). Most recently, Walker (1986b) analyzed theoretically the atmospheric loss due to impacts as a function of the impactor velocity and the escape velocity of the planet. He concluded that (1) escape occurs only if the impactor velocity is greater than the planetary escape velocity, (2) impact erosion does not occur from planets with escape velocities $>10 \text{ km s}^{-1}$, and (3) the amount of gas which escapes is roughly the amount intercepted by the impactor.

Titan's escape velocity is 3 km s^{-1} . Impact of Saturn-orbiting planetesimals with relative velocities lower than this would have led to net accretion of material. Solar-orbiting debris, on the other hand, would have eroded the atmosphere and surface upon impact. The epoch of the accretion of Titan and its primordial atmosphere from Saturn-orbiting material could have been followed by a period when projectiles external to the Saturn system removed most of the gas. The Saturnian satellite cratering record has not yet been definitively interpreted in terms of solar- or planet-orbiting projectiles (Chapman and McKinnon 1986). However, if the Shoemaker and Wolfe (1984) analysis of the Jovian and Saturnian cratering record is correct, several hundred Earth masses worth of debris existed in the outer solar system at the close of planet formation. These objects could have been of singular importance in the escape and chemical modification of a primordial Titan atmosphere.

Structure and Cooling of Primordial Titan Atmosphere. Figure 14 illustrates a model for an ammonia-rich primordial Titan atmosphere. The atmospheric ammonia and water, in gaseous and cloud form, maintain the high surface temperatures by virtue of their high infrared opacities. Giant impacts cause escape of the atmosphere and hence reduction in the infrared opacity, resulting in cooling and consequent condensation of ammonia and water at the surface. Impact heating also converts ammonia to nitrogen, and methane to complex hydrocarbons. Photochemical conversion of ammonia to nitrogen also takes place in the upper atmosphere. These processes are detailed in the following subsection. As temperatures drop below 200 to 250 K, clathrate

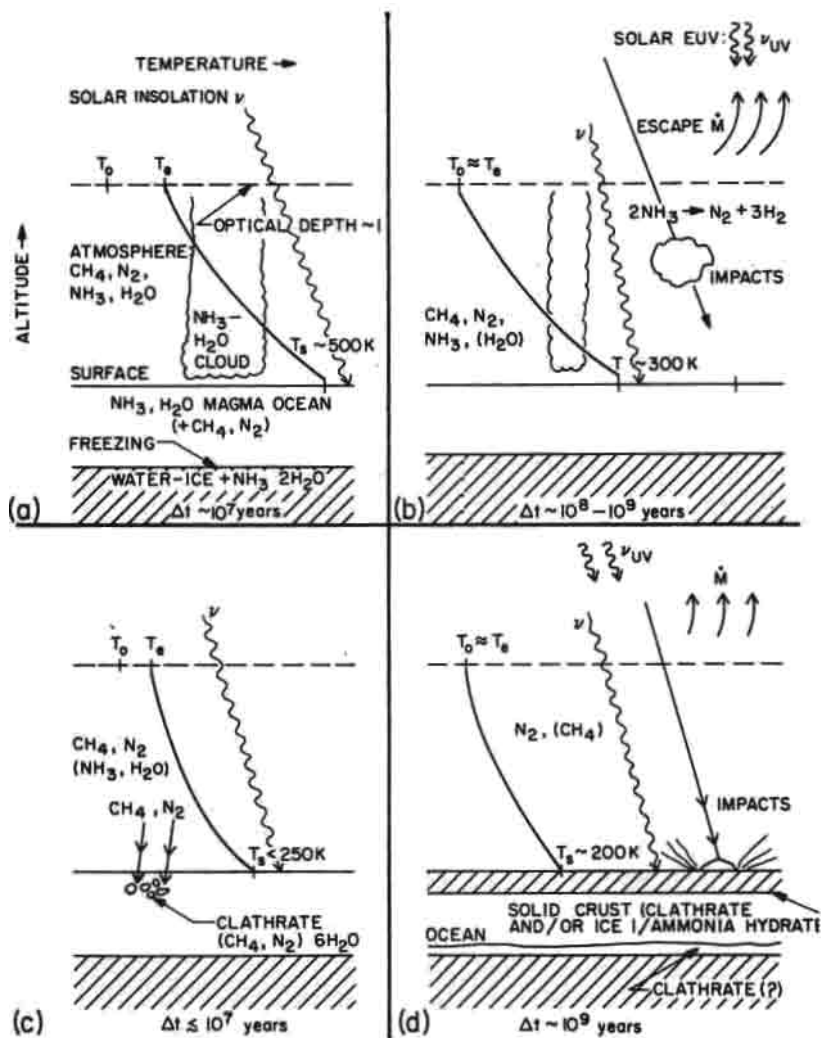


Fig. 14. Illustration of phases of atmospheric evolution after accretion. Temperature-altitude scale is schematic; time scales are typical for a model with atmospheric mass-loss rate of 10^{14} yr^{-1} and starting mass 10^{23} to 10^{24} g. Minor constituents are indicated in parentheses. A though some processes may occur in all panels, only those important to the particular stage a shown in a given panel. (a) Hot, post-accretional atmosphere cools down. (b) Atmosphere achieves thermal steady state in which effective temperature T_e is given by the insolation ν ; $T_e \approx T_o$. Cooling rate is now determined by mass-loss rate. Photochemical and impact-induced $\text{N}_2 \rightarrow \text{N}_2$ conversion may occur here (and in panel d). (c) Base of atmosphere enters clathrate stability field, dropping surface pressure rapidly and forcing $T_e > T_o$, increasing the cooling rate. (d) Ocean freezeover terminates clathrate formation; atmosphere returns to steady state (figure from Lunine 1985a).

formation at the base of the atmosphere may occur, causing a further drop in surface pressure and temperature. Eventually the surface freezes over.

The end state of such an evolution is hard to specify. If bombardment is efficient enough to remove 10^{25} g of atmosphere over 100 Myr, it is too much to ask that it leave behind 10^{22} g of nitrogen and methane. As discussed in Lunine and Stevenson (1987) the present surface methane complement was likely to have been outgassed from the interior during the overturning of Titan's core. If this occurred as late as 500 Myr after formation, the epoch of primordial atmospheric erosion would likely have been concluded. Was nitrogen outgassed with the methane, was it produced during the terminal bombardment and retained, or was it produced after the bombardment and methane outgassing? To address these questions we must consider the two processes by which ammonia can be converted to nitrogen in the early atmosphere of Titan: photolysis and shock heating due to impacts.

N₂ from NH₃ Photolysis. Ammonia can be efficiently converted to nitrogen photochemically (Atreya et al. 1977). The photolysis of NH₃ occurs following the absorption of solar ultraviolet photons with wavelengths between 1600 and 2300 Å. Neither CH₄ nor any other gas in significant proportion on Titan absorbs in this region. As a consequence, the photolysis of NH₃ would proceed unhindered by the presence of other constituents. Figure 15 shows a schematic of NH₃ photochemistry relevant to Titan. The photolysis of NH₃ yields amidogen radicals (NH₂) in the ground state. Production of NH (*a*¹Δ) is also likely, but with a low quantum yield of 4%. The maximum photolysis rate at Titan is on the order of 10^{-6} s⁻¹. Nearly 30% of NH₃ is recycled by the reaction of NH₂ with H. The reaction of NH₂ with itself yields hydrazine, N₂H₄. Hydrazine reacts with atomic hydrogen and also undergoes photolysis to yield hydrazyl, N₂H₃. The self-reaction of N₂H₃ then produces

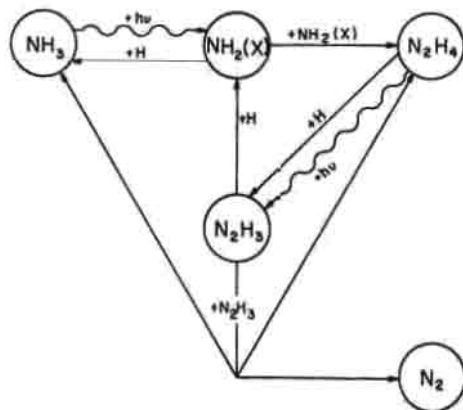


Fig. 15. Photochemistry of ammonia (figure from Atreya et al. 1978).

N_2 . Once N_2 is produced, it accumulates in the atmosphere, as it is inert and highly stable. A fraction (approximately 10%) of N_2 would, however, be lost due to the thermal and nonthermal escape mechanisms.

The scenario described works provided that the gas phase abundances of both NH_3 and N_2H_4 are appreciable. At the present-day surface temperature of Titan, 94 K, the vapor pressure and the corresponding mixing ratio (by volume) of NH_3 are, respectively, 2.7×10^{-8} mbar and 0.02 ppb. The low column abundance of NH_3 has not allowed detection of this species on Titan. The present abundance of NH_3 is too low to produce substantial amounts of N_2 by photolysis. If NH_3 photolysis were the source of Titan's N_2 , a warm temperature in the primordial atmosphere would be needed. Temperatures cannot be too high, however. Above approximately 300 K, comparable amounts of water and ammonia would be present in the vapor phase. The photolysis of H_2O would produce OH, whereas the photolysis of NH_3 would yield NH_2 . The reaction between NH_3 and H_2O and their radical products would entirely choke off the production of N_2H_4 and subsequently N_2 . Below 200 K, however, the saturation vapor pressure of NH_3 dominates that of H_2O . At the melting point of NH_3 (195.3 K), the ratio is nearly 100,000. Below 150 K, the saturated vapor density of the key intermediate constituent, N_2H_4 , drops dramatically with a corresponding drop in the yield of N_2 (Atreya et al. 1977). The photolysis of NH_3 leading up to the production of N_2 can thus proceed quite readily at temperatures between 200 and 150 K.

According to a pre-Voyager model of Atreya et al. (1978), the photolysis of NH_3 on Titan would proceed at a diurnally averaged rate of approximately $6 \times 10^{10} \text{ cm}^{-2} \text{ s}^{-1}$ assuming a temperature of 150 K. This implies that it could take up to 100 Myr, or 2% of the geologic time, to account for the present-day surface pressure of 1500 mbar on Titan. An epoch of enhanced solar ultraviolet flux would result in an increase in the rate of photolysis, and a corresponding decrease in the time constant for producing the present-day surface pressure of N_2 to as low as 10,000 yr (Atreya 1986). This estimate is based upon IUE observations of pre-main-sequence stars which suggest that the solar flux shortward of 2000 Å could have been as much as 10,000 times its present value (Zahnle and Walker 1982). Allowing for nonlinearities in the N_2 production rate due to the escape of N_2 , the decreasing vapor pressures of NH_3 and N_2H_4 as Titan cooled, and the effect on photolysis rate of the change with time of the solar ultraviolet flux, the above time constant could approach 50,000 to 100,000 yr—still short compared to geologic time scales (Atreya 1986).

The necessity for invoking enhanced solar flux to drive the conversion goes away if a long time period of ~100 Myr existed when Titan was warm. Even after the terminal bombardment phase erodes a primordial atmosphere, this is possible. Outgassing of all the methane required to produce the present ethane-methane ocean corresponds to a surface pressure of 20 bar, assuming no condensation. Pollack (1973) has calculated that a 0.5 bar surface pressure

of CH_4 alone would have led to enough greenhouse effect to raise Titan's surface temperature to 150 K. Rapid conversion of NH_3 to N_2 may still be necessary because of possible evolution of hazes and clouds that could prevent penetration of the photolyzing flux to the region where NH_3 was present.

Impact Production of Titan's N_2 . Projectiles passing through an atmosphere at supersonic velocities generate a shock in front of themselves. Atmospheric gas encountering the shock front is strongly compressed and heated to very high temperatures, on the order of thousands of degrees Kelvin. At these high temperatures thermodynamic equilibrium is very quickly realized, and a gas composition very different from the ambient atmosphere is produced. Reaction rates decrease very rapidly as the gas parcel subsequently cools by radiation, and the high-temperature chemistry is "quenched" into the parcel. In this manner, meteoroids passing through an early Titan atmosphere containing significant amounts of ammonia vapor may have converted a fraction of it to N_2 . Independent estimates of the amount of N_2 formed in this way during Titan's early history indicate that the shock-induced conversion of NH_3 to N_2 could easily have generated the satellite's current inventory of N_2 in ocean and atmosphere (Jones and Lewis 1987; Anderson and Stevenson 1987; McKay et al. 1988b).

The amount of nitrogen produced during passage of meteoroids through Titan's early atmosphere depends on the velocity and mass of the projectile, the temperature history of gas parcels, chemical reaction rates and the abundance of ammonia in the atmosphere. A convenient means for estimating the total amount of nitrogen generated by meteoroid passage through Titan's atmosphere is provided by the following equation:

$$[\text{N}_2] = E_K * F_K * Y \quad (14)$$

where E_K is the total kinetic energy of the projectiles participating in the conversion, F_K is the fraction of the kinetic energy going into shock heating, and Y is the number of moles of N_2 produced per unit of energy of shock heating. Projectiles with sizes between m and km are most effective at producing shock conversion since larger bodies pass through the atmosphere without losing much of their kinetic energy and smaller bodies dissipate the bulk of their kinetic energy above the cold trap, where little ammonia would be present (McKay et al. 1988b).

The yield Y depends on the quench temperature, the pressure of the shocked gas, and the mole fraction of ammonia in the ambient atmosphere. Jones and Lewis (1987) show that the value of Y is fairly insensitive to shock temperature and pressure over a wide range of reasonable values. Experimental simulations of the shock conversion of NH_3 to N_2 have been carried out by McKay et al. (1988b) who used a focused laser to generate a shock. They find that Y varies approximately linearly with ammonia mole fraction for fractions

above about 0.1, but that it sharply decreases with decreasing mole fraction below this value. Thus, significant shock conversion of NH_3 to N_2 occurred when ammonia was a major constituent of the lower atmosphere of Titan. This condition was most likely met during the satellite's accretion when heat deposited by impact raised the surface temperature well above its current value (McKay et al. 1988a,b).

Jones and Lewis (1987) estimated the shock production of N_2 during Titan's early history, subsequent to formation. Impactors derived from an early breakup of the neighboring satellite Hyperion and planetesimals scattered from the zone where Uranus and Neptune formed were studied as possible generators of Titan's N_2 atmosphere as well as a number of organic compounds. Using an estimate of the latter flux provided by Shoemaker and Wolfe (personal communication), they concluded that it was the dominant producer of shocked N_2 and that Titan's current N_2 volatile inventory could be generated by this source. In making this calculation, they assumed that the NH_3 mole fraction in the lower atmosphere was 0.5; this requires the hot gaseous accretion model described above.

Anderson and Stevenson (1987) and McKay et al. (1988b) advocated generating N_2 from NH_3 during accretion. In this case, the planetesimals that were adding mass to the satellite also chemically reprocessed some of the earliest atmosphere. Anderson and Stevenson (1987) obtained estimates of Y by using a laboratory-based reaction rate for the interconversion of N_2 and NH_3 and by calculating the temperature history of a gas parcel passing through a shock front. McKay et al. (1988b) derived Y from their laboratory data. Both groups concluded that Titan's N_2 volatile inventory could be generated by this shock processing.

Table III (McKay et al. 1988b) shows that a significant yield of organic compounds can be obtained in a mixture of NH_3 and CH_4 subjected to shock heating. For a laboratory simulation in which the starting materials were equal molar quantities of NH_3 and CH_4 , the yields of HCN and C_2H_2 are comparable to that of N_2 . The observed yields can be approximately reproduced by setting the quench temperature equal to 2000 K, as shown by the third column of the table. However, the much larger yield of C_2H_6 than expected on the basis of this quench temperature may reflect the role played by ultraviolet photolysis in the simulation (ultraviolet light is produced in the initial plasma discharge). Thus, copious quantities of organics, especially HCN and C_2H_2 , may have been produced by meteoroids passing through Titan's early atmosphere, ultimately to sediment out of the atmosphere onto the surface.

Photochemical Destruction of Primordial Carbon Monoxide. Incorporation of molecular nitrogen into Titan by accretion of clathrate brings in equal or greater amounts of carbon monoxide, as Fig. 12a shows. To reproduce the present atmospheric abundance of CO relative to N_2 , destruction of CO by photochemical or shock chemical processes must be invoked. Sam-

TABLE III
Gases Produced in a Laboratory Simulation of Shock Heating^a

Gas	Experimental Yield	Theoretical Yield ^b	Detection Method ^c
N ₂	1.2 × 10 ¹⁷	5.7 × 10 ¹⁷	1
H ₂	2.1 × 10 ¹⁸	4.0 × 10 ¹⁸	1
HCN	2.9 × 10 ¹⁷	2.6 × 10 ¹⁷	2
C ₂ H ₂	1.1 × 10 ¹⁷	4.8 × 10 ¹⁷	2
C ₂ H ₄	1.5 × 10 ¹⁷	4.8 × 10 ¹⁷	3
C ₂ H ₆	8.9 × 10 ¹⁵	9.2 × 10 ¹³	3
CH ₃ C≡CH	7.3 × 10 ¹⁵	1.4 × 10 ¹⁵	3
C ₂ H ₄	1.2 × 10 ¹⁵	2.2 × 10 ¹⁶	3
C ₃ H ₈	1.0 × 10 ¹⁴	4.7 × 10 ¹³	3

^aResults are from McKay et al. 1988b. The initial gases were CH₄ and NH₃ in equal molar proportions.

^bBased on thermodynamic equilibrium at a quench temperature of 2000 K.

^c1 = Thermocouple Gas Chromatography; 2 = Infrared Spectroscopy; 3 = Flame Ionization Detector Gas Chromatography.

uelson et al. (1983) formulated a photochemical scheme in which water from particulate material, raining down on Titan's atmosphere, could convert CO to CO₂, and reproduce the abundances of both in the atmosphere. Given a sufficient water influx rate, Samuelson et al. estimate that about 0.1 of a Titan atmosphere of CO could be destroyed over the age of the solar system. Whether the scheme is capable of destroying 100 times that amount (a conservative estimate of the amount of primordial CO brought in with nitrogen) has not been assessed.

Origin of Nitrogen on Titan: Observational Tests

We have enumerated two models for the origin of nitrogen on Titan: introduction of primordial nitrogen in clathrate hydrate formed in the nebula, and incorporation of ammonia into Titan followed by chemical conversion to molecular nitrogen. Both the bulk density of Titan and the atmospheric argon-to-nitrogen ratio provide tests of these models.

Test 1: Bulk Density of Titan. As noted above, Titan's density falls between that for a rock-water ice body formed from a methane-rich and carbon monoxide-rich gaseous nebula. (Again, the difference lies in the amount of oxygen available to form water after sequestration into rock and carbon species.) Since it is easier to envision the loss of water rather than rock during accretion, the measured density implies one of the following simple scenarios: (a) Titan formed in a relatively methane-rich environment and lost some water during accretion. Because CO is not the dominant carbon species in this model, most of the clathrate cages would contain methane, and nitrogen

would be largely excluded from the clathrate (Fig. 12). Hence the only source of nitrogen readily incorporated in Titan would be ammonia. (b) Titan formed in an environment containing comparable amounts of methane and carbon monoxide with a corresponding rock-to-ice ratio directly reflected in the present bulk density (corrected for compression). Again, because of the strong propensity for methane to occupy most of the cage sites, the amount of molecular nitrogen brought into Titan in clathrate is probably insufficient to account for the present-day nitrogen-to-(methane + processed hydrocarbons) ratio. Of course, more complex models are possible, in which the rock-to-ice ratio of planetesimals which formed Titan is decoupled from the amount of CO in the nebular gas (for example, due to processes involved in the spinout of a Saturnian nebula). The silicate mass fractions for various satellite systems, and corresponding amounts of CO and CH₄ in the primordial nebulae are quantified in Johnson et al. 1988).

Test 2: Argon to Nitrogen Ratio. Owen (1982*b*) first pointed out that if Titan's nitrogen were primordial, the argon-to-nitrogen ratio in the atmosphere should be approximately solar. He also showed that the low upper limit to neon in the atmosphere (1%) is inconsistent with an atmosphere captured directly from a solar composition gas. Thus the atmosphere was brought into Titan in ice phases condensed from the nebular gas out of which Titan formed. Lunine and Stevenson (1985*a*) quantified a compositional test of the origin of nitrogen in Titan's atmosphere using clathrate thermodynamics. If the present-day nitrogen is derived entirely from clathrate, then the Ar-to-N₂ ratio in Titan's atmosphere would be 10⁻² to 10⁻¹ (Lunine and Stevenson 1985*a*). The molecular properties of Ar and N₂ are such that their outgassing histories should be similar. If the N₂ were derived from photochemistry or shock heating, and any primitive N₂ transported in clathrate, then Ar/N₂ would depend on the amount of N₂ produced photochemically and on the argon outgassing and escape history. Since the clathrate is dominated by CH₄ for all but the most oxidized-nebula scenarios (Fig. 12*a*), the amount of argon brought in depends upon its propensity for incorporation in clathrate, which is similar to that of N₂. Then the Ar/CH₄ ratio in the clathrate is about 10⁻⁵. If argon outgassed to a similar extent as the CH₄ brought into Titan in clathrate, then the argon-to-N₂ ratio in the present atmosphere would be ~10⁻⁵, assuming (for example) a methane-to-nitrogen ratio in the current atmosphere plus ocean of order unity. The maximum possible argon abundance brought into Titan in methane-dominated clathrate could be as high as 1 to 10% of the atmospheric nitrogen abundance, but would require that all of the argon be outgassed and retained by the atmosphere, while only a small fraction of the methane did likewise. We regard this as unlikely.

Thus, a low value of argon in Titan's atmosphere (<<1%) would suggest nitrogen was derived from ammonia; a large argon abundance (>1%) would suggest that much of the nitrogen was brought into Titan as N₂.

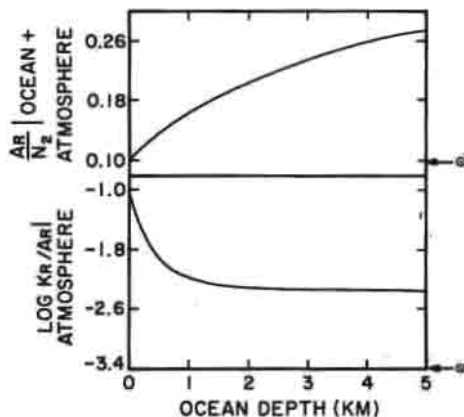


Fig. 16. Abundance patterns in Titan's atmosphere and ocean, as a function of ocean depth, predicted from solubility considerations. See text for details (figure from Lunine and Stevenson 1985a).

The above test will be affected slightly by the presence of the ethane ocean. Figure 16 plots the argon-to-nitrogen ratio in ocean and atmosphere, assuming the atmospheric value is measured at 10%. This figure also plots the logarithmic Kr-to-Ar ratio in the atmosphere assuming an ocean-plus-atmosphere ratio of 10%. Both fractionation effects are due to differential solubility of the gases in liquid hydrocarbons. Clearly, interpretation of atmospheric mixing ratios in Titan's atmosphere could require surface sampling if an ocean is present.

Origin of Methane on Titan

Lunine and Stevenson (1987) pursued a model in which methane is incorporated into Titan as clathrate hydrate, then outgassed during core overturn of the satellite induced by radiogenic heating. The model is described in the chapter by Schubert et al., and we therefore do not elaborate. However, the implications of the model are twofold: (1) Most of the methane brought into Titan is lost during accretion—only about 10% is retained in the deep interior beyond accretion; (2) Outgassing of methane from the interior must occur late, after $\sim 5 \times 10^8$ yr, to avoid trapping of methane in an aqueous ammonia upper mantle and to avoid loss during hydrodynamic escape. The subsequent transition to the present epoch has not been studied, but could involve complex climate changes as a methane-nitrogen ocean is formed and evolves to the present state.

Figure 17 presents two schematic timelines for the origin and evolution of Titan's atmosphere, based upon the primitive nitrogen and ammonia-converted nitrogen hypotheses.

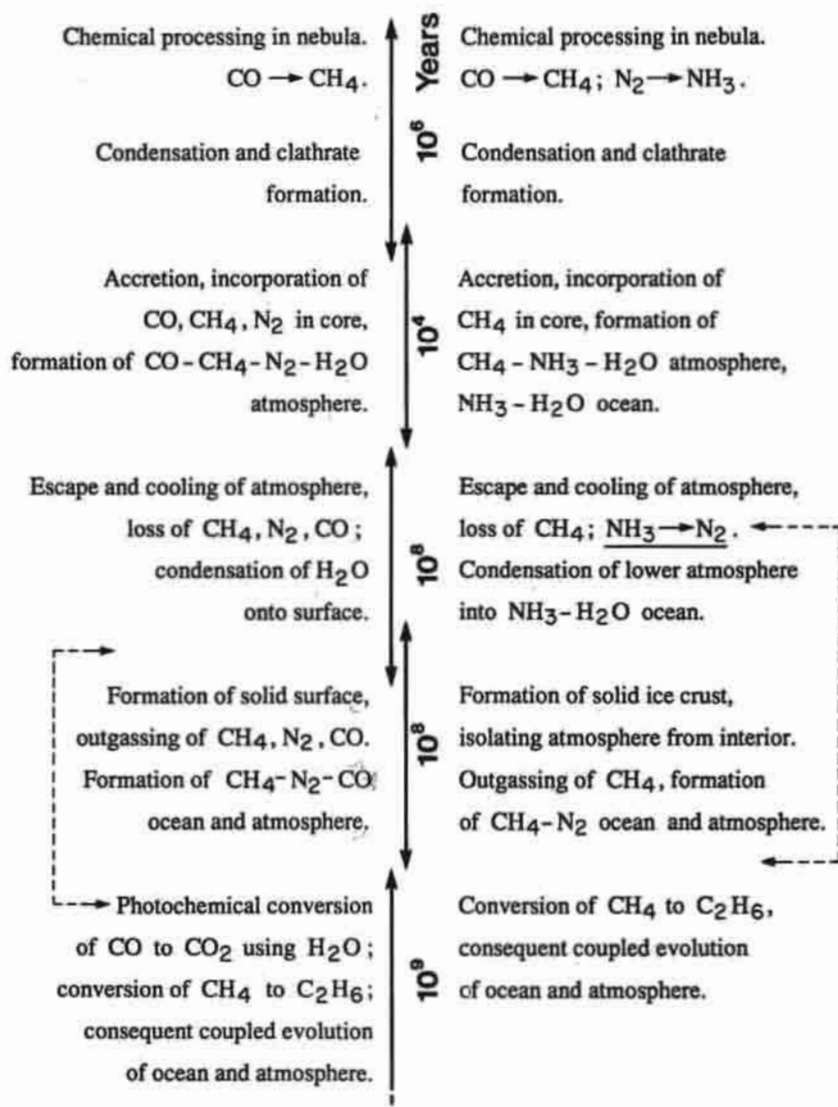


Fig. 17. Schematic timelines of Titan evolution, assuming (left) primordial N_2 scenario and (right) N_2 derived from ammonia.

Why do not Ganymede and Callisto have Nitrogen Atmospheres?

The absence of detectable atmospheres on Ganymede and Callisto, physically near-twins of Titan, requires explanation. The nebula around Jupiter was too hot to allow formation of methane clathrate (Lunine and Stevenson 1982), but could have allowed condensation of ammonia hydrates. We can only speculate on the essential differences between the evolution of the giant Jovian satellites and Titan, but three key differences suggest themselves: (1) Ganymede and Callisto never accreted significant quantities of ammonia, hence no source for a nitrogen atmosphere existed. (2) Ganymede and Callisto incorporated ammonia; a nitrogen atmosphere was raised but was eroded away by intense magnetospheric bombardment and/or a solid body bombardment flux more intense or longer in duration than at Saturn. (3) Ganymede and Callisto incorporated ammonia but not methane; as a consequence no methane outgassing occurred, a post-bombardment greenhouse phase never occurred and ammonia was converted to N_2 only in very small amounts.

Whether any of these scenarios is right requires spectroscopic observations of the poles of Ganymede and Callisto by Galileo, since molecular nitrogen and other volatiles could be cold-trapped at extremely high latitudes on those satellites (D. J. Stevenson, personal communication).

Implications of Deuterium Abundance for the Origin of Titan

Owen (1987) assessed the significance of the enhanced deuterium abundance in Titan's atmosphere for its formation. He concluded that it was unlikely that processes in the solar or giant-planet nebulae could have produced such an enhancement, and that some of Titan's atmosphere must have been contributed by interstellar material which never fully equilibrated with the hydrogen gas forming the solar nebula. Grinspoon and Lewis (1987a) have also found that it is difficult to obtain significant fractionation in the nebula, even in the presence of surface catalysis on grains. The delivery vehicle for the interstellar deuterium is uncertain. Although the deuterium enhancement seen in Titan's atmospheric methane is much less than that found in organic phases in meteorites (Yang and Epstein 1983), it is close to the D/H ratio in the water component of Halley's comet (1 to 5×10^{-4} ; Eberhardt et al. 1987a). The hypothesis that comets supplied deuterium-rich ices to Titan has yet to be quantified; the net gain of cometary material to the atmosphere depends upon a number of factors such as impactor velocity, size distribution and volatile content, as well as on the atmospheric mass of Titan at the time. In any event, Owen's assertion that the deuterium enhancement is interstellar cannot be tested until the origin of cometary material itself is determined. This will require *in situ* measurement of the D-to-H ratio in the ice component of a comet nucleus, together with analyses of molecular abundances of species trapped in the ice. Such a test awaits the development of the Comet Rendezvous Asteroid Flyby (CRAF) Mission. Observations of comets from the

next generation of infrared observatories, e.g., Stratospheric Observatory for Infrared Astronomy (SOFIA), Infrared Space Observatory (ISO) and Space Infrared Telescope Facility (SIRTF), will also be required.

Origin of Volatiles on Triton and Pluto

Questions which we can address about Titan's volatiles cannot be addressed for Triton until certain measurements are made. These include determination of bulk density and measurement of (or upper limits on) abundances of atmospheric argon and neon. These tests will be performed during Voyager 2's flyby in 1989.

The density derived for the Pluto-Charon system (Tholen et al. 1987; Tholen and Buie 1987) strongly suggests an origin in a water-depleted region; i.e., a CO-rich gas such as the solar nebula. However, the presence of methane shows that the carbon in the nebula was not purely in CO. Trapping of nebular gases in water ice, either by adsorption or clathration, necessarily results in chemical fractionation effects. Relative to carbon monoxide, methane is preferentially incorporated in water ice (Lunine and Stevenson 1985a). Hence, an origin for Pluto in a CO-rich nebula with traces of methane could lead to (a) a high bulk density, and (b) incorporation of some methane along with carbon monoxide during accretion. Lunine (1987) concluded that measurement by *Giotto* of comparable amounts of methane and carbon monoxide coming from the nucleus of Halley's comet is consistent with that comet's origin in just such a nebula, assuming the gases were trapped in clathrate hydrate.

Finally, scenarios for origin and evolution of Triton and Pluto's atmospheres must also consider the thermal effects of catastrophes such as orbital ejection or capture. This issue has been examined by McKinnon (1984).

V. RELATIONSHIP TO TERRESTRIAL-PLANET ATMOSPHERES

We consider the relationship of the atmospheric composition of Titan, Triton and Pluto to those of the terrestrial planets. Nitrogen- and carbon-containing gas species represent the major constituents of both types of atmospheres. For all of these atmospheres, except Venus', the abundance of water vapor is limited by the surface temperature, although this limitation is more severe in the case of the outer solar system objects.

Perhaps the most significant difference between the inner and outer solar system atmospheres is their state of oxidation. The Earth represents an extreme case in this regard due to the high abundance of molecular oxygen. This apparently reflects the Earth's unique position in the solar system as an abode of life. However, C is present in its fully oxidized state CO₂ in all the terrestrial atmospheres and in its fully reduced state in the outer solar-system objects. This difference could reflect the ability of water to buffer the oxidation state of the carbon species in the atmospheres of the terrestrial planets,

while the oxidation state of the C in the outer solar system atmospheres may be primordial, preserved because water buffering is not possible at the low temperatures obtained. Much of the terrestrial buffering is due to dissociated water in magma chambers.

Size may also have played an important role in the differing evolutionary history of these two classes of atmospheres. On the one hand, the terrestrial planets may be large enough so that their atmospheres evolved significantly over their lifetime due to volcanic and tectonic changes with time. Thus, for example, the Martian atmosphere may have been much denser during its early history and a clement climate may have prevailed due to more vigorous outgassing (Pollack et al. in preparation). By way of contrast, the outer solar system objects may have undergone early dramatic changes followed by tectonic quiescence; subsequent evolution would be externally driven by photochemical processes. (Since an ammonia-water magma beneath the surface of Titan could be maintained to the present day, that satellite may be tectonically active [Lunine and Stevenson 1987].)

Another parallel between the inner and outer solar system atmospheres has to do with partitioning of carbon and nitrogen species between the atmosphere and lithosphere. In the case of the Earth and probably Mars, much more C resides in the lithosphere than in the atmosphere at present, due to weathering processes that readily convert CO₂ gas into carbonate rocks, and in the case of Mars, to the large buffering capacity of the regolith. In the outer solar system objects, this buffering is due largely to the low surface temperatures which put most of the methane into surface frosts or oceans. Nitrogen is more volatile so that a much larger fraction of it is present in the atmospheres of Earth, Mars and Titan. Venus is, of course, a special case since its high surface temperature prevents the accumulation of large near-surface reservoirs of C and N.

VI. CONCLUSIONS

We have reviewed the current state of knowledge of the atmospheres of Titan, Triton and Pluto and theoretical models for their origin and evolution. All three atmospheres contain methane, while Titan and probably Triton also have nitrogen. The fundamental driving process for the evolution of Titan's atmosphere is the irreversible photolysis of methane. If a surface reservoir of liquid methane exists to resupply the atmosphere, then it is subject to enrichment in ethane due to the long-term photolysis of methane. The ocean in turn drives slow climate changes as the atmospheric composition changes in response to the ocean evolution.

The key issue in the origin and early evolution of Titan's atmosphere is the source of molecular nitrogen: was it brought into Titan as molecular nitrogen or ammonia? A diagnostic experiment to test the two models is measurement of atmospheric argon: a low ($\ll 1\%$) value of the atmospheric argon-to-nitrogen

ratio implies the present molecular nitrogen was derived from ammonia, while a high (>1%) value would suggest an origin as N_2 . Two schemes for conversion of ammonia to nitrogen are photolysis and shock chemistry during projectile impacts. Coupling of the early evolution of Titan to the slow evolution of atmosphere and (if existent) hydrocarbon ocean remains a major challenge.

Little can be said about the evolution of Triton's and Pluto's atmospheres until definitive compositional and physical measurements can be made. The Voyager 2 encounter with Triton in 1989 is expected to raise our understanding of that object's atmosphere to the point that useful comparative studies with Titan's can be made. The seasonal modulations of Triton's atmosphere may set limits on the abundance and distribution of volatiles on its surface; long-term Earth-based observations are required to observe such effects.

The parallels and differences between these outer solar system atmospheres and their terrestrial cousins challenge our understanding both of their origin, and of the operation of current physical processes in the atmospheres. Most challenging, and perhaps most rewarding, is to establish the interaction between the atmospheres and surface reservoirs. In every case except Venus, the atmospheres we observe on the "small" bodies of the solar system are in intimate contact with surface and subsurface volatiles, which in the long term control the composition and evolution of these thin gaseous envelopes.

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