2.5   INTERIOR AND ITS IMPLICATIONS FOR THE ATMOSPHERE

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Introduction

Up to now we have been talking about the atmosphere. We all know that
the atmosphere represents a negligible proportion of the mass of Titan and that
we know very little about it. I'm going to talk about the interior, which rep-
resents a much larger proportion of the mass of Titan, and we know almost nothing
about it.

Perhaps the best way to proceed is to review conceptually, several con-
trasting interior models for solar system bodies and then discuss in some detail
the thermal history of the model I prefer for Titan. To this I will add some
remarks on compatible atmospheric bulk composition and structure. It should
prove interesting to see how this blends with the Earth-based atmospheric data
presented so far today.

Conceptual Chemical Equilibrium Model

The first thing in dealing with the interior of Titan is to just list
those raw materials which might be of some significance in the interior; to draw
up a list of those abundant materials which one might expect to be present at
that point in the solar system. We need not be either very clever or very well
informed to draw up most of the list. We need only to ask what the most abun-
dant elements are and what materials are reasonably easy to condense.

These first results I will be giving are based upon the concept of chemical
equilibrium between the solid materials and the gas of solar composition. The
simplest way to run through this is to start with high temperatures and say that
first rock-forming materials (in other words, silicates, sulfides, and metals)
condense. We will assume that by the time we have reached the outer part of the
solar system, this entire process of condensing rocks has gone to completion and
substantial amounts of less dense and more volatile material have also condensed.
This is certainly borne out by the low observed densities of many of the satel-
lites and the low postulated densities of many of the smaller satellites.
Morrison might have something to say about the very low densities of some of
the satellites of Saturn. Perhaps this is a subject we can come back to later,
because I think you'll see that it's a very important point -- whether there
are satellites with densities as small as unity.

Below the temperatures at which rocks are formed (again thinking of a
sequence of decreasing temperatures, starting with a parent material which has
the same composition as the Sun) the next appreciable material to condense is
water ice. As the temperature continues to drop, the next major material to
form out of this gas of solar composition would be a solid hydrate of ammonia.
At yet lower temperatures, methane clathrate hydrate is condensed, which is not
strictly a chemically bound compound. This material represents simply sticking

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a methane molecule into each one of the large vacant sites in the ice lattice. This uses up all the water ice but some methane gas is left over. Further lowering the temperature, the next important thing to condense is the left-over methane, which condenses as a solid.

Now what are the densities of the objects which are formed during this cooling sequence? Densities of rock-like objects, depending upon formation temperature, are on the order of 4 gm cm^{-3}, but there is considerable detail ranging from the condensation of metallic iron (density ~ 7) on down to ~ 3 at lower temperatures. So 4 is just a round number. When water ice is condensed, the bulk density of everything, rock plus ice -- comes out to approximately 1.7 gm cm^{-3}.

I am going to give relative densities which are good to a few hundredths of a gram per cubic centimeter. The absolute densities are not good to anywhere near that accuracy because of the uncertainties in the cosmic abundance of the elements. I shall give three significant figures for the densities, and the ratios of those densities, or the differences between them, are both reasonably secure. However, the absolute densities may be slipped by as much as 0.3 gm cm^{-3} by changes, for example, in the abundance of carbon and oxygen relative to silicon.

Once the ammonia hydrate forms, the mass of condensed material goes up only slightly because the atomic abundance of nitrogen is 5 times less than that of oxygen, and the density would drop slightly. This would give a bulk density of around 1.65 gm cm^{-3}. Next, methane hydrate forms. Because a portion of the water has already been used up in making ammonia hydrate, and because about half of the oxygen has been used up in making silicates, the amount of methane that is retained is not terribly large and the density change is not very large. The bulk density after this step is ~ 1.60 gm cm^{-3}.

Note that these are zero-pressure densities, and certainly compression affects the icy materials quite substantially. For example, if you take the observed density of Titan, 2.2 gm cm^{-3}, and correct it to zero pressure, the density comes out about 1.8. So it's a fairly important correction for objects as large as Titan. Let me also say, parenthetically, that the bulk material which is formed, containing the four constituents down through methane hydrate, contains about 4% methane by weight. Once solid methane is condensed, the amount of methane present goes up by a rather substantial factor to something like 20%.

Notice that carbon is a very abundant material, far more abundant than any of the rock forming elements. It is more abundant than nitrogen, and it has about half the abundance of oxygen. Also, methane has a very low density, about 0.6. That means that, upon methane condensation, the bulk density must drop considerably, and in fact it drops to 1.0 gm cm^{-3}. I hesitate to quote three significant figures here for a simple reason, namely the density is quite temperature-sensitive and quite model-sensitive. Let us say that the zero pressure density is ~ 1.0 after solid methane condenses.

Conceptual Inhomogeneous Accretion Model

Now let us examine a very different but equally tractable formation process. This competing model assumes that the accretion of solid particles into large bodies takes place very rapidly. As soon as the temperatures get low enough for

something to condense, it accretes into a large body and is therefore unable to interact chemically with the gas beyond that point. It makes a profound difference in the chemistry because, for example, ammonia hydrate in a chemical equilibrium model is formed by chemical reaction of ammonia gas with ice which already exists, and requires intimate contact between gas and solid. Likewise, methane hydrate is formed by reaction of methane gas and solid ice, and requires contact between gas and solid.

So let's start again with very high temperatures and go through the calculations, but unlike the equilibrium case, as each new condensate appears from the gas, we will remove it. In physical terms, we accrete a layer of the most recently formed material on to the surface of a body which is now inhomogeneously accreted. This is a generalization of the inhomogeneous accretion model of Turekian and Clark (1969) as proposed for the Earth. The core forms first, then the mantle accretes on top of it, then the crust on top of that. Their model has numerous serious difficulties and I am not advocating it; and I don't believe they would for this case either, but it's the farthest removed from the simple, straightforward equilibrium approach that I can conceive of and certainly represents a polar extreme that should be studied.

The sequence begins again with rock, but with certain special differences. No water-bearing silicates are present, because we do not permit water vapor to equilibrate with high-temperature silicates. Also, there are no sulfides, and no iron oxides. This means that sulfur remains in the gas (H_2S) long after the condensation of rocky material is complete.

Then, continuing to cool this gas, which now has a different composition than in the equilibrium example, we would condense water ice first. After that, we would condense a material that does not appear at all in the first sequence. This is ammonium hydrosulfide, which we may also call an ice or a salt. It is a fairly stable solid which has a vapor pressure comparable to ammonium chloride. You can make it and hold it in your hands at room temperature, though it is exceedingly unpleasant. When freshly prepared and pure, it's just as colorless as any ice, or common salt.

Going to yet lower temperatures, ammonia, frustrated from its tendency to react with water to produce solid ammonia hydrate, must condense by itself as solid ammonia ice. This will occur at much lower temperatures than the temperatures at which the ammonia hydrate would normally form. In other words, the vapor pressure of ammonia ice is much higher than the vapor pressure of ammonia hydrate. Finally, going down to even lower temperatures, we get methane ice.

The bulk densities along this sequence look quite similar to those we calculated earlier. Because of the uncertainties in the cosmic abundances, there is no way to use the observed densities of bodies in the outer solar system to distinguish between the two models. Notice, however, that in the inner solar system, there is a very large difference in the chemistry. Just knowing the chemical composition of the Earth or meteorites, knowing the bulk densities of the planets, and knowing a great deal about the structure of the Earth and something (not much) about the internal structures of Mars and Venus, we can compare how the densities of the terrestrial planets ought to vary with

distance from the Sun (from the predictions of these two kinds of models) with the observed densities and to the observed compositional detail we have for the Earth. If that is done, the equilibrium model comes out looking very good. It predicts the observed density dependence, including such subleties as the increase in density going outward from Venus to the Earth. That's very rewarding.

I have, however, elected to give you the results of both models for the purpose of equipping you with a complete list of abundant materials that one might worry about as starting materials. By "abundant", I mean those materials abundant enough to effect the bulk density. Those which might be abundant enough to produce a visible trace of atmospheric gas would require pursuing this list down to much, much less abundant elements, because atmospheres represent such a small proportion of the total mass of bodies.

Working Compositional Model for Titan

Now, let us take the equilibrium concept as our working compositional model. We will then assemble these materials into objects comparable in size to the Galilean satellites or to Titan. In other words, large enough so that their internal thermal state is interesting, and they are not simple isothermal objects. Let us sketch how the internal structure of these objects depends upon their composition, and thus upon their formation temperature. The temperatures of formation or condensation for these materials range from about $170°K$ for water ice to about $120°K$ for ammonia hydrate, to about $80°K$ for methane hydrate, and down to about $50°K$ for solid methane. These condensation temperatures are computed for solar nebula pressures of about 10^{-6} to 10^{-7} atmospheres. Within a factor of 10 or even 100 in pressure, these temperatures simply all shift by a certain logarithmic increment up and down together. The sequence of reactions is immutable. We can, therefore, sketch cross-sections through these condensed objects as a function of the formation temperature, as shown in Figure 2-22.

At $200°K$, we have not quite condensed water ice yet, and we may represent the object as being all rock. If we like, we could permit this rock to differentiate by density, to permit the formation of a sulphide core with a silicate mantle on top of it, but this is a matter of taste.

At about $170°K$ ice will condense, and I will allow the ice to rise to the top via density-dependent differentiations. I will give my reasons for that eventually. With ice added, the structure changes abruptly. The top of the rock region will drop down, and we will have an ice layer on top. The "rock" here means a water-bearing silicate rock, perhaps like serpentine.

As we set the temperature yet lower, ammonia hydrate will be present in the parent material of the satellite. Upon partial melting and differentiation of the satellite the ammonia will partition itself between the various phases and, of course, ammonia is exceedingly soluble in water. The result will be to form a "mantle" of aqueous ammonia solution. A solid mixture of ice and ammonia hydrate begins to melt at a temperature of $173°K$ which is the eutectic temperature in the ammonia-water system. This means that an object with a surface temperature not much less than $170°K$ may have a thin ice crust, and, at a relatively shallow depth, the temperatures become high enough so that a melt or slurry (which is a suspension of ice in a liquid) is present.
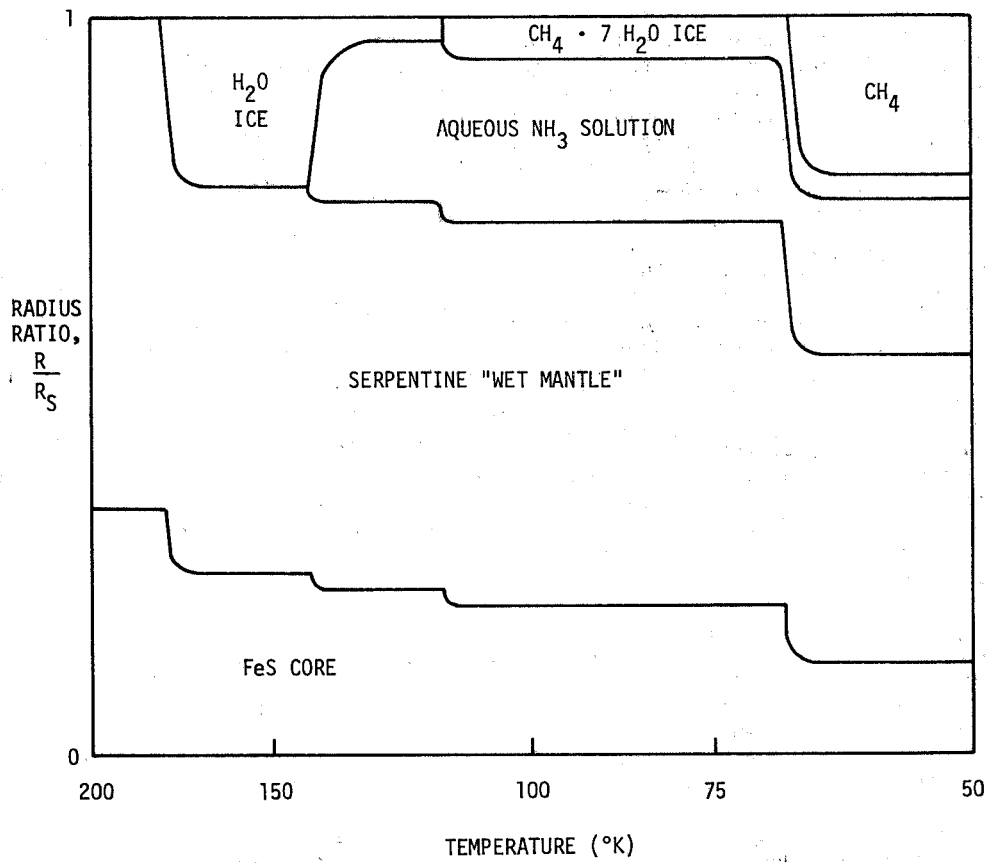
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Figure 2-22. Radial sections of condensed objects as a function of formation
temperature based on the chemical equilibrium model.

The next step is adding a solid methane hydrate to the parent material. The effect of making solid methane hydrate, you will recall, is to leave leftover methane gas and exhaust all the ice. That means that a differentiated object produced from this composition will contain not only an aqueous ammonia solution, but also a crust which now consists of methane hydrate. Methane gas will be given off due to melting of this ice mixture. Some proportion between zero and 100 percent of the methane will be released as a gas, which will produce an atmosphere.

Then, at temperatures low enough to condense solid methane, a very profound effect occurs, with the superposition of an enormous mass of methane on top of the ice crust. Now, the question is, what is the physical state of this methane? Is it solid, liquid, or methane gas? If a Titan-sized satellite contained such a large quantity of methane, we would find that the physical state of the methane versus depth would depend upon detailed physical considerations, such as the internal thermal structure of the satellite, that we have not yet considered.

An object formed with methane hydrate (but not solid CH_4) present contains enough methane so that, if it were fully outgassed, it would produce a one kilobar methane atmosphere. The total amount of methane obtainable when solid CH_4 is included could reach about 5 kb at the base of the methane, where we have indicated the presence of an ice crust.

It is necessary to point out at this juncture that, until we really know what the "surface temperature" is, we can't be certain that this ice layer will be present. What if the atmospheric mass is so large that it permits a surface temperature above the decomposition temperature of methane hydrate? Then there may be an interface between a methane atmosphere and an aqueous ammonia solution with no crust in between. You can't rule it out. It is an exceedingly interesting possibility.

Right now I am addressing myself to Saturn's system, so I would say the boundary temperature is so low that unless something like the presence of a methane atmosphere raises the surface temperature, you won't get ammonia in the atmosphere. Certainly if the atmospheric mass is large enough, and surface temperatures high enough, to have even aqueous ammonia solution in contact with the atmosphere, then the presence of a significant quantity of ammonia in the lower atmosphere is quite possible.

In the Jovian system, you might indeed have an ammonia-containing satellite, and it might indeed be possible to put ammonia into the atmosphere, but the partial pressure of ammonia would be so low that the atmosphere would be photochemically regulated.

Trafton: What happens to your diagram (Figure 2-22) with all the heats of solidification? Does that upset things?

Lewis: There are two effects. One is that it changes the static structure and the other is that it changes the thermal history.

Let me address the first point first. The ice layer we talked about is in fact ice-I only down to a level where the pressure is about 2 kb, at about 50 or 60 km depth. There we get a conversion of ice to a higher density form. Thus there should be a sequence of ice layers going on down to ice-VI. This could be most easily thought of as an isothermal structure in which you just take the isothermal conversion pressures of ice into the high pressure forms.

But now, let's switch over to the second point and ask about a thermal history in which we consider how to get from the homogeneously accreted primitive object, which contains all of these materials mixed together randomly, to a differentiated object. The question then is, what is the time scale for heating? We would like to know, first of all, the formation temperature in order to know what the bulk composition is. We would also like to know the accretion temperature, i.e., the characteristic internal temperature after the solid object is assembled, as a starting point in thermal history models. We would like to know the intensity of heat sources, and, of course, the equations of state and melting behavior of all components in it.

Here is how we do it: We set the accretion temperature equal to the formation temperature. If the object is heated during the accretion process by conversion of gravitational potential energy into internal heat, then it will be easier to melt. So, I am saying, let us make a pessimistic assumption here. Let us set these two temperatures equal. Then, with regard to the intensity of the heat sources, we dismiss gravitational energy as a source of heat. We will do away with adiabatic compression of the interior, and put the thing together isothermally. We will do away with short-lived radionuclides, because there is now some fairly good evidence from the study of meteoroids that the short-lived radionuclides, very popular a few years ago, almost certainly had nothing to do with the thermal history of meteorite parent bodies.

So, we are left with two heating mechanisms to consider, one of which cannot be quantified yet. That is solar wind heating, the Sonett mechanism. The other is long-lived nuclides. But, in the case of long-lived nuclides, we know the abundances of the radioactive elements in meteorites and in the Earth. We, therefore, can make quite reliable estimates of how large that heat source is. The sources of this heat are uranium, thorium and potassium, mostly potassium at this stage of the history of the solar system. The half-life for potassium decay is about a factor of three shorter than that for ^{235}U, ^{238}U, or ^{232}Th, which are about equal-sized heat sources nowadays. Thus, back at the origin of the solar system, potassium was about an order of magnitude more important as a heat source than uranium or thorium.

We are, therefore, taking only one heat source, the one we know must be there, present in the amounts which are needed in order to give the observed density. We want to know how well that heat source, by itself, can heat the parent material, which we start at the lowest possible temperature. For Titan, this is about 70°K. We then ask, how long does it take for that object to heat to the point where it begins to differentiate? Once it begins to differentiate, we have another heat source: the internal conversion of gravitational potential energy to heat, due to this settling of dense material through the light material. This heat source, let us call it ΔGPE, exists only as a result of having started differentiation. Therefore, that heat source has nothing to do with when it starts to melt. Under these assumptions, for an object the size of Titan, it takes ∿0.8 x 10^9 years to begin to melt.

The additional energy derived from gravitational separation is not by itself sufficient to supply all the heat for phase changes. The Earth differentiated catastrophically because the gravitational potential energy released from separating each part of the Earth was more than enough to melt an equal mass of material. For Titan, this would not be the case. Differentiation would be fairly rapid on a cosmic time scale, but it would not be catastrophic. The differentiation-produced heat source is about four times too small for that to happen. I could probably change that figure by a factor of 2, but, in round numbers, it takes about another 0.8 billion years to do the melting, to reach a steady-state structure. The elapsed time to this point is about 1.6×10^9 years. Thus, within two billion years, Titan would differentiate. Nowadays, it is probably fair to regard the satellites as being in a thermal steady state.

The heat flux that would be passing through the crust of this object to keep it in a thermal steady state is about a thousand times more than the heat flux needed to drive convection in a liquid interior. So heat will be transported rapidly. That means that the liquid mantle will be nearly isothermal. It will be adiabatic in structure, and we will have a thin conductive layer, the crust, on the surface. In the case of Titan, we don't know whether or not the atmospheric mass is large enough to make the surface warm. If it is warm enough, we won't have a crust, and there would be convective heat transport directly up into the base of the atmosphere. I haven't yet said how much atmosphere is needed to get rid of the crust. I said if all the methane were driven out of the interior, it could provide up to a kilobar of methane. It would require <u>at least</u> a 10 b surface pressure to melt and decompose the crust.

Pollack: If there is ammonia in the atmosphere, does your model imply that we are seeing the surface, the aqueous ammonia solution?

Lewis: That depends on what I calculate to be the temperature required to melt the crust. I don't see it necessarily requiring the surface be melted. It may just have ....

Pollack: ....like a volcano?

Lewis: Yes, a volcano, or even solid ammonia hydrate not too far below its eutectic melting temperature.

Pollack: Which one of those two methane compounds would you expect at the surface? If it is a methane hydrate its vapor pressure is a lot lower than that of methane, so if you find a lot of methane in the atmosphere, that implies a certain minimum surface temperature.

Lewis: The vapor pressure of methane over the methane hydrate is several orders of magnitude lower than the vapor pressure of methane over solid methane, so Pollack is saying that the composition of the surface material greatly influences your concept of how the atmosphere interacts with the surface.

Hunten: At 127°K the vapor pressure is 4 bars for methane and 3 x 10⁻³ bars for the hydrate (Lewis, 1971).

Pollack: You see, this has very strong impact on Danielson's model in the sense that he wants the temperature of the surface to be 80°K and, if that were true, I think it would be very hard to have methane as we observe it in the atmosphere with a clathrate surface.

Danielson: How rapidly do you achieve equilibrium with a clathrate of that kind, and if you once sublime it, which means you then form water, what happens? If you take a clathrate and dissociate it, you have water on the surface.

Lewis: Disordered ice, actually, or an aqueous ammonia solution....

Danielson: ....and then you condense out methane again. Then it's just solid methane, isn't it?

Lewis: No, actually, lab experiments were done by Delsemme and Miller (1970) looking at the stability fields of these hydrates to see how relevant they were to comets. They were able to make these hydrates at quite low temperatures. I would have to go back to the original article to say exactly how low the temperatures are. They found that granular ice subjected to the presence of methane gas did permit formation of methane hydrate.

Hunten: I have read that this hydrate is an important problem in natural gas pipelines.

Lewis: Yes, it builds up in natural gas pipelines. The gas must be dried quite scrupulously to keep it from happening. It is not just methane; all the light hydrocarbons form these hydrates.

Trafton: For the methane-rich models, what would be the physical character of the surface of the base of the methane?

Lewis: Let me answer that by proceeding to my second and last graph.

Compatible Atmosphere

     In this section I will address the relationship of atmospheric composition to bulk composition and interior models. Just for simplicity let us consider a pure methane atmosphere. We'll leave out temporarily, all consideration of ammonia, hydrogen, and other gases. Thinking about a single component is quite a bit easier. Figure 2-23 is the phase diagram for the system, pure methane. Note the triple point of methane at 91°K and 90 mb. By a curious coincidence of nature,
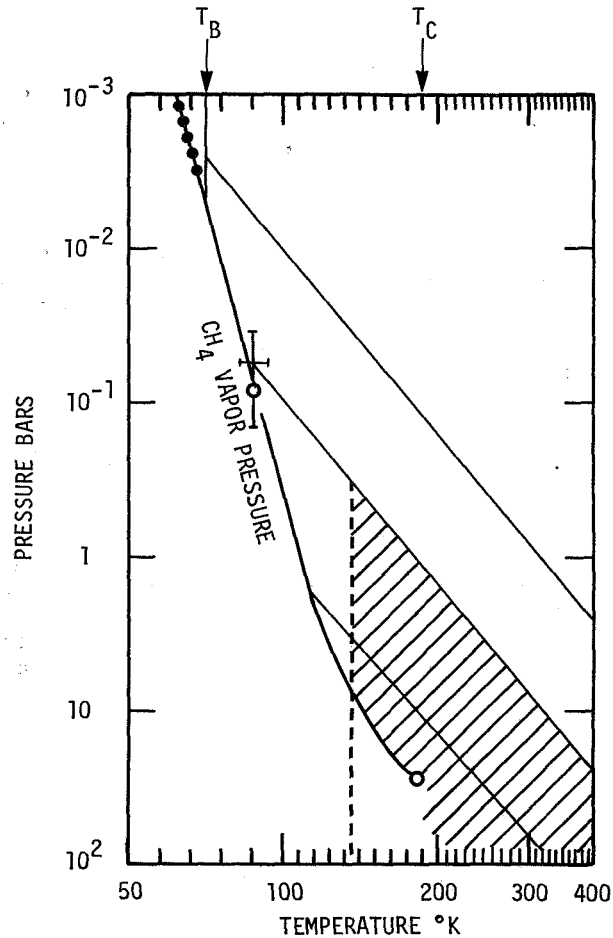
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Figure 2-23. Pure-methane atmospheric models for Titan. The heavy line is the vapor pressure curve of methane. T_B is the Gold-Humphreys boundary temperature (74°K), and T_C is the critical temperature of methane. The triple point of methane is indicated at 91°K and 90 mbar, in good accord with the effective temperature and CH_4 pressure for a pure-methane atmospheric model. The three diagonal lines are dry adiabats for pure CH_4. Note that the slope of the vapor pressure curve (a fully-saturated adiabat) equals that of a dry adiabat near the critical point. The cross-hatched region contains the allowable surface conditions ($T_s \geq 145°K$) for pure-CH_4 atmospheres. The visible level in Titan's atmosphere is presumably defined by the triple point of methane, above which level a bright solid-CH_4 particulate haze may be present, but below which only strongly forward-scattering liquid droplets would be stable. After Lewis and Prinn (1973). Reprinted from Comments on Astrophys. Space Phys., 5:4, with permission of Gordon and Breach Science Publishers, Inc. All rights reserved.

the pressures and temperatures observed for Titan correspond fairly well with the triple point of methane. This might be easy to rationalize if we were looking down from above into an atmosphere which contained condensed methane in which the temperature-pressure profile lay, at least temporarily, on the vapor-pressure curve of methane. Thus a thin cloud (or perhaps a thick cloud, depending on one's taste) of solid methane particles would be present down to the level where the melting temperature of methane was reached. Beyond that point, the cloud would be composed of droplets of liquid methane, or the atmosphere could be clear of clouds.

Now what is the real temperature structure of the atmosphere? We do not know, but greenhouse models seem plausible to me, implying an adiabatic lower atmospheric structure. The temperature probably follows the vapor-pressure curve of methane for some distance, but how far? Almost anything could happen. At one extreme, the lower atmosphere may be isothermal; then we are led to predict that there would be a surface of solid methane. Alternatively, the lower atmosphere may have clouds in it down to some greater depth and then the atmosphere may follow a dry adiabat to the surface.

There is a whole family of possible models. If we believe that the temperature of 145°K or 150°K refers to a lower limit on the surface temperature, then we would expect that the surface of Titan would lie to the right of the 150°K isotherm. If one imagines that the lower atmosphere is saturated, then the atmosphere may be saturated all the way to the 150°K level, where the atmospheric pressure is 12 b. On the other hand, 150°K is not an upper limit on the temperature of the surface for this model. It is a lower limit. If the lower atmosphere is saturated all the way down to the critical point of methane, then we may have a methane atmosphere merging gradually into a dense supercritical fluid interior with no phase change.

Alternatively we could follow an unsaturated dry adiabat from our postulated temperature-pressure point in the upper troposphere as far as one cares to do so. Assuming a minimum surface temperature of 150°K then, in the context of the atmospheric models, it means the ones with the lowest atmospheric pressure at the surface of Titan, compatible with the presence of clouds in the upper atmosphere, would have a total pressure of about 0.5 b on the surface.

Regarding models with high surface pressure, I have suggested already that we probably should not think of atmospheric pressures in excess of a kilobar. In the context of these pure methane models, I do not see how one can use present observational evidence to rule out the possibility of having an extremely deep, massive atmosphere. Of course, surface temperatures of about 150°K should inspire those interested in exobiology, because at that temperature ammonia gas appears. Also, 173°K is the eutectic temperature in the ammonia-water system, at which point melting begins.

We therefore must know exactly what that surface temperature is. A radio occultation experiment by Mariner Jupiter/Saturn (MJS) would plumb the atmosphere down to levels where pressures are about 10 b. One should not think that this pressure is significant to two places because the surface temperature is still negotiable. There is quite a variety of features which may be compatible with the notion of an atmosphere with temperature increasing with depth, mostly made of methane which may, by its own presence, make the lowest atmosphere warm enough for ammonia to be present.

Danielson: Why wouldn't your argument apply to some of the Galilean satellites?

Lewis: Well, first of all, they do not have methane atmospheres, which leads us to suspect we are talking about composition classes in which methane was never retained. Secondly, the presence of an equilibrium atmosphere on one of the Galilean satellites would be virtually unobservable. My estimate is about 2×10^{-7} atmospheres, based strictly on chemical equilibrium considerations. Photochemistry will turn over such an atmosphere very quickly. It is noteworthy that the upper limit set by the Io occultation is exactly the same, useless to all concerned. Thus, Io does not have an atmosphere that is capable of affecting the surface temperature.

Trafton: Where would you place Triton?

Lewis: I would place Triton in the solid-CH_4 region. The only thing that convinces me that Saturn's satellites may contain methane is that we see it on Titan. Otherwise, I'd have to conclude that it was a marginal situation. The satellites of Uranus would fall in the same class as Titan. Neptune's satellites should fall in the solid CH_4 region.

Sagan: Triton doesn't have any methane on it.

Lewis: It may, of course, because the boundary temperature is so low that it would all be frozen and thus unobservable. So on Triton, we would be talking about a solid methane surface.

Trafton: What about the density of Triton?

Morrison: John, quote your densities for Triton that you were telling me about.

Lewis: I did a literature search on this. I can't claim it was complete, but I took what I thought to be all of the reliable estimates of the mass and radius of Triton and I came to the conclusion that the density of Triton almost certainly lies between 0.2 and 40 gm cm^{-3}. It is very hard to use this information for subtle compositional discrimination.

Blamont: What about hydrogen and rare gases?

Lewis: I can say a few brief things about noble gases. One is that if we search for a mechanism for retaining helium, the formation of clathrate hydrate wouldn't help because the holes in the ice lattice are so large that helium circulates readily through it. So there is no mechanism for helium retention here.

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Sagan: Is that the result of a diffusion calculation?

Lewis: Yes.

Sagan: It's actually calculated?

Lewis: The holes are literally substantially larger than the helium atom. Also, in terms of forming small grains in the nebula, the question arises: what would the helium be doing in the ice lattice in the first place? Because we would form these grains at very low pressures, the amount of helium which might be randomly trapped inside the lattice, just by having a crystal grow around it, would be something like one part in 10^{10}.

Sagan: Occluded helium, I think, can be excluded!

Lewis: Yes, and also absorbed helium. Direct helium condensation requires a temperature which is below 1°K. Since the background temperature of the universe is about 2.6°K, I think we should not take that too seriously. Neon is also too small an atom to form a stable clathrate. Neon should condense eventually as solid neon at a temperature of about 12 to 15°K, which also seems unreasonably low.

Argon forms a clathrate hydrate which is rather less stable than the methane hydrate, and argon is quite a bit less abundant than methane. I did a calculation looking at the equilibrium partitioning of argon between gaseous methane and solid methane hydrate and came to the conclusion that one argon atom would be present in the solid for every 7,000 methane molecules. There are certain systematic uncertainties in deriving that number, but the number is not temperature sensitive because the vapor-pressure curves of the hydrates are quite nicely parallel.

Rasool: How about Argon-40?

Lewis: Radiogenic Argon-40, produced in the deep interior, might possibly make it to the surface particularly if we believe that potassium resides in solution rather than in mineral grains. The maximum amount of Argon-40 would be about 10 millibars.

Blamont: That may not be insignificant.

Lewis: If the total pressure is some tens of millibars then it might be quite significant. Finally, getting back to your question about other gases, hydrogen condenses at about only 7°K. Adsorption of gases on solid surfaces is negligible at temperatures more than about 3 times the condensation temperature of the pure substance, so, if we accept ∿70°K as the accretion temperature of Titan, no adsorbed hydrogen will be retained.

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Veverka: Can we get back to Saturn's other satellites? Did you say the other satellites should have solid methane surfaces?

Lewis: I said that, if they had a density of 1, then they would have enormous quantities of methane sitting on top of them. From outside, we would see gaseous methane, I should suspect, and they should have solid surfaces. Frankly, I am skeptical about such low densities.

Veverka: What actual surface material do you suspect?

Lewis: Asphalt.

Morrison: The inner satellites cannot be covered with a material as dark as asphalt unless either the measured masses are off by an order of magnitude or the densities are a great deal less than unity.

Conclusions

The bulk composition and interior structure of Titan required to explain the presence of a substantial methane atmosphere are shown to imply the presence of solid $CH_4 \cdot 7H_2O$ in Titan's primitive material. Consideration of the possible composition and structure of the present atmosphere shows plausible grounds for considering models with total atmospheric pressures ranging from ~ 20 mb up to ~ 1 kb. Our expectations regarding the physical state of the surface and its chemical composition are strongly conditioned by the mass of atmosphere we believe to be present. A surface of solid CH_4, liquid CH_4, solid CH_4 hydrate, H_2O ice, aqueous NH_3 solution, or even a non-surface of supercritical H_2O-NH_3-CH_4 fluid could be rationalized. It is an urgent necessity to determine the location of the surface of Titan; in other words, to find the surface atmospheric pressure.

Note: This article is, in part, a summary of publications and preprints by Lewis (1971, 1973), and Lewis and Prinn (1973).