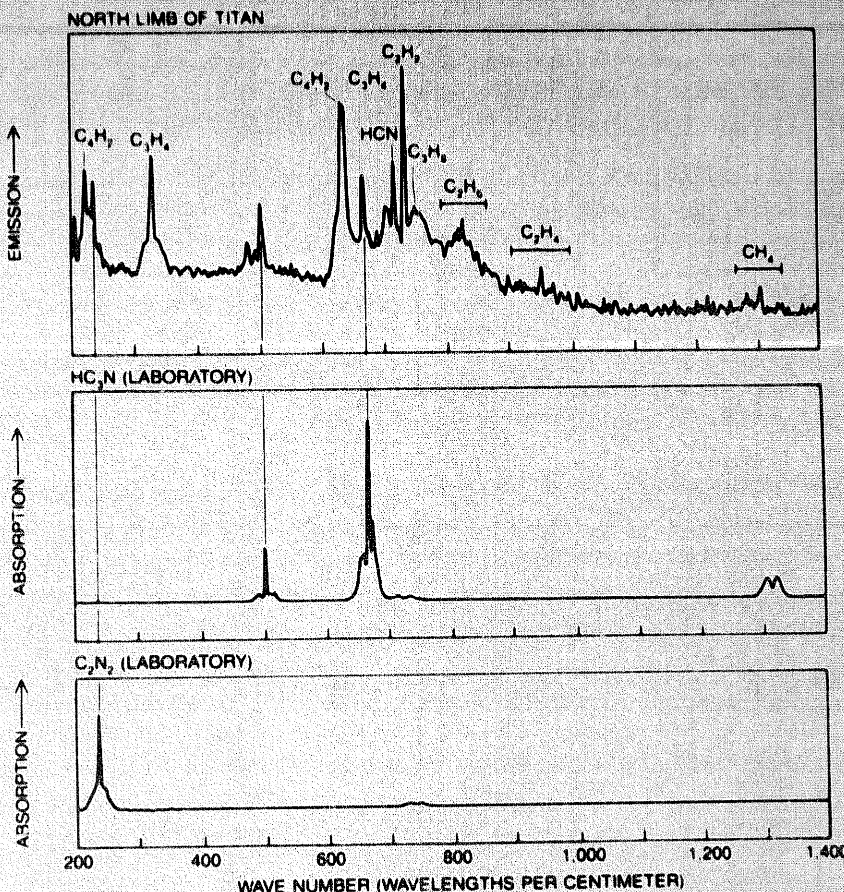
Titan failed to develop an atmosphere like that of Mars or Venus, an atmosphere rich in carbon dioxide? The reason is that oxygen is unavailable: it is trapped in water ice inside the solid moon. The unique combination of Titan's size and Titan's temperature has allowed the atmosphere of Titan to evolve and yet remain a reducing one.

It is generally accepted that Titan formed in a proto-Saturnian nebula, an isolated part of the cloud of dust and gas that became the solar system. Then too it seems reasonably certain that Titan formed with Saturn, Saturn's rings and Saturn's other moons some 4.5 billion years ago. The density of Titan measured today (1.9 grams per cubic centimeter) indicates that it consists of approximately 52 percent rock and 48 percent ices. The proportions represent a slight enrichment in rock compared with the composition of the solar system overall. The ice, however, would have been crucial for the subsequent evolution of Titan's atmosphere, because the ice would have trapped gases from the proto-Saturnian nebula to a far greater extent than the rock would have.

Twenty years ago Stanley L. Miller of the University of California at San Diego predicted that the icy moons of Saturn should include methane hydrate ($CH_4 \cdot 7H_2O$), that is, methane trapped in water ice. The known presence of methane in Titan's atmosphere supported his idea. The newly discovered presence of several additional gases suggests that they too were trapped as hydrates. In order to predict with assurance which substances really were trapped, one must know the values of temperature and pressure for which a given substance and its hydrate are in equilibrium. (At equilibrium the rate at which molecules or atoms of a substance escape from the hydrate equals the rate at which they are trapped, so that the quantity of the hydrate does not diminish and the hydrate is stable.) It is thought that the proto-Saturnian nebula's temperature did not fall much below 60 degrees K. At that temperature the equilibrium pressure for nitrogen molecules or argon atoms and their respective hydrates is less than 10^{-7} bar.

A pressure of 10^{-7} bar is lower than the pressure that nitrogen or argon is likely to have contributed to the proto-Saturnian nebula; therefore these gases should have been trapped in ices. On the other hand, the equilibrium pressure for neon atoms and their hydrate at 60 degrees K. is nearly 40 bars. Neon has a high cosmic abundance; hence the absence of a detectable amount of it in Titan's atmosphere means two things. First, neon could not be trapped as a hydrate; second, it was not trapped as a gas. That is, the gravitation of Titan as it was forming was not strong enough to trap neon directly from the proto-Saturnian nebula. (The atomic weight of the



SPECTRA MADE BY VOYAGER 1 in the infrared part of the electromagnetic spectrum allow the identification of several gases on Titan other than methane. In this case the identification of cyanoacetylene (HC_3N) and cyanogen (C_2N_2) is demonstrated by a comparison of absorption spectra made in the laboratory with an emission spectrum of Titan made by the spacecraft. The comparison is valid because the molecules of a given gas absorb and emit radiation at the same set of characteristic wavelengths. Spectral features of several other gases identified by similar comparisons are labeled in the spectrum of Titan. For all three spectra the horizontal scale represents wave number, or waves per centimeter. A wave number of 200 corresponds to a wavelength of 500,000 angstroms; a wave number of 1,400 corresponds to a wavelength of about 71,000 angstroms. The spectroscopy was done by a group led by Rudolf Hanel of the Goddard Space Flight Center of the National Aeronautics and Space Administration.

most abundant isotope of neon is 20, or four more than the upper limit set by Jeans's theory for escape from Titan at its present mass.) The absence of neon tends to confirm that Titan's atmosphere formed after the body itself accreted and that the atmosphere formed from gases trapped as hydrates.

How did the gases escape from the hydrates and get to the surface of Titan? In the first place the release of gravitational potential energy in the form of heat as Titan accreted would have been sufficient to vaporize a fraction of the ices in the body. Later the decay of radioactive nuclei inside Titan would have become the main source of heat inside it. According to models proposed by Mark Lupo and John S. Lewis of the Massachusetts Institute of Technology, the radioactive heating may have been sufficient to create a zone of liquid water deep in the mantle of the body. Gases could escape from the liquid.

Plainly there are ways in which gases once trapped in Titan's ices could escape and form an atmosphere. One sees evidence of such escape on other Saturnian moons. The cracks on Dione rimmed by material brighter than the surrounding terrain are the most conspicuous example. Dione was simply too small to retain an atmosphere. Other Saturnian moons show signs of fresh surfaces. The material that resurfaced the moons may have been driven upward to the surface partly by the internal pressure of gases escaping from hydrates.

The nitrogen in Titan's atmosphere calls for further discussion. In the events I have been describing it is assumed that the nitrogen in Titan's atmosphere today was incorporated into the accreting Titan as a hydrate. This assumption requires in turn that the dominant form of nitrogen in the proto-Saturnian nebula was molecular (N_2), which may not have been the case. To be sure, Ronald G. Prinn of M.I.T. has joined with Lewis in suggesting that N_2 was the stable form of nitrogen in the incipient solar system. Prinn and M. Bruce Fegley, Jr., of M.I.T. point out, however, that the increase of temperature near the incipient Jupiter and Saturn could have allowed ammonia (NH_3) to form. If it did and if Titan trapped it as a hydrate instead of trapping N_2, the subsequent history of Titan must have been substantially different.

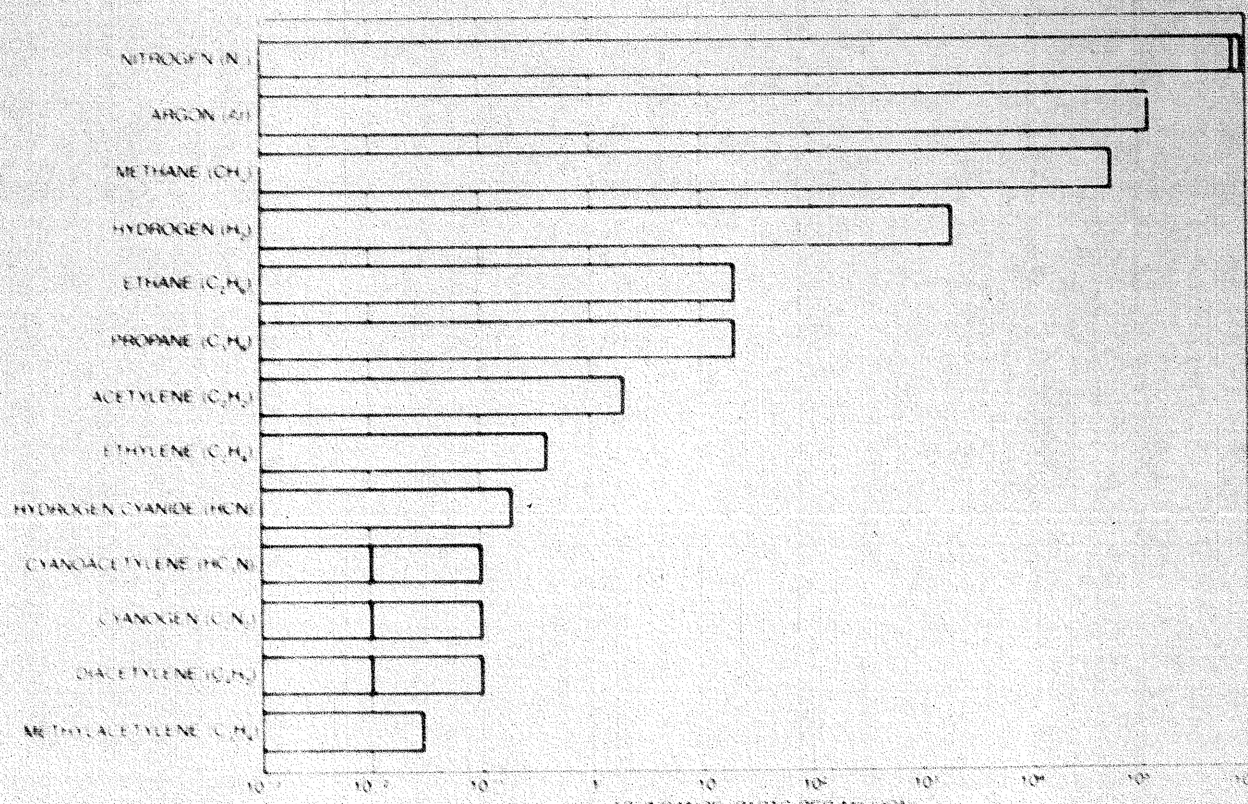
In particular, calculations made by Sushil K. Atreya and his colleagues at the University of Michigan show that one must postulate a "warm" epoch early in the history of Titan in which the surface temperature exceeded 150 degrees K. Throughout this epoch ammonia would have escaped from the interior and into the atmosphere, where it would have been broken up by solar ultraviolet photons. In this way the atmosphere would have lost its ammonia and gained the N_2 it has today. A temperature of 150 degrees K. is not out of the question; in principle a greenhouse effect created by hydrogen and ammonia in Titan's early atmosphere could have produced it. Still, the warm epoch is a complication that is avoided if nitrogen was trapped by Titan as a hydrate of N_2. Perhaps a combination of the two processes was involved, so that less of a constraint need be placed on the early surface temperature.

The argon in Titan's atmosphere also merits discussion. If it makes up 12 percent of the atmosphere, it must have come from trapped hydrates. The only competing possibility is that it came from radioactive decay. More than 99 percent of the argon in the atmosphere of the earth was made in just that way: it arose from the decay of the radioactive isotope potassium 40 into argon 40. Even if the rocky material in Titan had the same proportion of potassium as the rocky material in the earth, however, the current content of argon 40 in Titan's atmosphere would be about 70 parts per million, far from the predicted 12 percent, or 120,000 parts per million. The argon in Titan's atmosphere must indeed be primordial argon trapped as a hydrate from the proto-Saturnian nebula. It must therefore be argon 36 with an admixture of 20 percent argon 38.

The equilibrium pressures of nitrogen and argon with respect to their hydrates are sufficiently similar and sufficiently low to suggest that the proportions in which they become trapped as hydrates should be about the same as the proportions in which they later escape from those hydrates. A test of the presence of nitrogen instead of ammonia in the proto-Saturnian nebula begins, therefore, with an estimate of the amount of nitrogen that has escaped from the solid body of Titan. The estimate must include the nitrogen content of Titan's atmosphere today and also take account of how much nitrogen has escaped into space and how much has been incorporated into aerosol particles over the history of the body. It follows from Strobel's values for these two modes of depletion that the total amount of nitrogen that has entered Titan's atmosphere is about 1.7 times the atmosphere's current content of nitrogen, or 140 percent of the total content of Titan's atmosphere.

The amount of argon that has escaped from the solid body of Titan is easier to calculate. Argon is inert (it will not form chemical compounds), and it is too heavy to escape into space in appreciable quantity. The amount of argon that has escaped from the solid body is simply the 12 percent of the atmosphere. The ratio of nitrogen to argon is therefore 11.7. The ratio of nitrogen to argon in the cloud of matter that became the solar system was quite close to that: it was 11.

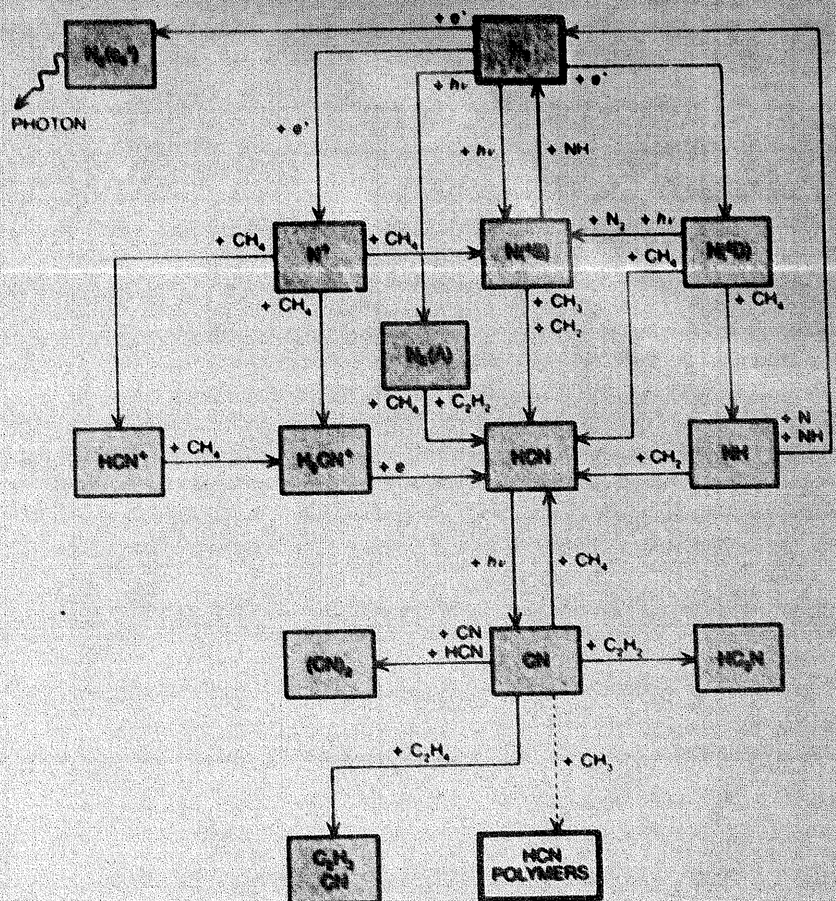
What can Titan tell us about the primitive earth? Opinion is shifting away



GASES IN TITAN'S ATMOSPHERE are now thought to vary in abundance from molecular nitrogen (set at 82 to 94 percent of the atmosphere, or 820,000 to 940,000 parts per million, as a result of Voyager data) to trace quantities of hydrocarbons such as methylacetylene and nitrogenous substances such as cyanogen. Several further trace constituents of Titan's atmosphere may remain to be discovered. The chart indicates some 12 percent (120,000 parts per million) of the inert gas argon. This 12 percent is required to raise the mean molecular weight of the gases that make up Titan's atmosphere to the value of 28.6 that tentatively emerges from the Voyager data.

from the view that the earth began with a highly reducing atmosphere consisting mostly of methane, ammonia, hydrogen and water vapor. The newer view is that the atmosphere was mildly reducing at first and that it consisted mostly of carbon dioxide, molecular nitrogen and carbon monoxide with no more than 10 percent of hydrogen. It is firmly agreed, however, that no free oxygen was present, because an oxidizing environment makes it extremely difficult for organic molecules to form. In an oxidizing environment the carbon is quickly locked into molecules no more complex than carbon dioxide.

Investigators working in laboratories on the earth have subjected gaseous mixtures of methane, ammonia, hydrogen and water vapor to repeated electric discharges. They have succeeded in producing, among other organic molecules, some of those that are constituents of DNA. What they have not been able to produce is something like DNA itself, or more broadly a molecule that can replicate itself by acting as a template for the assembly of a duplicate from the simpler molecules that are available. The problem seems to be a lack, in Andrew Marvell's phrase, of "world enough, and time." A test tube is simply too small and years may be too short for the advent of a self-replicating molecule to be likely.



CHEMISTRY FOR NITROGEN in Titan's atmosphere is proposed by Darrell F. Strobel of the Naval Research Laboratory. Here the main reactants and reaction products are shown; hydrogen atoms and molecules, among others, are omitted. The initial reactions involve the breaking of the N–N bond in a nitrogen molecule high in the atmosphere. The energy to break the bond is provided by the impact of solar ultraviolet radiation ($h\nu$) or of a high-energy electron (e^*) trapped near Titan by Saturn's magnetic field. (The latter process supplies Titan's atmosphere with about 10 times as much energy as the former.) The final reactions include the formation of the reddish aerosol particles observed in Titan's atmosphere. The final steps are not fully known because the chemical composition of the particles themselves is not yet established. It is, however, known that hydrogen cyanide (HCN) can form a reddish-brown polymer. In the illustration ^2D and ^4S signify excited atomic states, A and c_4' signify excited molecular states and e signifies an electron freed in the atmosphere by solar ultraviolet radiation.

Titan as a Laboratory

In this respect Titan offers what amounts to an immense natural laboratory free of experimental bias and the possibility of accidental catalysis or inhibition of chemical reactions by the walls of reaction vessels or the grease in the stopcocks of a vacuum system. Moreover, it is a laboratory where the reaction products over the history of the solar system have been collected into aerosol particles that rest at low temperature at the surface of the body, where we may one day be able to examine them at our leisure. Indeed, we may one day resolve to conduct experiments there ourselves. Heating up a few acres of Titan would produce more of the "primordial soup" than our terrestrial experiments could make in several lifetimes.

For now, NASA is contemplating a mission for the 1990's that would send a probe into Titan's atmosphere while a parent spacecraft was in orbit around Saturn, employing radar to pierce the opacity of Titan's atmosphere and make a map of the surface. We may expect much sooner than that to learn more about Titan from further analysis of the Voyager data, from the powerful new spectrometers now available on the earth and particularly from the instruments that will go into orbit around the earth with the Space Telescope in 1985.

Meanwhile the Voyager spacecraft continue their missions of exploration. *Voyager 1* is on its way out of the solar system. If its transmitters continue to function we can expect it to tell us the position of the boundary between the solar wind and the tenuous gas of the interstellar medium. The news should come within the next 10 years. *Voyager 2* is on its way to Uranus, which it will reach in January, 1986, and Neptune, which it will reach in August, 1989. The mechanism that points the cameras on the spacecraft suffered some damage when the spacecraft passed through Saturn's rings. Engineers at the Jet Propulsion Laboratory are confident, however, that *Voyager 2* will transmit valuable data from Uranus and Neptune if there are no further equipment failures.

Still, the Voyagers were not originally intended to travel to planets more distant than Saturn, and their instruments are far from optimum for that purpose. The change in plans was made in the mid-1970's when it became apparent that no specific missions to Uranus and Neptune would be undertaken for at least a decade. In the wake of the success of the Voyager program it is ironic that we find ourselves with no follow-on missions other than one that may be canceled: the Galileo project, which would send a probe into Jupiter's atmosphere to make measurements of such things as composition, pressure and temperature. We have already lost our chance to send a mission to Halley's comet. In effect we are retreating to the early 17th century, a time when the most distant known planet was Saturn and it was not understood that comets traverse the solar system. This is no time for such a retreat. There is much we need to learn about the worlds around us before we can fully understand the history of the solar system and that of the earth itself.