Rain and hail can reach the surface of Titan

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Abstract

We have calculated the condensation and evaporation of ternary CH4–N2–C2H6 liquid drops and solid CH4 hail as they fall through Titan’s lower atmosphere to determine the likelihood that precipitation reaches the ground. Assuming the humidity profile determined by the Huygens probe, binary liquid CH4/N2 condensate grows in the region from ~8 to 15 km in Titan’s atmosphere because the combined humidity of CH4 and N2 exceeds saturation. These drops evaporate below ~8 km. We determine the fate of 10 mm seeds composed of ethane, which is expected to provide condensation sites. In addition, we study the fate of already formed raindrops with radii of 1–4.75 mm falling out of the growth region. High (50%) and low (0%) ethane relative humidities (RH) are considered in the calculation. We find that drops with radii ~3 mm and smaller dropping from 8 km reach the ground in compositional equilibrium with the atmosphere in the high ethane RH case as a result of the stabilizing influence of the ethane, and evaporate in the atmosphere in the low ethane RH case. Large drops (>~3 mm) reach the surface large and cold because the latent heat loss due to the evaporation of methane cools the drop and slows the evaporation rate. Pure methane hail hits the ground if its radius is initially more than 4 mm at 16 km above the surface and sublimes in the atmosphere if its radius is smaller.

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1. Introduction

The role of methane in Titan’s atmosphere and on its surface is the subject of considerable debate. Early theories suggested a global methane ocean and a methane cycle similar to Earth’s water cycle. While it is now known that there is no global ocean covering Titan’s surface, there is evidence for liquid methane in localized lakes in the polar regions (Stofan et al., 2007). Dry streambeds have also been imaged by the Huygens probe (Tomasko et al., 2005). Further, the gas chromatograph mass spectrometer (GCMS) on the Huygens probe found evidence of methane and ethane vapor rising from the ground beneath the landing site, probably vaporized by the heated inlet of the instrument (Niemann et al., 2005; Lorenz et al., 2006). These new data indicate that liquid methane plays a key role in Titan’s surface geology, but the presence or nature of a methane cycle complete with rain has not been determined conclusively.

Toon et al. (1988) first predicted rain on Titan, suggesting that raindrops would be sparse and grow rapidly to a size larger than 50 μm, but without forming optically thick clouds (i.e., rain without clouds). Karkoschka et al. (2007) observed transitory cm-sized bright spots in Huygens probe images of Titan’s surface that could be raindrop splashes. Recent detailed models indicate that methane rain is indeed possible, and that ethane can act as the condensation nucleus (Barth and Toon, 2003, 2006). The Huygens probe directly measured the temperature (Fulchignoni et al., 2005) and methane concentration (Niemann et al., 2005) profiles of Titan’s atmosphere. The atmosphere’s ability to form condensates can be derived from these measurements. The surface humidity
with respect to pure CH$_4$ was 45%, increasing with altitude to about 80% at and above 8 km. Tokano et al. (2006a) suggested that the 80% RH of CH$_4$ was expected if the condensate was not pure CH$_4$ but a CH$_4$–N$_2$ binary as predicted by Thompson et al. (1985). Tokano et al. (2006a) argued for the presence of a non-convective liquid cloud growth region for the CH$_4$–N$_2$ binary from roughly 8–15 km, the possibility of a steady-state methane drizzle from this subvisible cloud, and the existence of a layer of CH$_4$ ice particles extending up to 30 km above this layer of condensing liquid.

Pruppacher and Rasmussen (1979) studied the behavior of falling water drops under Earth conditions, and Lorenz (1993) applied this method to methane on Titan. Lorenz (1993) modeled pure methane drops of various sizes falling from 3 km. His results suggested that methane drops evaporate before reaching the surface for a range of plausible methane relative humidities (RH), which include the Huygens probe values. However, he did not account for the presence of ethane or nitrogen in the raindrops and did not include evaporative cooling effects.

A number of studies have addressed the behavior of methane/ethane and methane/ethane/nitrogen condensates in Titan’s atmosphere. Barth and Toon (2003, 2006) discussed the fate of methane/ethane raindrops, but were concerned primarily with the formation of ethane condensation nuclei, and the subsequent growth of methane raindrops when ethane seeds fall through the growth region of the atmosphere. They accounted for the presence of nitrogen in the drop by adding a factor, but did not integrate nitrogen’s behavior into their equations for drop growth. Thompson et al. (1992) describe in detail the thermodynamics of binary N$_2$–CH$_4$ mixtures in Titan’s atmosphere to determine atmospheric properties such as cloud composition and latent heats of vaporization. Thompson (1985) studied the properties of possible N$_2$–CH$_4$–C$_2$H$_6$–C$_3$H$_8$ and N$_2$–CH$_4$–C$_2$H$_6$ oceans and clouds. McKay et al. (1993) considered ternary N$_2$–CH$_4$–C$_2$H$_6$ mixtures, but were more concerned with the overall evolution of Titan’s atmosphere and surface liquid reservoirs rather than with rainfall.

In this paper, we present calculations for the fall of liquid drops and solid hail in Titan’s lower atmosphere. We use the temperature and pressure data recorded by Huygens’ Atmospheric Structure Instrument (HASI) (Fulchignoni et al., 2005) and the atmospheric composition measured by the GCMS (Niemann et al., 2005) to determine the RH profiles of methane and nitrogen in Titan’s atmosphere. These profiles are shown in Fig. 1, as are the two cases of ethane RH we consider: 0% and 50%—a value comparable to the surface humidity of methane. We consider these two values of ethane RH because the actual value has not yet been determined. Due to the high atmospheric RH of CH$_4$ and N$_2$ in the region from ~8 to 15 km in Titan’s atmosphere, the presence of nitrogen in a drop is sufficient to suppress the vapor pressure of methane to below its atmospheric partial pressure. In this altitude range, methane/nitrogen drops grow steadily until dynamically unstable. Because these methane/nitrogen drops likely form onto ethane condensation nuclei falling from above this growth region (Barth and Toon, 2003), we consider ternary methane/ethane/nitrogen raindrops.

The growth region shown in Fig. 1 is indicative only because the saturation conditions for a binary mixture of N$_2$ and CH$_4$ depend on composition as well as temperature. Hence relative humidity is not well defined for this binary mixture. The growth region as shown refers to a particular binary mixture of N$_2$ and CH$_4$—that mixture in which the ratio of N$_2$ to CH$_4$ is in equilibrium with the atmosphere and the drop is growing uniformly with respect to both constituents. A naturally falling drop quickly comes to this equilibrium and so the growth region as we have defined it is useful as it defines the region over which a falling drop will grow.

We analyze several ternary rain cases as well as methane hail. Barth and Toon (2006) suggested an ethane seed radius range of 1–10 $\mu$m, while Samuelson and Mayo (1997) argued for a radius of 10–75 $\mu$m. We use a radius of 10 $\mu$m to maintain consistency with both calculations. We consider pre-formed raindrops from 1 to 4.75 mm in radius falling from 8 km, the bottom of the growth region of the atmosphere. Drops larger than 4.75 mm in radius would break up in Titan’s atmosphere (Lorenz, 1993). We also track condensation onto a 10 $\mu$m ethane seed falling into the top of the growth region (initialized at 16 km) for both ethane relative humidities considered (0% and 50%). While hailstones would also have an ethane seed, we only consider pure methane hail. This is because we assume the seed would be sequestered in the center of the solid hailstone, and therefore would have no effect on the fate of methane hail. Therefore, to study the behavior of hail in the troposphere, we consider methane hail particles 1–8 mm in radius initially at 16 km above Titan’s surface.
Raindrops and hail experience several processes as they fall through Titan’s atmosphere. Methane and nitrogen condense onto raindrops as they fall through the growth region. The final size to which they grow depends on how long they take to fall through the growth region. Once below this region the particles begin to evaporate, losing both N2 and CH4 as they fall. As the particles lose mass they cool due to the loss of latent heat. This effect slows the rate of evaporation of large raindrops as well as hailstones, and allows them to fall further. As is clear from Fig. 1, there is no equilibrium composition of CH4 and N2 that will stabilize a particle in the lower atmosphere. This is because their relative humidities with respect to the pure substances sum to well below unity. However, if the C2H6 humidity is high (~50%), then a mixture of N2–CH4–C2H6 could be in equilibrium with that atmosphere, due to the stabilizing effect of the ethane.

2. Methods

In this calculation, we are not concerned with the formation or frequency of raindrops on Titan, but rather with determining whether a drop of given size and composition, falling from a certain height, evaporates in the atmosphere or reaches the surface as drizzle. We assume ethane ice nuclei melt and mix completely with the condensed methane and nitrogen, and that this melting process has no effect on the thermal balance of the drop. A single drop is followed from a specified initial height until it either evaporates or reaches the surface. Its size, composition, and temperature are tracked as it falls. The drop is allowed to gain or lose mass and heat, based on its properties and those of the atmosphere it is falling through. We model methane/nitrogen/ethane drops and methane hail. A detailed description of the calculation of fall velocity, evaporation/condensation, and temperature of a raindrop, and the differences between the rain and hail velocity, evaporation/condensation, and temperature are given in Appendix A.

The evaporation or condensation of each drop component i is governed by (altered from Lorenz, 1993; Pruppacher and Rasmussen, 1979)

$$\frac{dM_i}{dt} = f_i \frac{\pi a_i^2 D_i m_{di}}{RT_i} (P_{\text{vapor}, i} - P_{di}),$$

(1)

where $P_{\text{vapor}, i}$ and $P_{di}$ are the atmospheric partial pressure and vapor pressure of i in the drop. $P_{di}$ is the product of the vapor pressure at saturation, the mole fraction of i present in the drop, and the non-ideal coefficient that accounts for the change in vapor pressure due to interactions between drop components. The relative values of $P_{\text{vapor}, i}$ and $P_{di}$ govern the sign of $dM_i/dt$, and therefore whether the drop is gaining or losing component i. The other terms in Eq. (1) are the ventilation coefficient ($f_i$), drop radius ($a_i$), diffusivity coefficient of i ($D_i$), molecular mass of i ($m_{di}$), universal gas constant (R), and $T_i = (T_{\text{atm}} + T_d)/2$, where $T_{\text{atm}}$ is the air temperature and $T_d$ is the drop temperature (Pruppacher and Rasmussen, 1979).

Since the drops are not always in thermal equilibrium with the atmosphere as they fall, drop temperature is tracked by calculating the heat transfer rate between drop and atmosphere:

$$M_{\text{tot}} c_p \frac{dT_d}{dt} = H_{\text{lat}} + H_{\text{cond}} + H_{\text{rad}},$$

(2)

where $M_{\text{tot}}$ is the raindrop mass, $c_p$ is the specific-heat capacity of the drop, $dT_d/dt$ is the rate of change of the drop’s temperature, and $H_{\text{lat}}$, $H_{\text{cond}}$, and $H_{\text{rad}}$ are the latent, conductive, and radiative heating rates, respectively. We include $H_{\text{rad}}$ for completion, but radiative heating is negligible compared to the conductive and latent heat flux. Latent and conductive heat fluxes do not exceed 0.1 K/s.

The atmospheric pressure, temperature, and density are extrapolated from Huygens HASI data (Fulchignoni et al., 2005), and atmospheric composition from Huygens GCMS data (Niemann et al., 2005). To aid numerical convergence particularly with respect to the nitrogen content of the drops, the computation steps explicitly in mass and then implicitly determines height. This guarantees that only a small amount of each component is transferred to or from the drop during each computational step, enhancing numerical stability.

Hail is treated in essentially the same way, except that the particles are pure methane, and the appropriate parameters are changed to represent ice rather than liquid. Our assumption of pure methane hail is possibly justified if the condensation is directly from vapor to solid on ethane ice grains falling from above. Hail may contain nitrogen if it forms from freezing liquid drops carried upward from lower in the atmosphere (Thompson, 1985).

3. Results

We first consider methane and nitrogen condensation and evaporation on an ethane seed particle 10 μm in radius that initiates its fall from 16 km altitude (just above the liquid growth region of the atmosphere). Because ethane’s atmospheric relative humidity is unknown, we run two trials: one with a relative humidity of 0% (case a), the other with 50% (case b). Gray lines a and b in Fig. 2a represent the results: in both cases drops grow to just over 0.9 mm in size before they fall out of the growth region and begin to evaporate, after which point their behavior deviates. The raindrop reaches the ground in case b, but does not in case a.

Regardless of ethane relative humidity, the drop falls slowly enough that it begins to equilibrate both compositionally and thermally with the atmosphere. Compositional equilibration is evident in Fig. 3, which charts the mole fraction of each component in the drop as it falls. There is a rapid shift in composition at 4600 m for case a and 6000 m for case b, where the fraction of ethane in the drop increases dramatically due to the evaporation of most of the nitrogen and methane. When compositional equilibrium is reached, the vapor pressures of methane...
because the mole fraction of ethane needed in the drop to stabilize the methane never exceeds the relative humidity of ethane (50%).

The drop in case a does not experience this long-lived stability because the low atmospheric ethane relative humidity results in the evaporation of the drop’s ethane over the fall time of the drop. As the ethane evaporates, the methane and nitrogen have to evaporate as well, which results in the shrinking drop falling more and more slowly until it entirely evaporates without reaching Titan’s surface. The curve for case a in Fig. 2a levels out at this evaporation altitude. The composition of the drop when it evaporates (4600 m above the surface) is indicated by the end points of the gray curves in Fig. 3.

The relative humidity of ethane in Titan’s atmosphere is not only an indicator of whether rain will reach the surface, but also has significant implications for the composition of liquids at Titan’s surface. If the ethane relative humidity is 0%, then over time any rain that reaches Titan’s surface will eventually evaporate. The methane in a ternary $\text{CH}_4$–$\text{N}_2$–$\text{C}_2\text{H}_6$ liquid is stable at Titan’s surface when the liquid has a mole fraction ratio of 40% methane/ 20% nitrogen/ 40% ethane because ethane in this concentration lowers methane’s partial pressure sufficiently. Accordingly, this liquid will be stable from evaporation if the relative humidity of ethane at the surface is above 40%. Otherwise, liquid $\text{CH}_4$–$\text{N}_2$–$\text{C}_2\text{H}_6$ will evaporate. Since raindrops in case b fall to Titan’s surface in compositional equilibrium, the composition of these drops when they reach the surface (shown in Fig. 3) represents this stable state, and therefore

and nitrogen match their respective atmospheric partial pressures. Thermal equilibrium is reached also, when the drop’s temperature matches the ambient atmospheric temperature.

For case b, the drop reaches compositional equilibrium and simply falls to the ground with only minimal further evaporation. Fig. 3 shows the steady decrease in mole fraction of methane and nitrogen and increase in ethane that occurs as the drop evaporates small amounts of methane and nitrogen in response to the lowering atmospheric relative humidity of each constituent as the drop approaches Titan’s surface. Stability is possible in this case
these small drops would not evaporate but remain liquid on the surface.

There is currently no known mechanism for producing large raindrops at the Huygens landing site. Nonetheless, we calculate the fate of pre-formed CH$_4$–N$_2$–C$_2$H$_6$ raindrops up to the maximum aerodynamically feasible drop size of 4.75 mm in radius (Lorenz, 1993). This is done because there may be updrafting or some other mechanism that keeps drops in the growth region longer, allowing them to attain larger sizes.

Fig. 2a also shows the results for raindrops of varying initial sizes, each containing a 10$\mu$m ethane seed (black curves). These larger drops are initiated at the bottom of the growth region with a variety of sizes from 1 to 4.75 mm in radius. Raindrops 3 mm in radius and less evaporate before reaching the ground (for zero ethane RH, shown in the figure) or stabilize to a size set by their ethane content (for high ethane RH, not shown in the figure). However, raindrops larger than 3 mm reach the ground with little mass loss. This is primarily due to the temperature difference between the drop and the surrounding air as the drop is cooled by evaporation. In Fig. 4, the temperature profile of the atmosphere is compared with the temperature history of a drop with an initial radius of 4.75 mm at the bottom of the growth region. Because of its high sedimentation rate, conductive heat flux cannot compensate for the drop’s latent heat loss, and the drop remains colder than the atmosphere for the remainder of its descent. Because it is cold, methane and nitrogen evaporate much more slowly from this drop, and it reaches Titan’s surface large, cold, and not in compositional equilibrium with the atmosphere.

These large drops cool primarily because of the evaporation of methane. Evaporating nitrogen also contributes to the temperature discontinuity; however, the evaporation of methane is 10 times more significant to the overall cooling of the drop. The cooling effect of each component is the product of its evaporated mass and its latent heat of evaporation. The latent heat of evaporation of methane is significantly higher than that of nitrogen, and more methane evaporates than nitrogen per unit time. For this reason, we expect that methane will be the primary cooling agent in the drop.

We expect these drops would warm and evaporate once they reach the surface if the relative humidity of ethane is below 40%. However, if the relative humidity of ethane is above 40% at the surface, we predict the drop would instead equilibrate with the atmosphere by evaporating methane and nitrogen, and leave a small ternary drop that would remain stable on the surface.

The fall times and properties at impact of the two types of raindrops that reach the ground (small and in compositional equilibrium with the atmosphere, and large and out of compositional equilibrium with the atmosphere) are compared in a summary table (Table 1). Properties of the case b ethane seed with condensed CH$_4$ and N$_2$, and the drop 4.75 mm in radius at 8 km are shown. The smaller drops fall more slowly than large drops throughout their descent, evidenced by the longer fall time listed in the table. Additionally, large drops impact the surface at 1.5 m/s, fast enough to potentially affect the mechanical properties of the surface material.

Finally, we consider pure methane hailstones with initial radii ranging from 1 to 8 mm at 16 km. We do not model hailstones greater than 8 mm in radius because the behavior of larger hailstones is not fundamentally different. Moreover, it is difficult to envision how hailstones more than twice the radius of the maximum raindrop size could form in the non-convective atmosphere of Titan’s equatorial region for which our calculations are most pertinent. Fig. 5 shows that large methane hail particles reach the ground, and small ones do not. No particles melt to become raindrops—large hail particles reach the ground as hail and small ones sublime entirely in the atmosphere. Note also in Fig. 5 that unlike for methane/nitrogen/ethane rain, there is no particle growth region for hail in the atmosphere below 25 km (Tokano et al., 2006a). This is because there is no ethane or nitrogen present in the hail to stabilize the methane, so it is always at saturation vapor pressure, which is always higher than the vapor pressure of methane in the atmosphere. This causes hail to sublime at

Table 1

<table>
<thead>
<tr>
<th>Property</th>
<th>Large drop (0% RH C$_2$H$_6$)</th>
<th>Small drop (50% RH C$_2$H$_6$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Drop radius at 8 km (mm)</td>
<td>4.75</td>
<td>0.92</td>
</tr>
<tr>
<td>Drop radius at ground (mm)</td>
<td>3.34</td>
<td>0.20</td>
</tr>
<tr>
<td>Fall time from 8 km (min)</td>
<td>78</td>
<td>361</td>
</tr>
<tr>
<td>Velocity at ground (m/s)</td>
<td>1.5</td>
<td>0.24</td>
</tr>
<tr>
<td>% Methane by mole at ground</td>
<td>77%</td>
<td>40%</td>
</tr>
<tr>
<td>% Nitrogen by mole at ground</td>
<td>23%</td>
<td>20%</td>
</tr>
<tr>
<td>% Ethane by mole at ground</td>
<td>$1.8 \times 10^{-8}$</td>
<td>40%</td>
</tr>
<tr>
<td>Drop temperature at ground (K)</td>
<td>90.0</td>
<td>93.5</td>
</tr>
</tbody>
</table>
atmosphere if the hail particle is small (4 mm). Methane hail does not melt, but sublimates entirely in the atmosphere, shrinks, and evaporates. Large drops reach the ground because they cool as they leave the growth region and begin to evaporate in the atmosphere. All drops there is a significant atmospheric ethane relative humidity. The drop temperature disequilibrium between large drops and the surrounding atmosphere is a key component to determining a raindrop's fate. Assuming that the temperature of the largest stable raindrop is the same as that of any raindrop on Titan and is the main constituent of the atmosphere. This has important effects on how atmospheric condensates behave. The nitrogen evaporating off of the drop is not diffusing through another medium (like methane diffuses through nitrogen), but is diffusing through itself. This process of self-diffusion is described by a different formula (see Appendix A). But because of some uncertainty in the literature about how to calculate the coefficient of self-diffusion for nitrogen (Colaprete and Toon, 2003; Winn, 1948), we tested the model's sensitivity to this value. Fig. 2b shows that the fall history of a 4.75 mm radius drop is relatively insensitive to variations in the self-diffusion coefficient, so we use the formula from Colaprete and Toon (2003).

Finally, it is clear from Fig. 4 that raindrops on Titan are not always in thermal equilibrium with the atmosphere. Therefore, tracking the heat transfer between a drop and the surrounding atmosphere is a key component to determining a raindrop's fate. Assuming that the temperature of the largest stable raindrop is the same as that of the environment underscores this strong dependency. Fig. 2b shows that under these conditions, even a large drop evaporates in the atmosphere. Accounting for how temperature disequilibrium between large drops and the environment affects the evaporation rate of these drops.

Fig. 5. Size evolution of 1, 2, 3, 4, 4.75, and 8 mm radius hail particles dropped from 16 km. Large hail particles (roughly 4 mm in radius and greater at 16 km) reach the ground, small ones (<4 mm) sublimate away in the atmosphere. Hail does not melt to become a liquid drop.

We ran several sensitivity tests on our calculations using the standard case of a 4.75 mm radius drop, falling though an atmosphere with a 0% ethane relative humidity. We consider uncertainties in the ventilation coefficient, the self-diffusion of nitrogen, and the drop temperature. Results are shown in Fig. 2b.

The ventilation coefficient governs how much the air rushing by the drop as it falls affects the drop’s evaporation rate (Lorenz, 1993). The ventilation coefficient for a 4.75 mm radius drop varies from 21 to 34 (23–28 for CH₄, 21–24 for N₂, 29–34 for C₂H₆). Fig. 2b shows that the model is quite sensitive to this coefficient: when it is pinned at 1 for all components, the evaporation rate is so low the standard drop loses almost no mass before hitting the ground, and when it is set at 10 times normal the evaporation rate is so high the drop entirely evaporates in the atmosphere nearly 3.5 km above the surface. Our baseline calculations followed Lorenz (1993) by using a formula for the ventilation coefficient experimentally determined by studying the behavior of water drops on Earth (Pruppacher and Rasmussen, 1979, see Appendix A). However, the behavior of methane/ethane/nitrogen drops on Titan may not be similar. So while the trend of bigger drops reaching the surface and smaller drops evaporating in the atmosphere would remain the same, the drop size where the transition between these two regimes occurs would change if the ventilation coefficient were found to be significantly different on Titan.

Alteration of the ventilation coefficient can also cause ethane seeds falling through the growth region to reach the ground as large drops. For these smaller drops the ventilation coefficient normally varies from 1 to 10 (1–9 for CH₄, 1–8 for N₂, 1–10 for C₂H₆). We set the ventilation coefficient for all components at a higher value, 15, when the ethane seed drop is growing (16–8 km), and at a lower value, 1, when the drop is shrinking (8–0 km). In this case, regardless of ethane relative humidity, the drop behaves like a large drop: it remains colder than its surroundings, is mostly composed of methane, and hits the ground 0.9 mm in radius (Fig. 2a, gray line c). Variation of the ventilation coefficient from Earth dependencies provides a possible way for our model to explain how large drops could form from ethane seeds and reach Titan’s surface.

As has been mentioned, nitrogen makes up a significant portion of any raindrop on Titan and is the main constituent of the atmosphere. This has important effects on how atmospheric condensates behave. The nitrogen evaporating off of the drop is not diffusing through another medium (like methane diffuses through nitrogen), but is diffusing through itself. This process of self-diffusion is described by a different formula (see Appendix A). But because of some uncertainty in the literature about how to calculate the coefficient of self-diffusion for nitrogen (Colaprete and Toon, 2003; Winn, 1948), we tested the model's sensitivity to this value. Fig. 2b shows that the fall history of a 4.75 mm radius drop is relatively insensitive to variations in the self-diffusion coefficient, so we use the formula from Colaprete and Toon (2003).
would impact the size distribution of rainfall and rainfall rates used in cloud models like those of Barth and Rafkin (2007) and Tokano et al. (2006a). Hueso and Sanchez-Lavega (2006) do consider the release of latent heat during the condensation of methane in their convective cloud model. Our results highlight the necessity of such calculation and suggest the need for greater rigor in this area.

5. Discussion

The Huygens probe found evidence of liquid methane and ethane on Titan’s surface (Niemann et al., 2005; Lorenz et al., 2006). How, then, does the ground near Titan’s equator become wet? Rain is one possible explanation. We find that a steady rain of large or small drops, or large hail could reach the surface. But there are energy and mass limits to consider on the rain’s sources and sinks when determining how much rain can occur in steady state.

\[ \text{CH}_4+\text{N}_2+\text{C}_2\text{H}_6 \text{ liquid} \] can be in compositional equilibrium with the atmosphere, because the presence of ethane stabilizes the drop. If there is a significant relative humidity of ethane in Titan’s troposphere, the drop’s ethane will not evaporate, but remain to stabilize the methane indefinitely. We found that if small drops reach the surface, they would have this stable ratio of methane, ethane, and nitrogen and therefore none of the constituents would evaporate from the surface. A steady rain of small drops could explain observations of a wet surface. However, since ethane would remain on Titan’s surface without evaporating, the mass of ethane deposited on the surface via rain would be limited by its photochemical production rate in the upper atmosphere. The standard value for the flux of ethane through the tropopause available for condensation is \( 9.1 \times 10^{-5} \text{kg/m}^2 \text{ per Earth year} \) (Atreya et al., 2006), and the value suggested by Atreya et al. (2006), accounting for additional carbon sinks and less eddy mixing, is \( 1.9 \times 10^{-5} \text{kg/m}^2 \text{ yr} \). These fluxes allow rainfall rates of \( 3.0 \times 10^{-4} \text{ and } 0.63 \times 10^{-4} \text{ mm/yr} \), respectively (Earth years). Thus, rain on Titan in this case would be limited by the mass of ethane available to form condensation nuclei.

Regardless of ethane relative humidity, large drops can reach the ground. These drops are not in compositional equilibrium with the atmosphere, and evaporate once they reach the surface. Such evaporation of methane and nitrogen requires energy. Radiative balance models (McKay et al., 1991) indicate that the non-radiative energy flux at Titan’s surface is about 1% of the incident sunlight. If all of this energy was being used to evaporate rain, it would imply a maximum evaporation rate of \( \sim 5 \text{ mm per Earth year} \). This corresponds to a maximum rainfall rate of \( 0.001 \text{ drops/m}^2 \text{ s} \) for drops \( \sim 3 \text{ mm in radius} \) when they reach the surface. At this maximum rainfall rate, it would take approximately 200 Earth years to rain out the total column methane in the growth region (8–15 km). If the deposition rate exceeded this maximum, we would either observe a colder surface, or there would be a net flux of liquid to the surface and puddles would be observed at the landing site.

There is also the question of whether the presence of tropospheric rain or mists which result from evaporated rain are consistent with Huygens probe findings. Rain may entirely evaporate, or the raindrop may become stable but so small that the turbulence in the atmospheric boundary layer keeps it suspended. This last option would result in a near-surface mist. Due to the low turbulence in Titan’s boundary layer—the eddy diffusivity is only roughly \( 7.4 \times 10^{-7} \text{ m}^2/\text{s} \) (Tokano et al., 2006b), as compared to \( \sim 2 \text{ m}^2/\text{s} \) over land on Earth (Pasquill, 1974)—the particle size that can be suspended in the atmosphere is quite small. This low eddy diffusivity would suspend particles with a drop size of \( 1.2 \times 10^{-4} \text{ mm} \) or smaller, corresponding to a sediment velocity of \( 2 \times 10^{-5} \text{ m/s} \) or less. A collection of such small particles is inconsistent with the results from the Huygens probe, which do not indicate a thick mist near the surface (Tomasko et al., 2005). This suggests that the smaller drops we consider are less consistent with data than the larger drops that reach the surface.

However, there is no clear mechanism for how large particles can currently form in the atmosphere above the Huygens landing site. It is possible that convective motions in the large cloud systems observed at \(-40^\circ \) latitude and at the south pole, 25–40 km above the surface (Griffith et al., 1998; Schaller et al., 2006) could suspend and cycle growing particles long enough for them to evolve into large hailstones. Barth and Rafkin (2007) model these clouds and find they can indeed produce a small number of ice particles that reach 5 mm in radius. Our calculations show that ice particles dropped from 25 and 40 km gain or lose hardly any mass above 16 km, and so arrive on the surface only slightly smaller than hail initialized at 16 km, assuming the Huygens temperature, pressure, and composition profiles. The relative humidity of methane may be different at higher latitudes, however. If the mole fraction of methane is 10% higher in the atmosphere (resulting in a higher methane relative humidity), hail reaches the ground much larger. If the mole fraction of methane is 10% lower instead, even large hailstones will sublime away. Our model only directly pertains to the Huygens landing site, but varying the methane relative humidity suggests that if atmospheric conditions are significantly different at higher latitudes, the fate of rain may be different there as well.

Our results differ from those of Lorenz (1993), who predicted that methane rain cannot reach the surface of Titan, except perhaps at raised terrain like mountaintops. He utilized the Voyager temperature and density profiles, and tried a range of reasonable methane relative humidities. We use the new temperature, pressure, and composition data from the Huygens probe to calculate the relative humidity profile of methane. Furthermore, we accounted for the effect of the presence of nitrogen and ethane in the drop on the evaporation rate methane, and tracked the drop’s temperature separately from the atmospheric
temperature. Each of these effects slows the evaporation rate of the drop. This is why our model, unlike that of Lorenz, predicts rain can reach Titan’s surface.

If the bright spots observed in surface images taken by the Huygens probe are raindrop splashes (Karkoschka et al., 2007), they may represent the large raindrops we show can reach the surface. However, detailed modeling of the splash and subsequent evaporation of these drops would be required to match the observations.

In summary, our calculations show that methane/ethane/nitrogen rain on Titan is consistent with the composition, pressure, and temperature profiles of Titan’s atmosphere as measured by the Huygens probe, and may help explain the methane- and ethane-wet surface. However, limits on the sources and sinks of rainfall will need to be further explored before conclusions can be made about the quantity of rainfall possible near Titan’s equator. Our results also indicate that the quality and fate of rain may be different in different latitudinal regimes.

6. Conclusions

We determine the fate of methane/nitrogen/ethane rain and pure methane hail in Titan’s atmosphere. We find that

- Small drops have two possible fates, depending on the relative humidity of ethane in the atmosphere:
  1. If the ethane relative humidity is high (50%), the drop reaches the ground as drizzle because of the stabilizing influence of the ethane seed.
  2. If the ethane relative humidity is low (0%), the ethane seed, and therefore the entire drop, evaporates and does not reach Titan’s surface.
- Big drops (>3 mm in radius) reach the ground because they cool relative to the surrounding atmosphere due to methane evaporation.
- Pure methane hail hits the ground if its radius is initially more than 4 mm at 16 km above the surface, and sublimates away in the atmosphere if smaller.

There remain several significant unknowns that would impact the results of the current study as well as the bigger questions of the overall global cycling and transfer of hydrocarbons on Titan. More research is needed into determining how the behavior of methane/ethane/nitrogen drops on Titan differs from that of water drops on Earth. Two key questions are whether drops on Titan can be approximated as oblate spheroids when they are compositionally different and falling through a different pressure and gravity regime than water on Earth, and whether the evaporation of a CH₄–N₂–C₂H₆ mixture on Titan responds to ventilation similarly to water on Earth. Additionally, constraining the relative humidity of ethane in Titan’s atmosphere is essential to improving the accuracy of calculations and predictions of liquid transport on Titan.

Acknowledgements

This research was supported by the Huygens Probe Project HASI instrument investigation. We thank Jonathan Lunine for useful comments related to the mass and energy limits on rain.

Appendix A

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
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<tbody>
<tr>
<td>(a_d)</td>
<td>spherical equivalent of drop radius</td>
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<tr>
<td>(C_d)</td>
<td>drag coefficient</td>
</tr>
<tr>
<td>(C_{do})</td>
<td>rigid sphere drag coefficient</td>
</tr>
<tr>
<td>(\epsilon_p)</td>
<td>specific-heat capacity of drop</td>
</tr>
<tr>
<td>(\epsilon_{pi})</td>
<td>specific-heat capacity of drop component (i)</td>
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<td>(D_i)</td>
<td>molecular diffusivity of component (i)</td>
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<tr>
<td>(\Delta M_i)</td>
<td>change in mass of drop component (i)</td>
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<td>(f_k)</td>
<td>ventilation coefficient for heat transfer</td>
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<tr>
<td>(f_c)</td>
<td>ventilation coefficient for mass transfer</td>
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<td>(g)</td>
<td>gravitational acceleration</td>
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<tr>
<td>(H_{rad})</td>
<td>radiative heat flux</td>
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<td>(K_n)</td>
<td>Knudsen number</td>
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<td>(k)</td>
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<td>(L_{ei})</td>
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<td>total drop mass</td>
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<tr>
<td>(\rho_a)</td>
<td>atmospheric density</td>
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the drag area (\(S_d\)). The drag reference area and drag coefficient of an oblate spheroid, because this is a good approximation for water drops on Earth (Pruppacher and Rasmussen, 1979).

\[\rho_{C_2H_6}\] density of liquid ethane
\[\rho_{CH_4}\] density of liquid methane
\[\rho_{N_2}\] density of liquid nitrogen
\[\rho_d\] average drop density
\[\kappa\] thermal conductivity
\[\sigma\] Stephan–Boltzman constant
\[\mathcal{N}_i\] number of moles of component \(i\) in drop

**A.1. Fall velocity**

We assume the drop is always at terminal velocity, so the drop’s velocity is dependent only on its mass and radius, and the local atmospheric properties. The fall velocity is calculated using equations from Lorenz (1993), altered when necessary to account for a multi-component drop. The drop’s velocity is represented by

\[m_{tot}g = \frac{4}{3}\pi \rho_d a_o^3,\] (A.3)

where \(V\) is the velocity, \(g\) is the gravitational acceleration (1.35 m/s\(^2\)), \(\rho_a\) is the atmospheric density, \(S\) is the drop’s drag reference area, \(C_d\) is the drag coefficient, and \(m_{tot}\) is the mass of the drop:

\[m_{tot} = \frac{4}{3}\pi \rho_d a_o^3,\] (A.4)

where \(a_o\) is the drop’s radius, and \(\rho_d\) is its density. \(\rho_d\) is found by adding the density contribution of each component in the drop. The density of liquid nitrogen is 808 kg/m\(^3\), and the densities of methane (\(\rho_{CH_4}\)) and ethane (\(\rho_{C_2H_6}\)) are functions of the drop’s temperature (\(T_d\)):

\[\rho_{CH_4} = 612 - 1.8T_d\] (kg/m\(^3\)), (A.5)
\[\rho_{C_2H_6} = 743 - 1.04T_d\] (kg/m\(^3\)), (A.6)

where \(T_d\) is in K (Tokano, 2005). Average density of the drop is given by

\[\frac{1}{\rho_d} = \sum_i \frac{Y_{d,mass_i}}{\rho_i},\] (A.7)

where \(Y_{d,mass}\) is the mass fraction of component \(i\), and \(\rho_i\) is its density.

Following Lorenz (1993), the drop is modeled as an oblate spheroid, because this is a good approximation for water drops on Earth (Pruppacher and Rasmussen, 1979). The drag reference area and drag coefficient of an oblate spheroid are found by applying a correction to the corresponding values for a rigid sphere. For a rigid sphere, the drag area (\(S_o\)) and drag coefficient (\(C_{do}\)) are

\[S_o = \pi a_o^2\] (A.8)

and

\[C_{do} = (24/N_{Re})(1 + 0.197N_{Re}^{0.63} + 2.6 \times 10^{-4}N_{Re}^{1.38}),\] (A.9)

where \(N_{Re}\) is the Reynolds number

\[N_{Re} = \frac{2a_o \rho_a V}{\mu}\] (A.10)

and \(\mu\) is the viscosity of the atmosphere. For Titan, as for Earth, the atmosphere is assumed to be 100% nitrogen for the purposes of determining viscosity, so

\[\mu = \mu_{N_2} = 1.718 \times 10^{-5} + [5.1 \times 10^{-8}(T_{atm} - 273)]\] (Pa s). (A.11)

\(T_{atm}\) is the atmospheric temperature in K. 

The drop’s velocity is represented by

\[S = S_o k^{2/3}\] (A.12)

and

\[C_d = \frac{C_{do}}{k},\] (A.13)

respectively, where \(k\) is the correction to an oblate spheroid from a rigid sphere:

\[k = 0.97 - 0.072N_{We}\] when \(N_{We} > 0.1,\] (A.14a)
\[k = [1 - (9/16)N_{We}]^{1/2}\] when \(N_{We} < 0.1\) (A.14b)

and \(N_{We}\) is the Weber number, described by

\[N_{We} = \frac{a_o V^2 \rho_a}{\gamma_i},\] (A.15)

where \(\gamma_i\) is the surface tension of the drop (0.017 N/m for methane).

The drop velocity is solved for iteratively, using an initial guess for the velocity found the first time by solving Eq. (A.3) using a value of 0.8 for \(C_d\), and subsequent times by using the velocity from the previous mass step.

**A.2. Drop evaporation**

The evaporation or growth of the drop is governed by the evaporation or condensation of its constituents, which is in turn determined primarily by the difference between the vapor pressure of each component in the drop (\(P_d\)) and its corresponding atmospheric partial pressure (\(P_{vapor}\)). The change in mass of each drop component is calculated separately (altered from Lorenz, 1993):

\[
\frac{dM_i}{dt} = \frac{f_i 4\pi a_o D_i m_i}{RT_i} (P_{vapor} - P_d),
\] (A.16)

where \(dM_i/dt\) is the change in mass of component \(i\) over a given time interval \(dt\), \(D_i\) is the component’s molecular diffusivity, \(m_i\) is its molecular weight, \(R\) is the universal gas constant, \(f_i\) is the ventilation coefficient, and \(T_i = (T_{atm} + T_d)/2\), where \(T_d\) is the drop temperature (Pruppacher and Rasmussen, 1979).

The diffusivities of methane (\(D_{CH_4}\)) and ethane (\(D_{C_2H_6}\)) through nitrogen are described by (corrected from Lorenz, 1993):

\[D_{CH_4} = 1.96 \times 10^{-5} \left(\frac{T_{atm}}{T_o}\right)^{1.75} \left(\frac{P_o}{P_{atm}}\right)\] (m\(^2\) s) (A.17a)
and (Barth and Toon, 2003)

\[ D_{C_2H_6} = 1.48 \times 10^{-5} \left( \frac{T_{atm}}{298.15} \right)^{1.94} \left( \frac{P_o}{P_{atm}} \right) \text{ (m}^2\text{s}), \quad (A.17b) \]

where \( P_{atm} \) is the total atmospheric pressure, and \( T_o \) and \( P_o \) refer to standard conditions (273 K and 101,325 Pa, respectively). Since nitrogen is the major constituent of Titan’s atmosphere, the possibility that the nitrogen leaving the drop is not diffusing, but rather flowing from the drop in a region around the drop called a Knudsen layer had to be considered (Young, 1991). This process is significant if the mean free path of nitrogen is comparable to or larger than the diameter of the drop. In other words, if the Knudsen number (\( K_n = \lambda/2a_o \), where \( \lambda \) is the mean free path) is equal to or greater than one (Colaprete and Toon, 2003). In Titan’s atmosphere, the Knudsen number is small (of order \( 10^{-6} \)–\( 10^{-5} \)), so rather than flowing, nitrogen diffuses. The self-diffusion coefficient (\( D_{N_2, self} \)) is used since the nitrogen is essentially diffusing through itself, rather than through another medium (Colaprete and Toon, 2003):

\[ D_{N_2, self} = \frac{2\mu}{\rho_o}. \quad (A.18) \]

The ventilation coefficient is defined by the Reynolds and Schmidt numbers:

\[ f_v = 1 + 0.108X^2 \quad \text{for } 0 < X < 1.4, \quad (A.19a) \]
\[ f_v = 0.78 + 0.308X \quad \text{for } 1.4 < X < 51.4, \quad (A.19b) \]

where

\[ X = \lambda^{0.5} \lambda_{Se}^{0.33} \quad (A.20) \]

and (Lorenz, 1993; Pruppacher and Rasmussen, 1979)

\[ N_{Se} = \frac{\mu}{\rho_o D}. \quad (A.21) \]

This formulation of the ventilation coefficient is empirically based on falling water drops subject to Earth conditions. Specifically, \( X \) is partially determined by the drop radius, via its dependence on the Reynolds number (Eqs. (A.10) and (A.20)). Maximum drop size on Earth is significantly smaller than the theorized values for Titan (3 vs. 4.75 mm in radius, Lorenz (1993)); therefore, values of \( X \) for large drops on Titan exceed 51.4, which corresponds to the maximum drop size experimentally tested by Pruppacher and Rasmussen (1979). For drops with values of \( X \) larger than 51.4 we continue to use Eq. (A.19b) to calculate the ventilation coefficient; however, pending further study, Eqs. (A.19a) and (A.19b) may need to be revised for appropriate application to Titan. See Section 4 and Fig. 2b for a description of the model’s sensitivity to variations in the ventilation coefficient.

The partial pressure of component \( i \) in the atmosphere is the product of the atmospheric pressure and the mole fraction of \( i \) in the atmosphere (\( Y_{atm} \)) (Lorenz, 1993):

\[ P_{vapor} = P_{atm} Y_{atm}. \quad (A.22) \]

And, via Raoult’s law, the vapor pressure of \( i \) in the drop is the product of the saturation vapor pressure of \( i \) (\( P_{sat, i} \)), the mole fraction, or volume fraction, of \( i \) in the drop (\( Y_{d, mol} \)), and the activity coefficient of \( i \), a non-ideal correction (\( \gamma_i \)) (altered from Lorenz, 1993):

\[ P_{d,i} = \gamma_i P_{sat, i} Y_{d, mol}. \quad (A.23) \]

The mole fraction of \( i \) is calculated from the mass fraction via:

\[ \chi_i = M_i / m_i, \quad (A.24) \]
\[ Y_{d, mol} = \chi_i / \sum_j \chi_j, \quad (A.25) \]

where \( \chi_j \) is the number of moles of component \( i \). Curvature can have an effect on the saturation vapor pressure of a liquid. This Kelvin effect, however, was found to be insignificant for the curvatures of the drop sizes in question, and \( P_{sat, i} \) is therefore calculated directly from fits to data (Weast, 1976):

\[ P_{sat, N_2} = (1 \times 10^5)(10^{1.95-306/T_d}), \quad (A.26) \]
\[ P_{sat, CH_4} = (3.4543 \times 10^9) \exp(-1145.705/T_d), \quad (A.27) \]

\( (T_d \text{ in K, } P_{sat, N_2} \text{ and } P_{sat, CH_4} \text{ in Pa}) \) and from Moses et al. (1992):

\[ \log_{10}(P_{sat, C_2H_6}) = 5.9366 - \frac{1086.17}{T_d} + 3.83464 \log_{10} \left( \frac{1000}{T_d} \right) \quad (A.28) \]

(\( T_d \text{ in K, } P_{sat, C_2H_6} \text{ in mmHg} \)).

As mentioned in the text, the drop is considered a non-ideal mixture, which allows for the calculation of the effect of the presence of methane on the vapor pressure and therefore the evaporation rate of nitrogen, and vice versa. \( \gamma \) is calculated by assuming the ternary drop (\( N_2, CH_4, C_2H_6 \)) behaves as a binary \( N_2–CH_4 \) mixture. This is done because the mole fraction of ethane in the drop is negligible for much of the drop’s descent, so the assumption that its presence has a negligible effect on the drop’s divergence from an ideal mixture is sound. We therefore assume the activity coefficient for ethane is 1, and follow Thompson et al. (1992) in the calculation of \( \gamma_{N_2} \) for nitrogen and methane.

Once the amount of each component leaving/entering the drop is determined via Eq. (A.16), these values are simply added to each component’s mass to find the new masses of methane, nitrogen, and ethane, and from that the new drop mass is found:

\[ M_{new} = M_{old} + dM_i, \quad (A.29) \]
\[ M_{tot} = M_{CH_4, new} + M_{N_2, new} + M_{C_2H_6, new}. \quad (A.30) \]

Note that these equations describe mass loss as well as mass gain, so they are applicable to both Titan’s growth and evaporation regions.
A.3. Calculation of drop temperature

The drop temperature was calculated, taking into account heat transfer due to conduction, radiation, and evaporation/condensation (latent heat):

\[ M_{\text{tot}} \frac{dT}{dr} = H_{\text{lat}} + H_{\text{cond}} + H_{\text{rad}}, \]  

(A.31)

where \( c_p \) is the specific-heat capacity of the drop in J/K/kg (\( c_p = \sum c_i M_i \)), and \( H_{\text{lat}}, H_{\text{cond}}, \) and \( H_{\text{rad}} \) are the latent, conductive, and radiative heat transfer rates, respectively:

\[ H_{\text{lat}} = \frac{dM_N dL_N + dM_{CH_4} dL_{CH_4} + dM_{C_2H_6} dL_{C_2H_6}}{dr}, \]

(A.32)

\[ H_{\text{cond}} = 4\pi k a_c (T_{\text{atm}} - T_d) f_h, \]

(A.33)

\[ H_{\text{rad}} = 4\pi k a_c^2 \sigma (T_{\text{atm}}^4 - T_d^4), \]

(A.34)

where \( L_{N_2}, L_{CH_4}, \) and \( L_{C_2H_6} \) are the latent heats of evaporation of nitrogen, methane, and ethane respectively, \( \kappa \) is the thermal conductivity of the atmosphere, \( \varepsilon \) is the atmospheric emissivity, \( \sigma \) is the Stephan–Boltzman constant, and \( f_h \) represents the effect of ventilation on heat transfer, where \( f_h = f_c \) (Pruppacher and Rasmussen, 1979).

The thermal conductivity is found by linear extrapolation from laboratory data for pure nitrogen gas (Weast, 1976):

\[ \kappa = 9 \times 10^{-5} T_{\text{atm}} + 0.0005 \]

(T\( \text{atm} \) in K, \( \kappa \) in W/m/K, accurate to 1.3% over 80–200 K), and the latent heats of methane and nitrogen from linear extrapolation from Thompson et al. (1992), accurate to 0.1% and 1%, respectively, over the range (71.2–94 K):

\[ L_{CH_4} = (10818 - 23.202 T_d)/m_{CH_4}, \]

(A.36)

\[ L_{N_2} = (8679 - 40.702 T_d)/m_{N_2}, \]

(A.37)

(\( T_d \) in K, \( m_{CH_4} \) and \( m_{N_2} \) in kg/mol, \( L_{N_2} \) and \( L_{CH_4} \) in J/kg). The latent heat of ethane is assumed to be roughly equal to its latent heat at boiling point.

A.4. Modeling methane hail

We calculate the size and fall rate of pure methane hail by making several small changes to the raindrop model to account for the physical differences between a liquid raindrop and a hail particle. An ethane seed is not included because in a hail particle the ethane would be sequestered in the center, and therefore would not affect the partial pressure of the methane ice. Nitrogen is not allowed to enter the hail particle as it descends. Additionally, the velocity of the hail particle is calculated assuming the hail is a rigid sphere (\( \kappa = 1 \)), rather than an oblate spheroid. The ventilation coefficient remains unchanged. There is also no size limit placed on the hail particle, since hail does not behave like a raindrop and break up once it reaches a certain size. The physical properties of the methane are changed to those of solid methane—namely specific-heat capacity (2641 J/kg/K, Colwell et al., 1963), density (519 kg/m\(^3\), Barth and Toon, 2006), and vapor pressure. The equation for the vapor pressure of methane is

\[ \log(p_{sat CH_4}) = 4.42507 - \frac{453.92414}{T_d} - \frac{4055.6016}{T_d^2} \]

\[ + \frac{115352.19}{T_d^3} - \frac{116556.7}{T_d^4} \]  

(A.38)

in atmospheres, where \( T_d \) is in K (Moses et al., 1992). Finally, in the calculation of latent heat transfer, the latent heat of sublimation is used instead of the latent heat of melting:

\[ L_{CH_4} = \frac{R}{m_{CH_4}} \left( \frac{453.92414 + 811.2032}{T_d} - \frac{346,056.57}{T_d^2} \right) \ln 10, \]

(A.39)

where \( T_d \) is in K (Barth and Toon, 2006).

References


