# The Greenhouse of Titan\*

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Both non-gray radiative equilibrium and gray convective equilibrium calculations for Titan indicate that the discrepancy between the equilibrium temperature of an atmosphereless Titan and the observed infrared temperatures can be explained by a massive molecular hydrogen greenhouse effect. The convective calculations indicate a probable minimum optical depth of 14, corresponding to many tens of km-atm of  $H_2$ , and total pressures of ~ 0.1 bar. The tropopause is several hundred km above the Titanian surface and at a temperature of about 90°K. Methane condensation is likely at this level. Such an atmosphere is unstable against atmospheric blow-off unless typical mesosphere scale heights are < 25 km, an unlikely situation. Blow-off can also be circumvented by exospheric temperatures near the freezing point of hydrogen. It is considered more plausible that the present atmosphere is in equilibrium between outgassing and blow-off of the one hand and accretion from protons trapped in a hypothetical Saturnian magnetic field on the other; or exhibits uncompensated blow-off of outgassing products. To maintain the present blow-off rate without compensation for all of geological time requires an outgassing equivalent to the volatilization of a few km of subsurface ices. Photo-dissociation of these volatilized ices produces the observed high abundance of  $H_2$  as well as large quantities of complex organic chromophores which may explain the reddish coloration of the Titanian cloud deck. An extensive circum-Titanian hydrogen corona is postulated. Surface temperatures as high as 200°K are not excluded. Because of its high temperatures and pressures and the probable large abundance of organic compounds, Titan is a prime target for spacecraft exploration in the outer solar system.

# **INTRODUCTION**

Allen and Murdock (1971) observing in the  $8-14\mu$  window in the Earth's atmosphere discovered a brightness temperature for the Saturnian satellite, Titan, of  $125^{\circ}$ K with a formal error of  $\pm 2^{\circ}$ . This is significantly higher than the equilibrium temperature of a rapidly rotating Titan of  $T_e \simeq 87^{\circ}$ K, appropriate for its probable Russell-Bond bolometric albedo,  $\overline{A} \simeq 0.2$ . As in the case of Venus, where a major discrepancy with the equilibrium temperature was discovered at microwave fre-

\* The bulk of the conclusions of this paper were presented (Sagan and Mullen, 1972a) at the Hawaii meeting of the Division for Planetary Sciences of the American Astronomical Society, March, 1972. quencies, this discrepancy strongly suggests a greenhouse effect. Because Titan is the only satellite in the solar system known to have an atmosphere, such a suggestion may perhaps be considered not implausible. Methane was discovered early (Kuiper, 1944) and at least fairly good evidence for molecular hydrogen has been found more recently (Trafton, 1972).

The abundance of hydrogen deduced by Trafton is, for an acceleration due to gravity  $g \simeq 150$  cm sec<sup>-2</sup>, ~ 6mb, with a comparable partial pressure of methane. However there is now significant evidence for the presence of clouds on Titan. Dollfus (1961) early described varying bright and dark patterns seen visually on Titan which he interpreted as cloud phenomena. However the angular size of

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Titan as seen from the Earth is extremely small. More recently, from the absence of a negative branch in the polarization/phase angle curve at small phase angles, Veverka (1973) has deduced that we are observing neither a solid surface nor a Rayleigh atmosphere at optical frequencies, but rather a cloud or aerosol. Veverka's observations have been extended and confirmed by Zellner (1973). If Titan were, for example, about half clouded, significant radiation would be scattered from the surface and a negative branch would be detected. We must therefore conclude that Titan has a dense cloud layer, a circumstance which again suggests in a general way the Venus case. The varying markings observed by Dollfus, if real, must then apply to a patchy higher cloud level than the clouds viewed polarimetrically. The remarkable reddish coloration of Titan (McCord et al., 1970) is unlikely to be due to a gas phase atmospheric constituent; at least no such constituent has been identified or suggested. The most reasonable alternative is that the coloration is within the lower complete cloud cover. The near ultraviolet optical depth for  $\sim 10 \,\mathrm{mb}$  of hydrogen and methane is quite small (Calvert and Pitts, 1966). Accordingly these clouds should be subjected to significant ultraviolet irradiation with attendant changes in their chemistry. We return to the question of the composition of these clouds later. But the existence of possibly complex cloud phenomena on Titan implies that the tentatively observed methane to hydrogen ratio may not necessarily be applicable to the lower atmosphere; more important it implies that the surface pressure on Titan may be considerably in excess of the characteristic spectrometric values ~ 10 mb.

The principal problem is to identify a plausible infrared absorber. Since the observation of Allen and Murdock, two further observations have been made in the  $8-14\mu$  window by Gillett and Forrest (1972). At the shorter end of the window a brightness temperature of  $144 \pm 3^{\circ}$ K is found. With a reasonable value for the surface emissivity this suggests a minimum value of the surface temperature  $T_s$  on

Titan of  $150^{\circ}$ K. If any significant atmospheric or cloud absorption occurs in the  $8-9\mu$  region, the surface temperature can of course be higher. A  $150^{\circ}$ K blackbody has the Wien maximum of its Planck distribution at about  $19\mu$ .

The temperatures on Titan are too low for greenhouse effects to be provided by carbon dioxide and water, the gases which produce greenhouse effects on the Earth and Venus. The spectroscopic observations of small quantities of methane and hydrogen suggest that, like the other atmospheres in the outer solar system, the Titanian atmosphere is reducing. The obvious first candidates by analogy with the Jovian planets, by cosmic abundances, and by their vapor pressures are hydrogen, methane and ammonia. The relative abundances of these molecules are not immediately obvious: The cosmic abundance of H<sub>2</sub> is  $\sim 10^3$  times that of methane and ammonia but, as is discussed below, H, should be lost at a very great rate from Titan. However the character of the lossthe blow-off mechanism---is such that all constituents should be approximately equally depleted. Thus from cosmic abundance arguments alone---and these may certainly be too simplistic-we would expect an  $H_2$  greenhouse. Even if the temperatures at Titan during its accretion were low enough for the condensation of methane but not for the condensation of hydrogen, considerable hydrogen may have been occluded and combined as clathrates among the ices of the accreting satellite.

If we restrict ourselves to permitted and pressure induced dipole and quadrupole transitions of water, ammonia, helium and methane, there is very little opacity to be found in the wavelength range around  $19\,\mu^1$ . Hydrogen on the other hand has quadrupole and pressure-induced dipole transitions in this region, which are well known in the calculation of the Jupiter greenhouse. Hydrogen satisfies the three

<sup>1</sup> Since presentation of this paper, Dr. J. B. Pollack has pointed out to me that octopole transitions of methane may be significant. We neglect such transitions in the present paper to preserve the argument originally presented at the Hawaii meeting.

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requirements for the Titanian greenhouse: high cosmic abundance, high vapor pressure, and high infrared opacity.

As a first attempt at calculating the Titan greenhouse, we consider a two-level step function transmissivity model which has been used previously (Sagan and Mullen, 1972b; 1972c). This is a pure radiative equilibrium model which furthermore neglects the possibility that there are wavelength regions which are neither negligibly nor totally absorbing. But because radiative gradients tend to be steeper than convective gradients, it provides a useful first approach to this problem. Figure 1 shows the results for  $T_s$  as a function of the assumed A for two values of the surface emissivity, e, and for various mixtures of methane, ammonia and hydrogen. We have taken several hundred m-atm of CH<sub>4</sub>, several m-atm of  $NH_3$  and ~ 100km-atm of  $H_2$ . We find that methane alone or methane and ammonia together provide at most a 20°K greenhouse effect, which is inadequate to account for the observations. However  $\sim 100 \, \text{km}$ atm of molecular hydrogen provides adequate opacity to match the observations; and the quantities of gases we have discussed are capable in this model of giving surface temperatures between 200 and 260°K.

This conclusion is supported, at least weakly, by the finding of Morrison et al. (1972) that the 20  $\mu$  brightness temperature of Titan is  $93 \pm 2^{\circ}$ K—higher than  $T_e$  but significantly lower than the brightness temperatures deduced in the 8-14 $\mu$  window. The pressure induced dipole transitions of hydrogen have significantly greater opacity in the  $20\mu$  than in the  $10\mu$ window, and Morrison et al. deduced the possible presence of  $H_2$  on Titan on these grounds. The preceding calculation was however the first quantitative attempt at calculating the Titan greenhouse. Because radiative gradients exceed convective gradients deep in a planetary atmosphere, the temperatures of Fig. 1 are somewhat high.

We now proceed to the simplest category of greenhouse models with convective equilibrium. The basis of these calculations is given by Sagan (1969). The procedure is essentially as follows: A surface temperature is assumed and the wavelength integrated equivalent gray optical depth above the surface calculated from

$$\tau = \frac{2}{3} (T_s/T_e)^{\eta_{\gamma(s+1)/\gamma-1}}$$
(1)

In Eq. (1)  $\gamma$  is the ratio of specific heats. Because vibrational transitions of H<sub>2</sub> are forbidden at low temperatures and permitted at high, within the temperature range appropriate to the Titan problem  $\gamma = \gamma(T)$ . Because it appears in the exponent, this can be a rather significant effect. In Eq. (1) *s* is the exponent on an assumed power law relationship between the gray absorption coefficient and the pressure. For pressure-induced transitions s = 1, which, through the Poisson equation, is equivalent to the statement that the optical depth is proportional to the square

1.0 A-0.1 Te-88.5\*K A=0.2 Te=86 A=0.3 Te=83 09 280 260 240 220 ----200 ¥ ŝ 180 •ب 160 140 120 100 S(CHa+ NHa); olso(NHa) 80 0,1 0.2 0.3 0.4 0.5 Τ FIG. 1. Radiative equilibrium surface tem-

FIG. 1. Radiative equilibrium surface temperatures on Titan, calculated as a function of the Russell-Bond bolometric albedo,  $\overline{A}$ , for two values of the surface emissivity, e, for mixtures of ~ 100 km-atm H<sub>2</sub>, ~ 300 m-atm CH<sub>4</sub> and ~ 3 m-atm NH<sub>3</sub>. An all-or-none step function transmissivity model was used.

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### TABLE I

$T_s$	130°K	150	180	210
$\lambda_{max}$	$22\mu$	19	16	14
$\hat{\tau}[\eta(1+s)=1]$	2	3	5	8
$\hat{\tau}[\eta(1+s)=2]$	6	14	42	107
$\tilde{\tau}[\eta(1+s)=3]$	18	64	330	1360
$P_s[\eta=1,s=0]$	0.03	0.05	0.08	0.13
$P_{s}[\eta=1,s=1]$	0.03	0.05	0.08	0.13
$P_s[\eta = 1.5, s = 1]$	0.05	0.10	0.22	0.45
$w_{\rm H_2}[\eta = 1, s = 0]$	$21\mathrm{km}$ -atm	32	55	88
$w_{\rm H_2}[\eta = 1, s = 1]$	21	32	55	88
$w_{\rm H_2}[\eta = 1.5, s = 1]$	36	68	154	310
$\Gamma_{\rm ad}[\eta=1]$	0.12K°/km	0.12	0.11	0.11
$\Gamma_{\rm ad}[\eta = 1.5]$	0.083	0.080	0.076	0.073
$T_t[\eta=1,s=0]$				
$T_t[\eta=1,s=1]$	101°K	100	99	98°K
$T_t[\eta = 1.5, s = 1]$	86°K	86	86	85°K
$Z_t[\eta=1, s=0]$				
$Z_t[\eta=1,s=1]$	230Km	420	710	1000
$Z_t[\eta = 1.5, s = 1]$	$530 \mathrm{Km}$	800	1200	1700
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of the pressure. Also in Eq. (1)  $\eta$  is defined by the equation

$$\left(\frac{dT}{dz}\right)_{\rm ad} = -\frac{g}{\eta c_p} \tag{2}$$

for the adiabatic gradient in a convective atmosphere;  $\eta$  represents the departure from the dry adiabatic lapse rate, due either to the latent heat of condensation or to atmospheric circulation. In the Earth's atmosphere  $\eta = 1.6$ . Table I shows, for four sample values of  $T_s$ , the resulting values of  $\tau$  for the cases  $\eta(1+s) = 1, 2, 3$ . Especially for the high temperature cases and  $\eta(1+s) \ge 2$ , quite high values of  $\tau$  are implied, approaching those necessary to explain the Venus greenhouse effect (Sagan, 1969). From these values of  $\tau$ , and the Poisson equation, the surface pressure,  $P_s$ , can be found:

$$P_s/P_0 = (1.5\tau)^{1/(s+1)} \tag{3}$$

where we have taken  $\tau = 2/3$  at the effective spectroscopic pressure level  $P_0 \sim 10^{-2}$ bars. If CH<sub>4</sub> is a major constituent,  $P_0 \sim 10^{-1}$  bars is possible. The resulting surface pressures  $P_s$  for an array of values of s and  $\eta$  are shown in Table I. We see that values of  $P_s \sim 0.1$  bar are required for pure H<sub>2</sub>, and  $P_s \sim 1$  bar for CH<sub>4</sub> as a major constituent. From the equation of hydrostatic equilibrium, corresponding values of  $w_{\rm H_2}$ , the hydrogen abundance, are also calculated. We see that, for the most likely (s-1) cases,  $w_{\rm H_2} \sim 100$  km-atm. From the results compiled by L. G. Young, whose opacities also served as the basis for the calculations of Fig. 1, the values of  $\tau$ , P, and  $w_{\rm H_2}$  exhibited in Table I are approximately consistent with the measured opacities of H<sub>2</sub>.

Table I also gives from Eq. (2) crude estimates of the adiabatic lapse rate on Titan for a pure H<sub>2</sub> atmosphere, and for  $\eta = 1$  and  $\eta = 1.5$ . In the latter case, the condensation of a minor constituent or atmospheric circulation can account for  $\eta > 1$  even though the atmosphere is composed primarily of H<sub>2</sub>. The level at which the convective and radiative temperature gradients are equal is a rough estimate of the temperature,  $T_t$ , at the Titanian tropopause. This temperature

<sup>(</sup>Errors due to averaging  $\gamma$  are about 10% in  $\tau$  and  $P_s$ . For CH<sub>4</sub> as a major constituent,  $P_s$  values are raised by a factor ~10.)

level is approximately given by (Sagan, 1969)

$$\left(\frac{dT}{dz}\right)_{\rm rad} / \left(\frac{dT}{dz}\right)_{\rm ad} = \frac{\gamma\eta(1+s)}{n(\gamma-1)} \left[1 - (T_0/T_t)^n\right] = 1 \quad (4)$$

where n is the exponent of a power law approximation to the wavelength integrated Planck function, and is here taken as 4;  $T_0$  is the planetary skin temperature here taken as  $2^{-1/4} \check{T}_e$ . Corresponding values of 83 to 106°K are displayed in Table I. These temperatures are sufficiently close to the frost point of 6mb CH4  $(73^{\circ}K)$  to suggest a tropopause methane cloud. Ultraviolet irradiation of such clouds should produce red organic chromophores (see below). The tropopause altitudes,  $Z_{t}$ , for both values of  $\eta$  are also given in Table I where we see characteristic values of several hundred km, implying a very deep troposphere.

[Note added October 14, 1972. Since the calculations for this paper were completed, J. B. Pollack (1973) has computed a much more exact non-gray radiative-convective greenhouse which invokes octopole pressure-induced transitions for methane. While Pollack concludes that the methane to hydrogen ratio is of the order of unity, his other conclusions concerning the partial pressure and tropopause temperature are of the same order as given here.]

Thus  $P_s \sim 0.1$  bars and an atmosphere composed largely of molecular hydrogen appears to be consistent to first order with all of the available observations, although we have made no attempt here to calculate an explicit emergent flux as a function of wavelength. There is however one difficulty with these ideas, first pointed out to me by John Lewis and R. G. Prinn of MIT in discussion at the Hawaii meeting after my paper was read, a problem having to do with blow-off. The blow-off of a planetary exosphere occurs when the root mean square velocity  $v_{\rm rms}$  is of the same order as the escape velocity,  $v_e$ . At this point the ordinary Jeans evaporative escape is replaced by hydrodynamic flow in which even high molecular weight constituents

can be carried by the low molecular weight blow-off flow.

The number density at the base of a planetary exosphere can be written

$$n(h_c) \sim (2\sigma \mathrm{H})^{-1}, \qquad (6)$$

where  $\sigma$  is the collision cross section and H is the scale height appropriate to the altitude,  $h_c$ , at the base of the exosphere. The composition of the exosphere specifies  $\sigma$  and the molecular weight; therefore  $n(h_c)$  is determined by  $h_c$  and by the exosphere temperature,  $T_e$ . If  $h_c$  is large,  $g \propto (R+h)^{-2}$  where R is the radius of the planet or satellite, becomes important. If we assume, as is crudely applicable to the Earth's atmosphere, a barometric equation from the tropopause to the base of the exosphere of Titan, the condition which must be satisfied to have a planetary exosphere at all, and therefore prevent blow-off is

$$\exp\left[-h_c R^2 / H_0 (R+h_c)^2\right] \simeq R^2 / [2 \times 10^{18} \sigma H_0 (R+h_c)^2]$$
(7)

where  $H = H_0(R + h_c)^2/R^2$ , R is taken as 2420 km,  $h_c$  is the altitude at the base of the exosphere and  $H_0$  is the scale height near the surface. We have assumed  $n(h_0) \sim 10^{18}$  $cm^{-3}$ , which will not affect the results at the tropopause significantly. For molecular hydrogen and  $T_0 \sim 100^{\circ}$ K,  $H_0 \sim 250$  km. The two sides of Eq. (7) are plotted in Fig. 2. We see that blow-off cannot be prevented unless  $H_0 \leq 25$ km; that is, for quite high mesospheric molecular weights and quite low tropopause temperatures. On the basis of considerations already mentioned, both of these alternatives seem unlikely. A much higher value of the mean molecular weight might be obtained by having molecular nitrogen in the atmosphere as proposed by Hunten (private communication, 1972); however,  $N_2$  is thermodynamically unstable in an excess of hydrogen (Lippincott et al., 1967) and, at least in the case for the Earth,  $N_2$  is a product of biological activity. However, some N<sub>2</sub> is in equilibrium with an excess of ammonia and hydrogen (Lippincott et al., 1967) and it would be interesting to see whether under photochemical pumping the nitrogen abun-

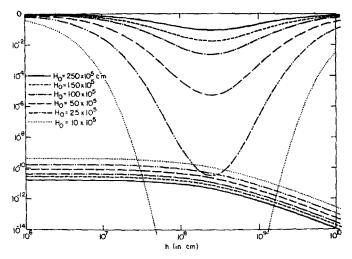


FIG. 2. Conditions for blow-off in the Titanian atmosphere, from Eq. (7). Blow-off is prevented when the two sets of curves intersect, i.e., for values of the tropospheric scale height  $\leq 25$  km. The abscissa is the altitude above the surface of Titan.

dance might increase. Helium is an additional, perhaps not implausible, possible constituent of the Titanian atmosphere, at least on cosmic abundance grounds. However, not much helium could be expected to be occluded in the interior of Titan during its formation, and very large quantities of helium would be required to affect the blow-off problem. We note parenthetically that cases which avoid blow-off have  $h_c \simeq R$ .

There are three other alternatives which may be more palatable: In the first, a cold trap exists somewhere in the upper Titanian atmosphere at temperatures of the order of  $15^{\circ}$  K at which hydrogen freezes. In the absence of blow-off, complete evaporative escape of a constituent in geological time from an atmosphere of this sort as a whole (not just depletion of the exosphere) can be calculated (Sagan, 1967) and corresponds to the condition  $H(h_c) \simeq R/24$ . Assuming that  $h_c$  is not > R and that the mean molecular weight of the exosphere is 2, the required exosphere temperature turns out to be  $T_c \simeq 35^{\circ}$ K. Were molecular hydrogen entirely photodissociated at this altitude, as is not improbable, the required  $T_c$  would be the freezing point of hydrogen-which would be a very effective impediment to the escape of hydrogen.

In the second alternative, blow-off indeed occurs, but the atmosphere is being replenished by outgassing from the interior, as has also been mentioned by Trafton (1972). There seems to be no difficulty with this suggestion. Lewis (1971) has proposed that the low mean density of Titan and its probable content of radioactive materials imply an interior composition of a molten slush of methane, ammonia and water, not very many tens of kms subsurface. Volcanism and outgassing are expected on Titan, as for example on Mars. It is well known that the effects of electrical discharge or ultraviolet irradiation on such gases is to produce (a) large quantities of hydrogen (Miller, 1957; Sagan and Khare, 1971) and (b) large quantities of organic molecules some of which are brightly colored red (Sagan et al., 1967). Typical molecules made in such experiments include amino acids, sugars, purines and pyrimidines (see, e.g., Horowitz et al., 197●), as well as a characteristic reddish-brown intractable polymer. This material probably includes polynitriles and polycyclic aromatic hydrocarbons-tars and asphalts. These polynitriles are known under aqueous hydrolysis to yield amino acids. It may therefore be that the greenhouse problem, the blowoff problem and the problem of the reddish

coloration of the clouds are all explained in a straightforward manner by the outgassing and photochemistry of high cosmic abundance volatiles.

There is a very interesting third alternative, that blow-off happens but is compensated by the accretion of hydrogen escaping from Saturn, by the sweeping of the Saturnian protons by Titan as it plows through the conjectured magnetosphere. Trafton (1972) estimates an escape rate of hydrogen ~  $1 \times 10^8$  to  $3 \times 10^9$  molecules cm<sup>-2</sup>sec<sup>-1</sup>. I calculate somewhat smaller values. Brice and McDonough (1973) calculate accretion rates onto Titan from a hypothetical Saturnian magnetosphere ~  $10^9$  cm<sup>-2</sup>sec<sup>-1</sup>. The two numbers are in excellent agreement.

It is also of interest that  $\sim 10^9 \,\mathrm{cm}^{-2} \mathrm{sec}^{-1}$ corresponds to an outgassing over all of geological time of only  $\sim 100 \mathrm{g} \mathrm{cm}^{-2}$  of hydrogen. Trafton's highest calculated outgassing value, even if constant over all of geological time, corresponds to only  $\sim 10^5 \mathrm{g} \mathrm{cm}^{-2}$ , or a few kms of equivalent ice outgassed. Compared to outgassing rates on Venus, the Earth, or probably even Mars, these rates seem quite modest.

# Conclusion

Thus the picture which emerges of Titan is of a place with an atmospheric density approaching that of Earth, with surface temperatures of at least  $150^{\circ}$ K and possibly as high as  $200^{\circ}$ K, and with abundant organic compounds in the clouds, atmosphere and surface. Biology under these circumstances is by no means out of the question, and organic chemicals which react at respectable reaction rates even at much lower temperatures are known (Pimentel *et al.*, 1966).

If surface temperatures on Titan are in the 150 to 200°K range they may be detectable by improved microwave interferometric observations of the sort described by Briggs and Drake (1972). The upgraded Arecibo radar system may be capable of determining the microwave reflectivity of Titan, an experiment which might just conceivably have surprising results. If the blow-off is occurring with very large scale heights, then Titan should be surrounded by a hydrogen corona of considerable dimensions. Such a corona might be considerably larger than the planet itself and still have detectable absorption and emission. This idea can be tested with high spatial resolution ultraviolet studies from the latest generation of orbiting astronomical observatories, and from the occultation, either at visible or microwave frequencies, of natural or artificial radiation sources.

Titan is the only object in the outer solar system with such conditions and on which an unmanned (or manned) landing is feasible any time in the next few decades. This can be accomplished under moderate atmospheric densities and low gravities, unlike the conditions in the Jovian planets themselves. Titanian organic chemistry is probably quite similar to that in the upper layers of the clouds of the Jovian planets above the aqueous cloud layers expected there (Sagan, 1971; Sagan and Khare, 1971b). It is also an ideal target for a Mariner class flyby mission in which organic compounds could be sought in the ultraviolet and near infrared, the atmospheric structure probed by radio occultation experiments, and the structure, coloration and polarization of the clouds examined by television systems.

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