Microphysical modeling of ethane ice clouds in Titan’s atmosphere

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Abstract

A time-dependent microphysical model is used to study the evolution of ethane ice clouds in Titan’s atmosphere. The model simulates nucleation, condensational growth, evaporation, coagulation, and transport of particles. For a critical saturation of 1.15 (a lower limit, determined by laboratory experiments), we find that ethane clouds can be sustained between altitudes of 8 and 50 km. Growth due to coalescence is inefficient, limiting the peak in the size distribution (by number) to 10 μm. These clouds vary with a period of about 20 days. This periodicity disappears for higher critical saturation values where clouds remain subvisible. Rainout of ethane due to methane cloud formation raises the altitude of the ethane cloud bottom to near the tropopause and may eliminate ethane clouds entirely if methane cloud formation occurs up to 30 km. However, clouds formed above the troposphere from other gases in Titan’s atmosphere could be sustained even with rainout up to 30 km. Although the optical depth of ethane clouds above 20 km is typically low, short-lived clouds with optical depths of order 0.1–1 can be created sporadically by dynamically driven atmospheric cooling. Ethane cloud particles larger than 25 μm can fall to the surface before total evaporation. However, ethane clouds remain only a small sink for tholin particles. At the peak of their cycle, the optical depth of ethane clouds could be comparable to that of tholin in the near-infrared, resulting in a 5% increase in Titan’s albedo for wavelengths between 1 and 2 μm. A number of factors limit our ability to predict the ethane cloud properties. These factors include the mixing time in the troposphere, the critical saturation ratio for ethane ice, the existence of a surface reservoir of ethane, the magnitude and timing of dynamically driven temperature perturbations, and the abundance and life cycle of methane clouds.

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1. Introduction

Titan’s temperature profile allows for the condensation of many of its atmospheric constituents throughout the troposphere and lower stratosphere. Sagan and Thompson (1984) showed that most of the known hydrocarbons and nitriles can condense in the stratosphere while methane condensation could occur in the troposphere. The only known nuclei for tropospheric clouds on Titan are aerosol particles sedimenting from the stratospheric haze layers. However, cloud formation may be a sequential process in which condensation first starts in the stratosphere, proceeds through the addition of a series of hydrocarbons and nitriles, and finally ends with methane condensation in the middle troposphere.

The first observational evidence for clouds in Titan’s lower atmosphere was reported by Griffith et al. (1998). From ground-based near-infrared data they concluded that increases in reflectivity at several wavelengths observed during 2 out of 18 sampling periods indicate the temporary presence of methane clouds in the troposphere around 15 km. Later Griffith et al. (2000) found similar evidence for short-lived methane clouds at a higher tropospheric altitude, around 30 km. These clouds may be indicative of a methane cycle on Titan similar to the Earth’s hydrological cycle.

McKay (1996) found that tholin (laboratory produced analogs for Titan’s haze particles) are virtually insoluble in polar solvents such as methane and ethane, concluding that large supersaturations must build up before tholin particles
could serve as acceptable condensation nuclei. However, observations of water ice clouds in the terrestrial atmosphere indicate that the ice nuclei involved are most commonly solid, insoluble particles. Hence, the methane ice nucleability of tholins, which needs to be measured, is probably not related to the solubility of tholins.

The major hydrocarbon product of methane photolysis is ethane. Gillett et al. (1973) used ground-based telescopes to make the first detection of ethane in the 12-μm region. Later observations from Voyager IRIS (in the same spectral region) identified the v₁ band of ethane in Titan’s stratosphere and set the ethane mixing ratio at 2 × 10⁻⁵ (Hanel et al., 1981). Calculations from more recent ground-based measurements give mole fractions ranging from 4 × 10⁻⁶ to 1.6 × 10⁻⁵, depending on the thermal profile used (Kostiuk et al., 1997). If we were to assume this mixing ratio is independent of altitude, then comparison with the ethane vapor pressure curve shows that ethane would be supersaturated between approximately 5 and 62 km.

Sagan and Thompson (1984) calculated that ethane should condense around an altitude of 58 km. This same study estimated a visible optical depth of about 200 for the resulting ethane clouds (assuming 1 μm particles in the geometric limit).

Although definitive observations of ethane clouds have not been made, Samuelson et al. (1997) believe ethane clouds could provide some of the observed opacity between 300 and 600 cm⁻¹. By including scattering in their radiative transfer modeling, they found, in addition to the condensed C₄N₂ at the north pole, a second component whose neutral wavenumber dependence was consistent with a thin, larger particle hydrocarbon cloud. They assumed the cloud was composed of ethane in order to allow methane to remain supersaturated and provide the rest of the opacity between 300 and 600 cm⁻¹. They compared several cloud models and found the best fit to the IRIS data called for an ethane cloud of τ = 0.17 ± 0.28 and rₗ = 66 ± 36 at 40 km (fixed altitude), and a methane supersaturation of 1.48 ± 0.11.

Despite the paucity of observations of lower atmospheric ethane clouds, methane clouds have been considered in many radiative transfer models (Courtin et al., 1995; Samuelson et al., 1997). Ethane is the dominant product of methane photolysis, and will condense at altitudes higher than that of methane. Condensed ethane could then serve to lower or raise the contact parameter necessary for methane nucleation on tholins. Given the impending Cassini/Huygens data, we feel it is important to understand the processes that could lead to ethane cloud formation and to determine the likely physical properties of these clouds. Some questions we address are:

1. Can the removal of ethane and other vapors by methane precipitation in the troposphere limit the production of clouds in the stratosphere?
2. What is the likely vertical extent of ethane clouds?
3. Will ethane clouds produce rain by either condensational growth or coalescence? How does ethane precipitation compare to that of methane raindrops as studied by Lorenz (1993)? Could ethane precipitation reach the ground?
4. Are the cloud particle radii of 10 and 75 μm suggested by Samuelson and Mayo (1997) plausible?
5. Will nucleation or scavenging of tholin particles by ethane change the tholin profile?
7. What is the relaxation time for ethane cloud perturbations?
8. Can ethane clouds be observed from Earth or Cassini?
9. What are the major unknowns limiting our ability to predict or simulate ethane clouds on Titan?

The layout of this paper is as follows: Section 2 describes the life cycle of a cloud starting with nucleation, condensational growth, coagulation, and destruction through rain-out or evaporation. Section 3 describes the microphysical model; results of model simulations are given in Section 4 and discussed in Section 5. Relevant Cassini and Huygens observations are outlined in Section 6. We conclude by addressing the questions above in Section 7.

2. Cloud formation & evolution

Nucleation or activation are the first steps in cloud formation (Pruppacher and Klett, 1997). Activation occurs when liquid solution aerosols adsorb their solvent with rising humidity to become cloud droplets. No phase change occurs in this process, which is the dominant one for liquid water in the terrestrial atmosphere (the latent heat release as a result of condensation is accounted for in the growth process). At Titan’s much lower temperatures, where ethane will mostly exist in the solid state, this process is unlikely to occur. This leaves nucleation, which requires much higher supersaturations to surpass the energy barrier. For ethane ice clouds at the low temperatures on Titan, it is most likely that ethane vapor condenses onto existing aerosol particles (heterogeneous nucleation). Clusters randomly form on the surface of the aerosol. Some small fraction of these will be large enough to reach the critical germ radius, given by

\[ a_c = \frac{2\sigma_s M_w}{RT \rho_s \ln S} \]  

where \( \sigma_s \) is the surface free energy of the solid–vapor interface of the condensing species, \( M_w \) is the molecular weight of the condensing gas, \( R \) is the universal gas constant, \( T \) is the atmospheric temperature, \( \rho_s \) is the density of the condensate, and \( S \) is the saturation ratio (explained below). Once the germ reaches the critical size, it is energetically favorable for it to grow once a single molecule has
been added. The nucleation rate is then determined from the number of aerosols present and the time it takes for one cluster to grow past this critical size by colliding with a single molecule of the condensing vapor. Obviously, the nucleation rate depends on particle size, since more clusters are present on a larger aerosol.

The onset of nucleation is determined by the degree of saturation of the vapor. The saturation ratio, \( S \), is the ratio of the partial pressure of the vapor to its saturation vapor pressure. The value of \( S \) determines which of three states the vapor is in: \( S < 1 \), subsaturated; \( S = 1 \), saturated; and \( S > 1 \), supersaturated. We note that \( S \) is directly proportional to relative humidity, such that \( S = 1 \) corresponds to 100% relative humidity. Nucleation cannot occur until the vapor becomes supersaturated, but how high \( S \) needs to be to obtain a given value of the nucleation rate depends on the particular gas, the temperature and the ice nuclei (the aerosol particles on which the cloud forms). Fig. 1 shows the sensitivity of the nucleation rate to variations in supersaturation.

By measuring the saturation ratio in the laboratory and using the equations of classical nucleation theory, we calculate the contact parameter, \( m \). The contact parameter is determined by the condition of mechanical equilibrium that there must be no net force component along the solid surface. This condition can be expressed through Young’s relation

\[
\cos \theta = \frac{\sigma_{Na} - \sigma_{Ni}}{\sigma_{Na}} = m,
\]

where \( \sigma \) is the surface free energy for the air–substrate (\( N/a \)) interface, substrate–ice (\( Ni/i \)) interface, and ice–air (\( i/a \)) interface. We call \( \cos \theta \) the contact parameter, \( m \). The contact parameter characterizes the nucleability of the aerosols such that \( m = 1 \) indicates a perfectly wettable nucleus and \( m = -1 \) indicates an unwettable nucleus. It is important to note that experimental evidence indicates nucleation onto solid substrates tends to favor nuclei with similar lattice spacing to that of the ice, and may occur in surface defects in the lattice. Nonetheless, the classical nucleation theory still appears to be the best description for heterogeneous nucleation for Titan conditions (Guz et al., 1997).

The contact parameter is related to the nucleation rate through the free energy of germ formation (Helmholtz free energy),

\[
\Delta F_g = \frac{4 \pi a_s^2 \sigma_{sv} f}{3},
\]

and \( f = (2 + m)(1 - m)^2/4 \) for a planar substrate. In our case, we have nucleation onto spherical particles, so \( f \) becomes a much more complicated function of the contact parameter and the ratio of the germ radius to the substrate radius. For simplicity of presentation, though, the planar substrate formula is used here in the derivation of the critical nucleation rate. In our numerical model we use the actual form that contains the radius of the germ (see Pruppacher and Klett (1997) for complete equation). Solving for \( \Delta F_g \) at the critical radius gives the energy barrier to stable embryo formation. \( \Delta F_g \) is \( \sim 10^{-13} \) ergs and \( a_s \sim 0.05 \mu m \) for nucleation of ethane vapor (onto tholin) at a saturation (\( S \)) of 1.15.

The rate (cm\(^{-2} \cdot s^{-1} \)) at which nuclei appear at the surface of a single aerosol of radius \( r \) per unit area is

\[
J = \kappa \exp \left\{ -\frac{\Delta F_g}{k_B T} \right\},
\]

where the prefactor (kinetic term) is given by \( \kappa = \pi Z_s a_s^3 \beta c_i \) and \( k_B \) is Boltzmann’s constant. \( Z_s \) is the Zeldovich factor,

\[
Z_s = \sqrt{\frac{\Delta F_g}{3 \pi k_B T \gamma^2}},
\]

which accounts for the nonequilibrium nature of the cluster size distribution (\( \gamma \) is the ratio of the germ volume to that of the aerosol particle); the flux of monomers to the spherical cap per unit surface area of the particle is
\[
\beta = \frac{p_v}{\sqrt{2\pi m \cdot k_B T}},
\]

where \(p_v\) is the vapor pressure and \(m\) is the mass of a condensate molecule. In our model \(\beta\) ranges from \(-10^{15}\) to \(10^{20}\) cm\(^{-2}\) s\(^{-1}\). The surface concentration of adsorbed monomers is

\[
c_1 = \frac{p_v}{\sqrt{2\pi m \cdot k_B T} v_s} \exp \left(-\frac{\Delta F_{\text{des}}}{k_B T}\right),
\]

where \(\Delta F_{\text{des}}\) is the desorption energy per molecule and \(v_s\) is the frequency of vibration of an adsorbed molecule normal to the surface. The nucleation rate is multiplied by an additional factor of \(4\pi r^2\nu\) for nucleation onto a spherical substrate of radius \(r_s\) to get the rate at which the particle nucleates to form ice. The exponential term dominates the \(J\) equation (Eq. (4)).

The critical saturation ratio (\(S_{\text{crit}}\)) marks the boundary between insignificant nucleation rates (\(S < S_{\text{crit}}\)) and those leading to visible particle formation (\(S > S_{\text{crit}}\)). Values of \(S_{\text{crit}}\) for homogeneous nucleation are often 10 or greater (Moses et al., 1992). Observations of the Earth’s atmosphere for heterogeneous nucleation of water ice crystals show \(S_{\text{crit}}\) is about 1.5 for nucleation (Heymsfield et al., 1998; Jensen et al., 2001). Once the critical saturation ratio is known, we can use the equations of nucleation theory, setting \(J = 1\) cm\(^2\) s\(^{-1}\) at \(S = S_{\text{crit}}\) for nucleation onto a planar substrate of area 1 cm\(^2\), to solve for the contact parameter. Then the contact parameter determines the nucleation rate for the modeled atmospheric conditions.

Homogeneous nucleation tends to be an inefficient method for the development of condensation, as the vapor pressure of the condensing gas must exceed its saturation vapor pressure by several hundred percent before condensation can begin. However, the presence of seed nuclei—heterogeneous nucleation—only requires \(S \sim 1\) or 2 for condensation to begin. Titan tholin is a likely candidate for seed nuclei for ethane, methane, or liquid ethane or methane. After being created in the photochemical haze layer, it sediments down through the atmosphere. As it is falling, the tholin may become coated with other condensation products before reaching the altitudes of methane/ethane condensation.

Once a cloud particle has formed, it can grow through the condensation of additional gas while the surrounding atmosphere remains supersaturated. The condensational growth of a cloud particle is described by

\[
\frac{dM}{dt} = \frac{g_0}{1 + g_1} \frac{(S - A_v A_i)}{\rho_a \rho \cdot v},
\]

where \(M\) is the particle mass, \(t\) is time, \(S\) is the saturation ratio, and \(p_v\) is the saturation vapor pressure. \(A_v\) is the Kelvin correction to account for the effects of particle curvature on the vapor pressure

\[
A_v = \exp \left(\frac{2m \cdot \sigma}{\rho_a r \cdot RT}\right),
\]

where \(\sigma\) is the surface tension and \(\rho_a\) is the density of the condensate (as in Eq. (1)). \(A_i\) is a solute term and is taken to be equal to 1 in our case since tholins are not soluble in liquid ethane or methane. The \(g_i\) terms are growth kernels that relate the growth to vapor diffusivity (\(D'\)), thermal conductivity (\(\lambda'\)) of the atmosphere, and latent heat of condensation (\(L\)):

\[
g_0 = \frac{4\pi rD' f_m}{RT},
\]

\[
g_1 = \frac{mL^2}{RT^2 f \lambda' 4\pi r}.
\]

The \(f\) terms are ventilation factors to account for the motion of the particle through the air as condensation occurs. \(f_v\) is the mean ventilation coefficient and is proportional to \((\text{Sc}^{-1/3} \cdot \text{Re}^{-1/2})\), where \(i = 1\) if the quantity in parentheses is greater than unity or 2 otherwise (Sc is the Schmidt number and Re is the Reynolds number). For a motionless drop, \(f_v = 1\). \(f_1\) is the ventilation effect on heat transfer and follows the same convention as \(f_v\) but with the Schmidt number replaced by the Prandtl number. The primes on \(D\) and \(\Lambda\) indicate a correction for the free molecular limit (the full equations can be found in Pruppacher and Klett (1997), Chap. 13). Substituting \(\frac{4\pi r^2}{RT^2 f \lambda'}\) for \(M\) in Eq. (8) shows that the droplet size increases as the inverse of the radius. So during the growth phase, smaller drops will grow much faster and thus catch up to larger drops. Condensational growth works to create a more monodisperse distribution of cloud drops.

As the cloud particle grows, it will fall through the atmosphere with a velocity dependent on the particle size and mass and the atmospheric viscosity (for \(r >\) mean free path),

\[
V_{\text{fall}} = \frac{2B \rho_s r^2 g}{9\eta},
\]

where \(\rho_s\) is the particle density, \(g\) is acceleration due to gravity, \(\eta\) is the dynamic viscosity of air, and \(r\) is the radius of the particle. \(B\) is a correction for both particle shape and mean free path and is of order unity in the troposphere. Equation (12) applies only in the low Reynolds number regime (\(\text{Re} < 10^{-2}\)). For the large Reynolds number regime, the Reynolds number is calculated as described in Chap. 10 of Pruppacher and Klett (1997). The fall speed can then be derived using the definition of the Reynolds number.

As particles move through the atmosphere, they may collide with other particles and so grow through coagulation,

\[
\frac{dn(v)}{dt} = 0.5 \int_0^v K_{\text{coag}}(v', v - v') n(v') n(v - v') dv' - \int_0^v K_{\text{coag}}(v', v) n(v) n(v') dv',
\]
where $K$ is the coagulation kernel. The two terms in Eq. (13) represent the creation of particles of size $v$ through the coagulation of smaller particles and the loss of particles of size $v$ as they coagulate to form larger particles, respectively. Toon et al. (1980) found that Brownian coagulation is the dominant coagulation process for tholin in Titan’s atmosphere. The Brownian coagulation kernel is given by

$$K_{br} = 2\pi(D_{p1} + D_{p2})(\mathcal{D}_1 + \mathcal{D}_2)b,$$

where $D_{p_i}$ is the diameter of the $i$th particle and $\mathcal{D}_i$ is the diffusivity. The parameter $b$ is a correction term for when the mean free path of the aerosol particle is comparable to the radius of the absorbing particle. In the continuum regime, $b = 1$ and the diffusivities can be represented by the Stokes–Einstein formula (where $\eta$ is the atmospheric viscosity):

$$\mathcal{D}_i = \frac{k_BT}{3\pi\eta D_{pi}}.$$  

In our model $\mathcal{D}_i$ is $\sim 10^{-2}$ cm$^2$ s$^{-1}$ at the bottom of the atmosphere and increases to $\sim 1$ cm$^2$ s$^{-1}$ at 100 km. In Titan’s atmosphere the particles are subject to charging below 300 km. This particle charging makes coagulation less efficient for small tholin particles. Brownian coagulation is not an important process for Titan cloud particles due to their low number density and large size.

Coalescence is an accretional process. Falling large drops overtake slower falling small drops, and collect these smaller drops with an efficiency defined by the ratio of the actual collision cross section to the geometric cross section (Seinfeld and Pandis, 1998). An additional efficiency, the coalescence efficiency, describes whether drops on collision trajectories will coalesce or bounce off one another. Then the coagulation kernel is described by

$$K_{coal} = \frac{\pi}{4}E_{coal}E_{coll}(D_{p1} + D_{p2})^2(v_{p1} - v_{p2}).$$

where $D_{p_i}$ has the same meaning as described above and $v_{p_i}$ are particle velocities. We use terrestrial data from Hall (1980) and Beard and Ochs (1984) to determine the collision and coalescence efficiencies, $E_{coll}$ and $E_{coal}$, respectively. Once particles reach millimeter sizes, through either growth or coalescence, they are considered raindrops.

Raindrops will either quickly fall to the surface or evaporate in subsaturated regions of the atmosphere (evaporation is described by Eq. (8) when $S < 1$). Lorenz (1993) described evaporating methane raindrops in Titan’s atmosphere. The raindrops were modeled as spheroids subject to the effects of aerodynamic drag and gravity. Growth was described by a simplified version of our Eq. (8), $dM/dt = g_\text{d}d\rho_v$. Collisonal growth was not treated (we show below that this type of growth is inefficient for our ethane clouds). Lorenz’s study concluded that for surface relative humidities allowed by the Voyager data (maximum value of 70%), methane rain from a 3-km cloudbase cannot reach the surface before total evaporation occurs. However, ethane condensation nuclei, dubbed “rain ghosts,” will remain after the methane clouds have evaporated. Lorenz’s calculations indicate extinctions of $0.5$ km$^{-1}$ for 1-μm-radius particles and $10^4$ times less for 10 μm particles (compare to our ethane clouds which have extinctions ranging from $10^{-3}$ to $10^{-1}$ at 3 km, particle sizes from $\sim 1–25$ μm). Due to the lower vapor pressure of ethane and consequently its slower evaporation rate, we find that ethane raindrops may reach the surface, as we show below.

Samuelson and Mayo (1997) used methane condensation onto precipitating ethane ice crystals as the loss process in their steady-state methane model (this was balanced by resupply from eddy diffusion). Maintaining methane supersaturation required a small ethane particle flux into the methane supersaturated region (to limit the number of nucleation sites). A small ethane particle flux implies large ethane particle radii (since the downward ethane transport rate is equal to the product of the number of ethane molecules per particle and the particle sedimentation flux at the tropopause). To match the latitudinal dependence of the methane supersaturations implied by the IRIS data simultaneously with the ethane flux, they required ethane particle radii of 10 μm at the north pole and 75 μm in equatorial regions.

3. The microphysics model

The parameters described in this section are summarized in Table 1. The table is divided into four sections: Atmospheric properties, Aerosol properties, Gas properties, and Nucleation and growth properties.

The microphysics model simulates particle nucleation, condensational growth, evaporation, coagulation, sedimentation, eddy diffusion, and aerosol electrical charging. The aerosol particles are created above the modeled domain by unspecified photochemistry. The model extends from the surface to 100 km altitude with 50 equally spaced bins. Aerosol processes above this region are accounted for by a flux of aerosol particles into the top layer. This flux was determined based on a previous model of Titan’s aerosols that covered the first 600 km of Titan’s atmosphere (Toon et al., 1992). Particles are lost to the surface by deposition. The steady-state aerosol profile used to define the flux at the top of the model is shown in Fig. 2. Steady state in the aerosol model is defined to be reached when the flux of particles out the bottom of the model is equal to the production rate.

The aerosol particles are segregated into 35 bins that double in volume. The bin-mean radii range from 13 Å to 3.35 μm. Fig. 3 shows the tholin size distribution at various altitudes used to initialize the cloud model and which the model finds in steady state if no condensational clouds are allowed to form. Cloud particles are contained in 41 size bins from about 0.1 μm to 1 mm. The aerosol particles grow
Table 1
Microphysics model equations

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Formula*</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Atmospheric properties</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Temperature</td>
<td>Recommended model (Fig. 4)</td>
<td>Lellouch and Hunten (1987)</td>
</tr>
<tr>
<td>Density</td>
<td>Recommended model</td>
<td>Lellouch and Hunten (1987)</td>
</tr>
<tr>
<td>Pressure</td>
<td>Ideal gas law</td>
<td></td>
</tr>
<tr>
<td>Viscosity</td>
<td>$\mu = 1.718 \times 10^{-8} + 5.1 \times 10^{-8} \times (T - 273)$</td>
<td>Lorenz (1993)</td>
</tr>
<tr>
<td>Thermal conductivity(^b)</td>
<td>$\lambda = \lambda_0(T) + \Delta \lambda_b(\rho)$</td>
<td>Stephan et al. (1987)</td>
</tr>
<tr>
<td>Eddy diffusion(^c)</td>
<td>$K_{diff} = 5000$ below 90 km</td>
<td>Toon et al. (1992)</td>
</tr>
<tr>
<td>Rainout rate(^c,d)</td>
<td>$3.1688 \times 10^{-8} \text{ s}^{-1}$, $3.8580 \times 10^{-7} \text{ s}^{-1}$</td>
<td></td>
</tr>
<tr>
<td>Rainout altitude(^c,d)</td>
<td>30 km, 20 km</td>
<td></td>
</tr>
<tr>
<td><strong>Aerosol properties</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Particle size</td>
<td>$r_{min} = 13 \text{ Å}$, bins double by mass</td>
<td>Toon et al. (1992)</td>
</tr>
<tr>
<td>Initial size distribution(^d)</td>
<td>Fig. 2</td>
<td>Toon et al. (1992)</td>
</tr>
<tr>
<td>Particle flux (into model top)</td>
<td>$1.22 \times 10^{-14} \text{ g/cm}^2\text{s}$</td>
<td>Toon et al. (1992)</td>
</tr>
<tr>
<td><strong>Ethane vapor properties</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Initial distribution</td>
<td>Mixing ratio = $10^{-3}$ or 75% relative humidity for 5–62 km</td>
<td>Kostiuk et al. (1997)</td>
</tr>
<tr>
<td>Vapor pressure(^e) (ice)</td>
<td>$\log(P) = 10.01 - 1085.0/(T - 0.561)$</td>
<td>Moses et al. (1992)</td>
</tr>
<tr>
<td>Gas flux (into model top)</td>
<td>$5.8 \times 10^6 \text{ molecules/cm}^2\text{s}$</td>
<td>Yung et al. (1984)</td>
</tr>
<tr>
<td><strong>Nucleation and growth properties</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sticking coefficient</td>
<td>$\leq 1$</td>
<td></td>
</tr>
<tr>
<td>Thermal accommodation</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>Shape</td>
<td>Spheres</td>
<td></td>
</tr>
<tr>
<td>Density of ethane</td>
<td>0.5446 g/cm(^2) (liquid), 0.713 g/cm(^2) (ice)</td>
<td></td>
</tr>
<tr>
<td>Diffusivity of ethane in (N_2)</td>
<td>$D = 0.148 \times 10^{12} \times \left(\frac{T}{298.15}\right)^{1.34}$</td>
<td>Boyd et al. (1951)</td>
</tr>
<tr>
<td>Latent Heat of ethane ice</td>
<td>$L_v = \frac{R}{M}[-5.25147 - (-1.1341 \times 10^3 \times 9.8774 \times 10^{-11}T^2 + 1.3466 \times 10^{-9}T\ln(10)]$</td>
<td>From vapor pressure eqn.</td>
</tr>
<tr>
<td>Surface free energy</td>
<td>$C_{2}H_{6}$ liquid–air</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$\sigma_{vi} = 21.517\left(\frac{305.42 - T}{305.42 - 153.2}\right)^{11/9}$</td>
<td>Yaws (1992)</td>
</tr>
<tr>
<td></td>
<td>$C_{2}H_{6}$ ice–air</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$\sigma_{vi} = \frac{L_{vap}}{T_{vap}} \sigma_{vb}$</td>
<td>Guez et al. (1997)</td>
</tr>
<tr>
<td></td>
<td>$C_{2}H_{6}$ ice–C(_2)H(<em>6)</em> liquid</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$\sigma_{di} = \sigma_{vi} - \sigma_{vb}$</td>
<td></td>
</tr>
<tr>
<td>Critical saturation(^e)</td>
<td>$S_{sat} = 1.15, 1.5$</td>
<td>Measured for liquid ethane, solid butane</td>
</tr>
<tr>
<td>Contact parameter(^e)</td>
<td>$m = 0.986, 0.9589$</td>
<td>Derived from $S_{sat}$ at 72.7 K</td>
</tr>
<tr>
<td>Surface concentration</td>
<td>$c_3 = 10^{15} \text{ molecules/cm}^2$</td>
<td></td>
</tr>
</tbody>
</table>

* All units are cgs unless otherwise noted.

\(^b\) Thermal conductivity in W/m/K, valid for $T = \text{triple point} - 3000 \text{ K}$, $\rho < 1.09 \text{ g/cm}^3$, $\lambda_0 = 0.03926390 \sqrt{T} \exp\left[-\frac{T}{\tau_{99}} \text{ Alog}\left(\frac{k_B T}{138.0848 \times 10^{16}}\right)\right]$, $\Delta \lambda_b = 4.17\sum_i^\infty C_i \left(\frac{\rho_i}{\rho_{air}}\right)^{1/3}$; $A_i = [0.46649, -0.57015, 0.19164, -0.03708, 0.00241]$; $C_i = [3.3373542, 0.37098251, 0.89913456, 0.16972505]$; $k_B$ is Boltzmann’s constant, $T$ is temperature, $\rho$ is density (of air, critical density of N\(_2\))

\(^c\) Variable parameters (not well constrained by observations).

\(^d\) Not included in base model.

\(^e\) Pressure in mmHg, valid 30–90 K.

by coagulation, which is limited by charging (reducing the sticking coefficient to less than 1). They are removed by ethane nucleating on them, by coagulating with ethane cloud particles, or by vertical transport. The cloud particles grow by both coagulation and condensation, and shrink due to evaporation (we assume a thermal accommodation coefficient of unity).

The atmospheric temperature and density profiles (Table 1) are from the Lellouch and Hunten (1987) recommended model. The pressure profile is calculated from the ideal gas law, assuming a pure N\(_2\) atmosphere.

Recent data (Kostiuk et al., 1997) indicate an ethane mixing ratio $\sim 10^{-5}$ in the stratosphere. Assuming a constant mixing ratio to the surface leads to $S$ values greater
than 1 over a substantial portion of the troposphere and lowermost stratosphere (Fig. 4). In order to initialize the model with subsaturated conditions, the initial ethane profile follows the vapor pressure curve, but is reduced to 75% relative humidity for altitudes where the vapor pressure curve would lead to supersaturation, and has a constant mixing ratio of $10^{11}$ elsewhere. Ethane is continuously added by a flux of $5.8 \times 10^9$ molecules cm$^{-2}$ s$^{-1}$ at the top of the model, based on the value of the flux at high altitudes calculated by Yung et al. (1984). We have no loss of ethane vapor at the bottom of the model.

An eddy diffusion coefficient controls the vertical transport of gas in the model and is therefore of great importance in determining the supply of vapor to the regions of nucleation and growth. The diffusion coefficient used in this model, taken from Toon et al. (1992), is a constant $5000$ cm$^2$ s$^{-1}$ for the first 90 km of Titan’s atmosphere. Such a diffusion coefficient implies a mixing time of 57 years over a scale height of 30 km (Fig. 5). Titan’s diffusion coefficient is not heavily constrained by observations. Other models employ different eddy diffusion profiles, as will be discussed in Section 4.

Fig. 5 also shows typical fall times for Titan cloud and aerosol particles. These fall times give the particle sedimentation rate (i.e., the rate at which the particles settle under the influence of gravity). For low Reynolds numbers the particle fall velocities are calculated from the Stokes relationship given in Eq. (12). Comparing diffusion and sedimentation times shows clearly that the vertical distributions of particles larger than 1 $\mu$m are controlled by sedimentation-
tion, while the distribution of smaller ones and of gases are controlled by diffusion.

Unfortunately, most nucleation parameters for ethane are unknown. The critical saturation value was obtained from lab experiments (Curtis et al., in preparation) to be 1.15 for liquid ethane condensing on tholin. Most of the region of Titan’s atmosphere in which we are interested actually lies below ethane’s freezing point of 89.9 K (Fig. 4). However, we do not yet have data on $S_{\text{crit}}$ for ethane ice. However, based upon butane ice formation experiments (Curtis et al., in preparation), the $S_{\text{crit}}$ should actually be higher than 1.15. Because we have no information on the ethane desorption energy (see Eq. (7)), we assumed adsorption as a monolayer on the surface, giving a constant value for $c_1$ of about $10^{15}$ molecules/cm$^2$. As no experimental data can be found on the surface free enthalpy for solid ethane (Eqs. (1)–(3)), we followed Guez et al. (1997). They show that the surface free enthalpies of solids can be linked to material properties for which laboratory measurements exist. Specifically, the surface free enthalpy of the solid is shown to be a function of the liquid enthalpy and the latent heats (as shown in Table 1).

4. Model results and sensitivity tests

4.1. Microphysics calculations for the formation and evolution of ethane clouds

Using the parameters specified in Section 3, the aerosol model was run to study ethane cloud formation and evolution. We used a contact parameter of 0.986, which corresponds to $S_{\text{crit}} = 1.15$ at $T = 72.7$ K, the tropopause temperature in our standard model. This value of $m$ is relatively large, so this calculation provides an upper limit to the nucleation rate for ethane.

Nucleation initially occurs about 40 days into the model run, at 58 km. (The altitude values in the following section are for a layer bottom with 2 km resolution, i.e., 58 km means the bin ranging from 58 to 60 km.) This is the same altitude where Sagan and Thompson (1984) predicted ethane would condense to form clouds! The ethane for the cloud particles is supplied by the initial ethane just above 58 km as the timescale for mixing ethane over a distance of 50 km is much longer than 40 days (160 years). Over the course of the model run, nucleation occurs at all altitudes between 8 and 58 km. Nucleation at the higher altitudes and the net diffusion of ethane vapor to the tropopause reduces the ethane content in the lower stratosphere to the extent that the atmosphere becomes subsaturated above 48 km by 100 years. Nucleation continues to occur between 8 and 46 km at steady state. We consider steady state to have been reached when the ethane flux out of a layer (including both ethane vapor and ethane ice in cloud particles) is equal to the ethane flux at the top boundary of the model (given in Table 1) within machine precision. It should be noted that cloud formation is driven in this steady-state model by vapor transport driving $S$. However, an alternative growth model is for dynamically induced temperature declines to drive $S$ up, by drawing the vapor pressure down. This latter process dominates terrestrial cloud formation, and will be discussed later.

At steady state we see periodic cloud formation with most of the activity confined to the troposphere (Fig. 6a). The greatest mass and number of cloud particles is located between 5 and 10 km. This mass is about the same order of magnitude as that of typical terrestrial subvisible cirrus (Jensen et al., 2001). Concentrations reach about 0.5 cm$^{-3}$, which is at most one-tenth that of typical terrestrial subvisible cirrus clouds (Jensen et al., 2001).

Fig. 7 shows size distributions of cloud particles for various altitudes. Forty kilometers is near the top of the cloud-forming region where particles are smaller. As the particles fall to lower altitudes, growth continues, as seen by the peaks at increasingly larger sizes in the 10- and 20-km curves. The bimodal distributions result from both nucleation and growth occurring at the same altitude. The ethane being removed by the falling cloud particles is being constantly resupplied by an upward ethane vapor flux due to eddy diffusion. The largest particles formed are just below Samuelson’s (Samuelson et al., 1997; Samuelson and Mayo, 1997) requirement that ethane cloud particles have radii between 30 and 100 μm.

The timescale for condensational growth can be estimated from Eq. (8). A coalescence timescale can be found in a similar manner to the growth timescale. Accretional growth of a drop of mass $M$ can be found by multiplying Eq. (16) by the liquid water content ($w_{\text{L}}$) of the small drops:

$$\frac{dM}{dt} = \frac{\pi}{4} E_{\text{coal}} E_{\text{coll}} (D_{p1} + D_{p2})^2 (v_{p1} - v_{p2}) w_{\text{L}}. \quad (17)$$

Fig. 8 shows coalescence times for some of the cloud particle sizes in the model. The long timescales indicate that this process is not important for growth of ethane clouds in Titan’s atmosphere. (This conclusion was also confirmed through a model run with coalescence turned off.) Therefore, the maximum particle size achieved will be limited by the efficiency of condensational growth of large particles. Thus, no significant number of millimeter-sized particles form.

4.2. Radiative transfer modeling of ethane clouds

Since Titan’s haze obscures much of the lower atmosphere at visible wavelengths, it is interesting to look at wavelength-dependent optical depths in the near-infrared. We consider IR wavelengths where cloud observations have been reported. We used a plane-parallel radiative transfer model (Toon et al., 1989) to determine albedos at various wavelengths. Optical parameters (optical depth $\tau$, single-
scattering albedo \( \omega \), asymmetry parameter \( g \)) were calculated for the tholin and cloud particles using Mie theory. Table 2 shows the wavelength-dependent values used in the calculation of the cloud and gas optical depths. Methane and tholin parameters were taken from Toon et al. (1992).

Ethane optical constants are not very well known. Values for \( \lambda > 1 \text{ \mu m} \) were taken from Quirico and Schmitt (1997). At shorter wavelengths, the ethane absorption was considered negligible. The real part of the refractive index for ethane was taken to be 1.45 for all wavelengths following

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**Fig. 6.** Mass mixing ratio and number density for Titan’s ethane clouds. The contours are 0.1, 1, 10, 25, 50, 75, and 95% of the maximum value. (a) For the normal eddy diffusion coefficient, clouds appear within a period of 20 days at the tropopause and 40 days near 10 km. The periodicity of the clouds changes for higher eddy diffusion coefficients: (b) \( 2 \times K_{\text{diff}} \), (c) \( 5 \times K_{\text{diff}} \) and (d) \( 10 \times K_{\text{diff}} \).
Pearl et al. (1991). The methane abundance was assumed to be 1% above 30 km and to vary linearly to 4% at the surface, following Toon et al. (1992). We take the ground albedo to be 0.1. Rayleigh scattering is related to atmospheric pressure (p) as

\[ \tau_{\text{Ray}} = 0.0088 \frac{p}{1013 \text{ mbar}} \lambda^{(-4.15+0.2\lambda)}. \]  

The optical depth of the ethane clouds, which is the same order of magnitude as that of terrestrial subvisible cirrus,

Fig. 7. Size distribution of ethane cloud particles at steady state, for various altitudes. The left plots correspond to a time when the optical depth was at a minimum at 10 km; the right plots are when optical depth was at its peak at 10 km.

Fig. 8. Growth times for various cloud particles. Dashed lines indicate times for condensational growth (long dashes) and evaporation (short dashes). Dashed–dotted lines indicate times for accretional growth. The saturation ratio used to calculate the condensational growth time (see Eq. (8) for \( S \) dependence) was taken from the cloud model; i.e., \( S \) is altitude dependent.
can exceed that of the tholin at some wavelengths and at some times (Fig. 9). This opacity results in a 5–10\% increase in Titan’s albedo for wavelengths between 1 and 2 \(\mu m\) when the clouds are at peak optical depth. (Optical depths of cloud particles at the minimum of the cloud cycle are negligible compared to the tholin.) To increase the albedo further requires a larger number of cloud particles to be formed. If the number of cloud particles is uniformly increased by a factor of 10, a 50–150\% increase in albedo \((\lambda = 1 - 2 \mu m)\) results (Fig. 10).

Note that in the model atmosphere we have assumed that methane clouds do not form, so there is no rainout of the ethane particles. In fact, the lower altitude ethane cloud may be impacted by the formation of methane clouds. The cloud particles produced in the model atmosphere are large enough that we can approximate their visible wavelength optical depth in the geometric limit. Sagan and Thompson (1984) estimated the optical depth from

\[
\tau_v = \frac{3 \mu X p f_c}{2 \mu g \rho r},
\]

where \(\mu\) and \(\tilde{\mu}\) are molecular weights for ethane and Titan’s atmosphere, respectively; \(X\) is the ethane mole fraction; \(p\) is atmospheric pressure; \(g\) is Titan’s gravity, \(\rho\) and \(r\) refer to the cloud particle density and radius; and \(f_c\) is the ratio of ethane in the solid state to that in the gas state. From this equation, their estimate of the ethane optical depth is about 200; using results from our model we find a value closer to 0.4, \(10^{13}\) times smaller! For their calculations, they assumed that the amount of ethane present as cloud particles was equal to that in the gaseous state \((f_c = 1)\). This is the major difference between our results and theirs; from our modeling, we find \(f_c \lesssim 10^{-3}\). In our model, the particles quickly fall rather than remaining suspended as a cloud, resulting in the small value of \(f_c\).

Another possible way to detect the presence of ethane clouds would be by their effect on the tholin and ethane profiles. Changes to the tholin profile as a result of cloud formation are only evident in Titan’s troposphere. Even though clouds do deplete a significant amount of the larger tholin particles, they do not exhaust the supply of available tholin CN. The tholin loss reaches a maximum of about 30\% at an altitude of 10 km (Fig. 11). This change in tholin is included in Fig. 10, and produces small drops in the albedo. If the amount of tholin condensation nuclei are decreased by a factor of 10 (to account for a similar increase in cloud particles as described above, shown in Fig. 11) the albedo decreases between 10 and 50\% for wavelengths less than 1 \(\mu m\) (Fig. 10).

### 4.3. Sensitivity tests for the ethane cloud model

One of the factors controlling particle size and mass is the atmospheric transport in our model. The mean transport is controlled by our eddy diffusion profile. The eddy diffusion coefficient of Toon et al. (1992) was based on a profile of Yung et al. (1984), modified so that a model without a chemical sink agreed with the observed HCN profile (Tanguy et al., 1990). The Voyager IRIS and UVS data points used as boundary conditions to constrain the HCN profile were at 75 and 1125 km. Recently, McKay (1996) has determined that haze production may be a significant sink for N in Titan’s atmosphere. Such a sink will affect the HCN profile and hence change the eddy diffusion profile. Lara et al. (1996) undertook a study of various eddy diffusion profiles and found that none could satisfactorily fit both the HCN distribution and the mixing ratios of various hydrocarbons. Their best-fit case \(K_T\) was a combination of the profiles suggested by Toublanc et al. (1995), \(K_L\), and

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**Table 2**

Methane, tholin, and ethane properties for RT calculations

<table>
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<tr>
<th>Wavelength ((\mu m))</th>
<th>CH(_4) absorption coefficients (km amagat)(^{-1})</th>
<th>Tholin refractive index</th>
<th>C(_2)H(_6) index</th>
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</tr>
</tbody>
</table>

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**Fig. 9.** Optical depths of tholin and ethane cloud particles from the microphysics model. Cloud optical depths are shown for a minimum and maximum in the cloud cycle.
Strobel et al. (1992), $K_s$, or, $K_L = (K_T^2 K_S)^{1/3}$. Below 100 km Toublanc’s profile is constant, $K_T = 2000$ cm$^2$/s. Strobel’s profile follows the form $K_S(z) = K_{S0} \exp(\frac{z}{H_{9264}})$, where $\xi(z) = 1.76 \times 10^5$ km $(z - Z_0) / (R_T (R_T^2 + z))$ is the normalized geopotential height with respect to the homopause at $Z_0 = 985$ km ($R_T$ is Titan’s radius and $R_0 = R_T + Z_0$) and $K_{S0} = 4 \times 10^8$ cm$^2$/s, $K_L$ varies linearly on a log plot from about 3000 to 4000 cm$^2$/s over the altitude range of our model. We substituted Lara’s profile for our constant profile, $K_{diff} = 5000$ cm$^2$/s, and found that the altitude variation of the diffusion coefficient and the relatively small decrease in $K_{diff}$ did not change the placement of the cloud layers or their optical depth significantly. The only substantial changes were an increase in the amount (both mass and number) of cloud particles above the tropopause and non-variable cloud features above 30 km, as shown in Fig. 12. The size distribution of these particles did not change from that found with our original eddy diffusion coefficient.

It is noteworthy that both these alternative diffusion coefficient profiles have values of $K_{diff}$ smaller than that in our model. To produce large cloud optical depths, larger values of $K_{diff}$ are needed. With larger $K_{diff}$ values (increase by factors of 2, 5, and 10), we see both an increase in the maximum optical depth and a change in the periodicity of the cloud features at 10 km. Figures 6b and 6c show that as the eddy diffusion coefficient is increased, the length of time between cloud formation events decreases. However, due to less ethane vapor present near the tropopause in the higher eddy diffusion cases, the optical depths of clouds features there are an order of magnitude less than in the nominal case.

The periodic cloud features result from the competition between nucleation and growth in depleting the ethane vapor content of an atmospheric layer and transport resupplying vapor. When the relative humidity gets above 112% (for a critical supersaturation of 0.15 as in our base model), many cloud particles can be formed from nucleation before condensational growth becomes efficient (Fig. 13). Particles have time to grow and fall before ethane is resupplied through eddy diffusion. A higher eddy diffusion coefficient brings in ethane faster; however, the majority of the excess vapor is then incorporated into the preexisting cloud particles, rather than building up to form more cloud particles.
We believe that the periodicity is an artifact of the modeling process since eddy diffusion is an artificial process; however, these results can be used to characterize cloud lifetimes.

While eddy diffusion may approximate the mean behavior of Titan’s atmosphere, there will in reality be organized mean motions as well as waves propagating in the atmosphere. Such motions can lead to temporarily increased supersaturation via decreased vapor pressures due to lowered atmospheric temperature. To partially investigate such waves we show a simulation of the cloud optical depth in Fig. 14 and size distribution in Fig. 15 in which we allowed a sinusoidal temperature oscillation between 40 and 50 km, with an amplitude of 1 K and a period of 1 month. The atmosphere responds to the first such wave by creating an ethane cloud that has a significant optical thickness compared with the cloud that was present previously. The presence of this cloud results in a 1% increase in Titan’s albedo between wavelengths of 1 and 2 μm. However, subsequent waves produce only very minor clouds since the first one depletes the available vapor. Hence sporadic clouds of moderate optical thickness may occur but will probably be rare. The rarity is due to a fundamental mismatch in timescales on Titan. Clouds are able to quickly remove vapor, once formed. However, the sluggish dynamics on Titan makes it difficult for the atmosphere to transport the vapor needed to create saturation. If a similar temperature wave is included between 6 and 12 km, the area of highest cloud formation in the base model, the maximum number of cloud particles formed increases by a factor of nearly 100. A similar increase is seen in the optical depth, but effects are limited to the region of the temperature changes. Fig. 16 shows that the 30-day timescale of the temperature wave becomes the dominant periodicity in the clouds.

Nucleation is a significant process controlling particle size in our model. While results for liquid ethane suggest a value of 1.15 for $S_{\text{crit}}$, this is likely to be somewhat low for ice clouds. However, from running the model with higher $S_{\text{crit}}$ values, such as those measured for solid butane, we no longer see periodic cloud formation ($S_{\text{crit}} = 1.4 - 1.5$). Once clouds reach a steady-state configuration, their maximum optical depth is less than 0.03. At $S_{\text{crit}} = 1.3$ periodic clouds remain at 10 km. These clouds have a period of 11 days at 10 km and an optical depth centering around 0.05 (Fig. 17).

Ethane is just one of the many photolysis products that will condense in Titan’s atmosphere. We doubled the flux of gas to simulate the addition of other similar hydrocarbons. The location of the clouds remains the same as that described above for the initial case. Fig. 18 shows that there is a significant increase in the amount of cloud particles above the tropopause, but comparable (to the base case) mixing ratio and number in the troposphere. The periodicity of clouds at 10 km is still about 40 days; however, clouds vary only slightly with time above about 30 km. Despite the increased amount of ethane being added to the atmosphere, the number of cloud particles formed in the troposphere is still limited by the amount of ethane present, not the number of tholin CN.

5. Discussion

5.1. Ethane precipitation

A comparison of the evaporation and sedimentation timescales (Figs. 8 and 5) shows that particles larger than 30 μm can fall from 6 km to the surface before total evaporation. Our ethane particles can reach the surface, whereas the methane particles of Lorenz (1993) could not because the methane vapor pressure near Titan’s surface is about 1000 times higher than that of ethane, so its
evaporation rate is correspondingly 1000 times greater. However, because most of the cloud particles only reach \( \frac{1}{3} \) of this size, there is only a small flux of particles across the bottom boundary of the model as shown in Fig. 19. This averages to a rate of about \( 2 \times 10^{-5} \) cm per terrestrial year, which is much smaller than the average terrestrial value of 1 m yr\(^{-1}\). Our calculated rainfall rate is only a small fraction of the flux Titan is energetically capable of producing. Lorenz (2000) argues from planetary energetics that there is enough energy available on the planet to drive about 1.5 cm of rainfall. Our model involves a recycling of ethane. However, the loss of ethane through rainout of cloud particles to the ground is consistent with the photochemical production of ethane.

Fig. 13. Comparison for nucleation and growth timescales in the cloud model at 10 and 40 km for different relative humidities.
A significant increase in the rainout rate (\(\sim 0.02\) cm per terrestrial year) is seen in cases where a surface source of ethane is added (this case is described more fully in Section 5.4).

### 5.2. Influence of methane cloud formation on the ethane clouds

Toon et al. (1988) described a case where, due to the scarcity of nucleation sites for methane condensation, any cloud formation would be followed by rapid growth and rainout. We simulate such a process by raining out all particles (from the base model) in the bottom 30 km of the atmosphere (altitude chosen based on recent cloud observations, Griffith et al. (2000)). A rainout time of 1 year was chosen. By raining out the ethane in the bottom 30 km of the atmosphere, the clouds above 30 km also disappear within 20 years, and the relative humidity around the tropopause drops below 100\%. This indicates that the lower atmosphere is the important supplier of ethane to the clouds. Transport of air with a low ethane vapor content from the lower troposphere into the tropopause region reduces the mixing ratio of ethane at the tropopause, thereby preventing clouds from forming. A steady-state model where ethane clouds remained at some altitudes is found if rainout only occurs below 20 km (same rainout time). The resulting cloud profile (Fig. 20) shows clouds at the tropopause with a maximum concentration of \(10^{-3}\) particles/cm\(^3\). These clouds have an effective radius around 1 \(\mu\)m, but are too sparse to have a significant optical depth (\(\tau \sim 10^{-4}\)).

### 5.3. Effects of rainout on the transport of gases

Assuming constant mixing ratios, as given by Cabane and Chassefière (1995), we find that acetylene will be supersaturated below 62 km, propane will be supersaturated below 64 km, and hydrogen cyanide will be supersaturated below 70 km. (Vapor pressures for these compounds are given in Table 3 and shown in Fig. 21. Note that although all condensed forms of these compounds will be frozen at Titan temperatures we were unable to find data for the solid vapor pressure of propane.) We used the microphysics model to look at the transport of these gases in Titan’s atmosphere. For the purpose of this test, the growth algorithms were turned off. Since each of these gases is soluble in methane, we studied the effects on the mixing ratios of rainout through methane cloud formation (Fig. 21). For comparison, we performed calculations with constant rainout rates at altitudes of 20 and 30 km for all of the gases (1 year and 30 days). It is evident from the plots that ethane clouds cannot remain in the atmosphere for either choice of rainout times (if

Fig. 14. Optical depth (visible wavelengths) of Titan’s ethane clouds after the addition of a sinusoidal temperature perturbation (at \(\sim 125\) days). Optical depth values before the temperature change were \(10^{-6}\) at the tropopause and \(10^{-3}\) at 30 km.

Fig. 15. Size distributions of Titan’s ethane clouds corresponding to the optical depth spikes in Fig. 14 (tropopause, dash dotted line; 30 km, long dashes). Size distributions before the temperature change are shown for comparison (tropopause, dotted line; 30 km, short dashes).
there is no evaporation at altitudes surrounding the tropopause to resupply ethane, as was the case in the model described in Section 5.2). The vapor pressures of the other gases, however, are much lower than that of ethane, so that they may remain supersaturated in parts of the lower stratosphere. For a rainout time of a year, the mixing ratios differ little between the 20- and 30-km cases.

5.4. Addition of ethane from surface sources

We chose to study ethane sources further by adding a surface source such that the relative humidity of the bottom layer remained at 75%. Even with a surface source of ethane, the cloud layers still form at the same altitudes described above, the only difference being that nucleation can now occur down to 6 km. It is evident from Fig. 22 that the surface ethane source is only effective for the bottom 10 km of the atmosphere, resulting in an increased number of particles (peaks in number concentration can increase by 3 orders of magnitude when a surface source is added). The average rainfall rate increases by about 3 orders of magnitude as well. However, the greater number of cloud particles is insufficient to raise the optical depth by an order of magnitude (Fig. 23). For this to occur, a much larger source of ethane is needed. Such a larger source might occur if the eddy diffusion coefficient near the surface were larger than we have assumed.

![Fig. 16. Optical depth (visible wavelengths) of Titan's ethane clouds after the addition of a sinusoidal temperature perturbation (at ~125 days) between 8 and 11 km.](image1.png)

![Fig. 17. Optical depth profiles for various critical saturation values. The shaded regions show the variation in optical depth for periodic clouds. For $S_{\text{crit}} = 1.15$ (dark shaded region), the clouds are periodic over their entire vertical extent. Cloud features become constant with time above 20 km when $S_{\text{crit}}$ is raised to 1.3 (light shaded region). For higher values of $S_{\text{crit}}$ such as those measured for solid butane nucleation onto tholin ($S_{\text{crit}} = 1.4$, diamonds and $S_{\text{crit}} = 1.5$, squares), clouds are no longer periodic for any altitude.](image2.png)

![Fig. 18. Particle number density and mass mixing ratio plots for comparison between different ethane fluxes. The profiles show a time-average over several cycles (~120 days). Doubling the ethane flux only affects the clouds in the stratosphere.](image3.png)
5.5. Variations with latitude

Our model was run as a column using only the temperature profile from the Voyager radio occultation experiment. However, we can draw some conclusions as to how our ethane clouds may vary with latitude. Using IRIS data, Samuelson et al. (1997) extended the radio occultation data from 7.8°N latitude to get a latitudinal distribution of temperature at the surface, tropopause, and 1-mbar levels. At the tropopause they found variations of about 1 K (as in our temperature perturbation case). At the other altitudes temperature variations were as great as a few Kelvin, symmetric about the equator. Since our ethane clouds form over about a 20-K range of temperatures, the cloud profile at another latitude will most likely not appear significantly different as that shown in this paper. However, as shown by our sensitivity tests with the temperature perturbation, if a parcel is carried horizontally, the 1 K temperature change is enough to enhance cloud formation such that the optical depth of the cloud will increase.

6. Cassini measurements

The Cassini spacecraft will reach the Saturn system in 2004. The Composite Infrared Spectrometer and the Visible and Infrared Mapping Spectrometer, both on the orbiter, will be capable of observing clouds below the haze layers. The Descent Imager/Spectral Radiometer on the Huygens probe is equipped with upward and downward spectrometers and downward and side-looking imagers. The infrared spectrometer operates from 0.87 to 1.64 μm, a region where some ethane absorption features (distinguishable from methane) exist. The tholin CN are optically thin, but the clouds may be thick enough to be seen by the side-looking camera. The best region to observe these clouds would be between the surface and 20 km, where the highest extinctions occur.

Another way to detect the presence of ethane in the clouds will probably be through the Aerosol Collector and Pyrolyser on the Huygens probe. Through heating at three increasing temperatures, this instrument will be capable of detecting the presence of an ethane layer around particles collected from Titan’s atmosphere. Particle collection will occur twice, at altitudes of 150–40 km and 23–17 km. Should optically thick ethane clouds be observed, it would indicate either a very lucky chance encounter or that Titan’s lower atmosphere is dynamically much more active than is currently thought.
7. Conclusions

Microphysical modeling has shown that conditions allow for ethane cloud formation in Titan’s atmosphere. Unfortu-
nately, our poor knowledge of ethane physical chemistry and of Titan limit our ability to predict cloud properties. The most important uncertainty is the contact parameter for ethane forming on (possibly hydrocarbon-rich) tholins. The

<table>
<thead>
<tr>
<th>Compound</th>
<th>Vapor pressure equation</th>
<th>Temperature range</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>C\textsubscript{2}H\textsubscript{2}</td>
<td>(30.895 - \frac{1645.9}{T} + 8.6252\log(T))</td>
<td>(98 &lt; T &lt; 115) K</td>
<td>1</td>
</tr>
<tr>
<td>C\textsubscript{2}H\textsubscript{4}</td>
<td>(9.130 - \frac{1149}{T - 3.84})</td>
<td>(115 &lt; T &lt; 145) K</td>
<td></td>
</tr>
<tr>
<td>HCN</td>
<td>(189044.86\exp\left(-\frac{1176^2}{T}\right))</td>
<td>(105 &lt; T &lt; 165) K</td>
<td>2</td>
</tr>
</tbody>
</table>

Note. Equations are for \(\log(P)\) with \(P\) in mmHg except for HCN where \(P\) is in dynes/cm\(^2\). (1) Romani and Atreya (1988). (2) Moses et al. (1992). (3) Calculated from Clausius–Clapeyron, latent heat of sublimation from Stull (1947).

Fig. 21. Mixing ratio profiles for various gases in Titan’s atmosphere. Rainout occurred up to 30 km (darker lines) or up to 20 km (lighter lines). The initial profile follows the saturation vapor pressure at 75% relative humidity at altitudes where the initial mixing ratio value would result in saturation. Clouds will remain in the atmosphere where the rainout profiles are greater than the saturation vapor pressure.
results are also limited by not knowing the frequencies of methane cloud formation, the eddy diffusion coefficient in Titan’s lower atmosphere, the magnitude and timing of dynamically driven temperature perturbations, and whether there is a surface reservoir of ethane on Titan. Assuming the only source of ethane vapor is from methane photolysis, the number of cloud particles forming will be limited by the flux of vapor or the presence of temperature perturbations rather than the abundance of condensation nuclei. Whether clouds will be observable depends on the critical saturation at which ethane will nucleate onto tholin particles. For low enough \( S_{\text{crit}} \) values we see a cloud cycle where enough particles are formed at peak production, to raise Titan’s albedo by about 5% at some infrared wavelengths. The majority of the cloud particles remain in the troposphere, but clouds can exist at much smaller optical depths throughout the bottom 10 km of the stratosphere. The size distribution is generally bimodal, with peaks at 1 and 10 \( \mu \text{m} \). The maximum cloud particle size is limited by the inefficiency of coalescence. Particles greater than 25 \( \mu \text{m} \) can fall to the surface before total evaporation in the bottom 6 km of the atmosphere. The formation of ethane clouds has only a small effect on the tholin profile. However, because the ethane cloud particles tend to congregate in the lowest 20 km of the atmosphere, they could provide sites for the nucleation of observable methane clouds. Depending on the altitude of methane cloud formation, ethane vapor may be removed near the tropopause to levels below saturation (but other hydrocarbon clouds can be sustained). Sporadic clouds with modest optical depths (~0.1–1) may occur due to temperature perturbations, but these must be very rare even if the perturbations are common. Their frequency of occurrence is limited by the low transport rates (diffusion coefficients) in Titan’s lower atmosphere. Should current estimates of these \( K_{\text{diff}} \) values be much too low, then optically thick clouds may occur.

**Fig. 22.** Particle number density and mass mixing ratio plots for comparison to a surface source of ethane. The profiles show a time-average over several cycles (~120 days). Ethane from the surface only affects the profiles up to 10 km.

**Fig. 23.** Optical depth profiles (time-averaged over 120 days) for two cases of the cloud model. The dashed line shows the case of no surface ethane source, and the solid line describes the optical depth when the bottom of the atmosphere is kept at 75% relative humidity. These optical depth calculations considered only the cloud particles in the geometric limit. For particle sizes of 1–1000 \( \mu \text{m} \), this corresponds to visible and near-infrared wavelengths. The optical depth above a given altitude is shown.

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