

The Greenhouse and Antigreenhouse Effects on Titan

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There are many parallels between the atmospheric thermal structure of the Saturnian satellite Titan and the terrestrial greenhouse effect; these parallels provide a comparison for theories of the heat balance of Earth. Titan's atmosphere has a greenhouse effect caused primarily by pressure-induced opacity of N_2 , CH_4 , and H_2 . H_2 is a key absorber because it is primarily responsible for the absorption in the wave number 400 to 600 cm^{-1} "window" region of Titan's infrared spectrum. The concentration of CH_4 , also an important absorber, is set by the saturation vapor pressure and hence is dependent on temperature. In this respect there is a similarity between the role of H_2 and CH_4 on Titan and that of CO_2 and H_2O on Earth. Titan also has an antigreenhouse effect that results from the presence of a high-altitude haze layer that is absorbing at solar wavelengths but transparent in the thermal infrared. The antigreenhouse effect on Titan reduces the surface temperature by 9 K whereas the greenhouse effect increases it by 21 K. The net effect is that the surface temperature (94 K) is 12 K warmer than the effective temperature (82 K). If the haze layer were removed, the antigreenhouse effect would be greatly reduced, the greenhouse effect would become even stronger, and the surface temperature would rise by over 20 K.

THE PLANETARY GREENHOUSE EFFECT results when atmospheric gases are transparent in the visible, allowing solar radiation to penetrate to the planet's surface, but are opaque in the thermal infrared and hence trap the outgoing thermal radiation. By contrast, the antigreenhouse effect is the result of a high-altitude atmospheric layer that is strongly absorbing at solar wavelengths but weakly absorbing in the thermal infrared and so acts to cool the planet.

The atmosphere of Titan, the largest moon of the planet Saturn, has a surface pressure of 1.5 atm and is composed primarily of N_2 with several percent CH_4 and about 0.3% H_2 (1, 2). The Voyager 1 flyby of Titan revealed that there is an optically thick organic haze in the upper atmosphere (3). The surface temperature is near 94 K and declines with altitude to a minimum of about 71 K near 40 km (4). The temperature then increases sharply, reaching a value of about 170 K in the stratosphere. This temperature structure has been successfully reproduced with the use of one-dimensional (1-D) radiative convective models (5). Titan may have thin clouds in the troposphere (6), and the atmospheric concentration of CH_4 is thought to be determined by the vapor

pressure of a condensed surface reservoir, possibly an ocean (7).

On Titan, the greenhouse effect is dominated by the collision-induced absorption of N_2 - N_2 , CH_4 - N_2 , and H_2 - N_2 . Although there is a small contribution due to CH_4 - CH_4 , its relative importance would increase with increasing temperature because it scales as the square of the CH_4 concentration. The spectral distribution of thermal infrared opacity for the present Titan atmosphere is shown in Fig. 1 (5). Also shown is the Planck curve for the present surface temperature of 94 K.

On the basis of a 1-D radiative convective model (8), the energy balance of Titan can be constructed as follows: the globally averaged sunlight incident on the top of Titan's

atmosphere is $3690 \text{ erg cm}^{-2} \text{ s}^{-1}$, of which about 30% is reflected back to space; only about 10%, $350 \text{ erg cm}^{-2} \text{ s}^{-1}$, reaches the surface. To maintain thermal equilibrium at the surface, warming due to absorbed solar radiation must be balanced by cooling due to a net loss of thermal radiation and by convection. The surface emits as a blackbody at 94 K, equivalent to $\sim 4400 \text{ erg cm}^{-2} \text{ s}^{-1}$, but receives most of this back as thermal infrared radiation from the atmosphere. The net infrared emission from the surface is only $311 \text{ erg cm}^{-2} \text{ s}^{-1}$ (5). An additional $40 \text{ erg cm}^{-2} \text{ s}^{-1}$ is carried from the surface by convective motions balancing the solar energy deposition. This analysis illustrates the importance of the greenhouse effect, the atmospheric back-radiation, in the surface energy balance. If there is a change in the surface energy balance, there will be a corresponding change in the surface temperature; the factor relating the two is $0.02 \text{ K erg}^{-1} \text{ cm}^2 \text{ s}$ (5).

Because the opacity of the atmosphere is very high for wave numbers less than 400 cm^{-1} (see Fig. 1), the surface of Titan receives almost precisely the same amount of reradiation from the atmosphere in this spectral region as it emits. The cooling of the surface is dominated by emissions within the 400- to 600- cm^{-1} region of Titan's infrared spectrum (5). As suggested by Samuelson (9), this region is therefore the "window region" and opacity sources in this region will have a disproportionate effect on the surface energy balance.

H_2 is a key absorber because it is primarily responsible for the absorption in this window region. CH_4 is also an important absorber, but its concentration is set by the saturation vapor pressure. The mixing ratio of H_2 on Titan is $\sim 0.3\%$ (1, 2, 5) and appears to be controlled by photochemical production balanced by escape to space (10). There is a similarity between the roles in climate control of H_2 on Titan and CO_2 on Earth. H_2 on Titan and CO_2 on Earth have

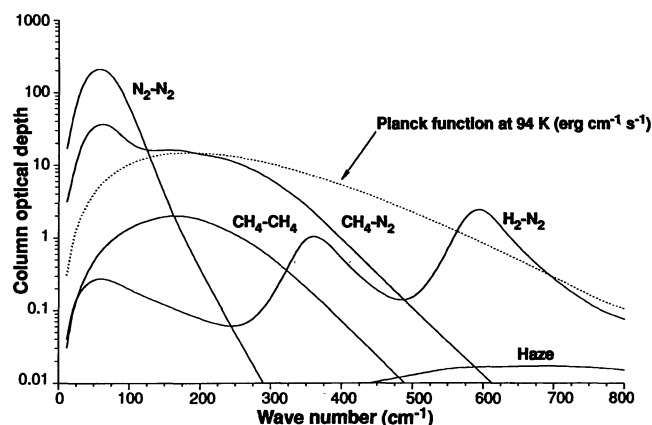


Fig. 1. Total column optical depth in the thermal infrared for Titan's atmosphere. Absorption is due to collision-induced transitions. Also shown is the total column opacity of the haze layer. The dotted line is the blackbody flux emitted from the surface at a temperature of 94 K. [Adapted from McKay *et al.* (5)]

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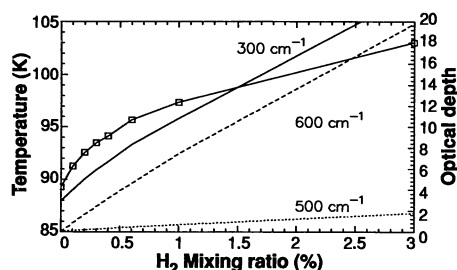


Fig. 2. Surface temperature (curve with square symbols) and opacity at 300, 500, and 600 cm^{-1} as a function of H_2 mixing ratio. The present H_2 mixing ratio is 0.3%. As H_2 , and hence the temperature, increases, the CH_4 in the atmosphere also increases, accounting for the increase in opacity at 300 cm^{-1} . In this sense, CH_4 on Titan is a condensable greenhouse gas similar to H_2O on Earth.

lower concentrations and play smaller roles in the thermal balance than the main condensable gases CH_4 and H_2O , respectively. However, they are not limited by saturation and hence their concentration can change, thereby altering the thermal profile. Any temperature change due to changes in these gases is amplified by corresponding, and much larger, changes in the condensable species (CH_4 on Titan and H_2O on Earth), resulting from the steep dependence of the saturation vapor pressure on temperature. Furthermore, CH_4 and H_2 on Titan are similar to H_2O and CO_2 on Earth in that the absorption of each individual gas is in a different, and complimentary, region of the spectrum. Thus, H_2 on Titan, like CO_2 on Earth, plays a key role in climate evolution, and understanding the processes that control its concentration is critical to developing models of the history of Titan's atmosphere. Because the production of H_2 is controlled by photochemistry, there is a link between climate and photochemical processes on Titan.

The effect on the surface energy balance of changing the H_2 concentration in Titan's atmosphere is shown in Fig. 2. As the amount of H_2 increases, the surface temperature rises, quickly at first and then more slowly once even the window region has become optically thick. Figure 2 shows the change in opacity as H_2 is increased for three key points in and near the window region: 300, 500, and 600 cm^{-1} . At 300 cm^{-1} the dominant absorber is $\text{CH}_4\text{-N}_2$, which has more opacity by about a factor of 10 than $\text{CH}_4\text{-CH}_4$. As the temperature rises, the CH_4 concentration increases and the $\text{CH}_4\text{-N}_2$ opacity increases proportionally to CH_4 . However, the opacity due to $\text{CH}_4\text{-CH}_4$ varies as the square of the CH_4 concentration. By comparing values shown in Fig. 1, one can see that the $\text{CH}_4\text{-CH}_4$ opacity will become larger than the $\text{CH}_4\text{-N}_2$ opacity if the CH_4 concentration increases

by about a factor of 3 over its present value. The minimum opacity in the window region occurs at 500 cm^{-1} . Here, both $\text{CH}_4\text{-N}_2$ and $\text{H}_2\text{-N}_2$ opacity are contributing to the opacity. Thus, at this wave number, opacity will increase directly owing to the increase in H_2 as well as indirectly owing to the temperature rise and the concomitant enhancement in CH_4 concentration. The value of the opacity at this wave number becomes equal to unity at a H_2 mixing ratio of about 2%, about seven times the present value (Fig. 2). At 600 cm^{-1} only $\text{H}_2\text{-N}_2$ absorption is significant and thus the opacity at this wave number will increase linearly with the increase in H_2 . In this region the opacity is near unity at present levels of the H_2 mixing ratio (Fig. 2).

One can understand the antigreenhouse effect by considering the energy balance at the top of a planetary atmosphere and within the atmosphere itself. We begin with an idealized case: a layer that completely absorbs the incoming solar radiation over a surface, with no opacity sources between them. If the layer is also optically thick in the thermal infrared, then energy balance at the top of the atmosphere implies that as much thermal infrared radiation must be emitted from the top of the layer as solar energy that is absorbed. If the layer is isothermal, then the same amount of radiation is emitted from the bottom of the layer toward the surface (11). Thus, the surface is warmed by an amount of thermal infrared that is equivalent to the amount of solar energy that it would receive if the absorbing layer was absent. Because there is no visible radiation reaching the surface, the temperature gradient in the lower atmosphere will become zero and the surface (and the high-altitude layer) would therefore be at the same temperature, the effective temperature (12). In this case the net greenhouse warming of the surface is zero.

If instead of being optically thick, the isothermal high-altitude layer has a very low optical depth in the infrared, then the radiation leaving the planet would include the thermal infrared emissions from the upper layer plus the thermal infrared radiation emitted directly from the surface. The upper layer absorbs the incoming solar radiation, emitting half to space and the other half toward the surface. The surface absorbs this half of the reemitted solar energy and then reradiates it directly to space, through the optically thin upper layer. Thus, the surface is receiving an amount of radiation that is half the incident value and is radiating directly to space. In this situation, the surface temperature is less than the effective temperature by the factor $(1/2)^{1/4}$ (13). Because the upper layer is optically thin, and hence has

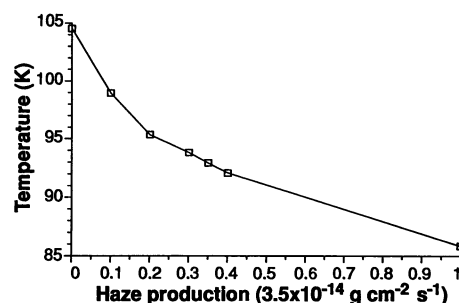


Fig. 3. Surface temperature as a function of haze production rate. The present value is 0.35 (5). As the haze becomes thicker the antigreenhouse effect becomes stronger, and in the limit of very thick haze the surface temperature should approach 69 K. Without any haze present (surface temperatures reach 105 K), there is still a slight antigreenhouse effect due to CH_4 absorption in the stratosphere. If both these effects are removed, the surface temperature is determined by the greenhouse effect only and reaches 115 K, 33 K warmer than the effective temperature.

low emissivity, in the thermal infrared it must warm to a high temperature in order to emit the absorbed solar energy; the emitted flux is proportional to $B(T)d\tau$ (B is the Planck function, τ is optical depth, and T is temperature) and, if $d\tau \rightarrow 0$, then $T \rightarrow \infty$. This is a characteristic of the antigreenhouse effect: a hot upper layer above a cold surface.

Now suppose that there is an appreciable amount of infrared opacity but negligible visible opacity below the absorbing layer. In the absence of the absorbing layer a substantial greenhouse warming of the surface occurs. When an upper layer that is opaque in the visible is added, the region of the atmosphere below this layer becomes isothermal. The infrared opacity of the lower atmosphere now loses its potency, and the surface becomes colder than it was before the upper layer was added.

The Earth's O_3 layer and the thermosphere are partially antigreenhouse layers (they have low spectrally averaged thermal opacities and high temperatures); however, they absorb only a fraction of the incident solar energy—the ultraviolet and extreme ultraviolet, respectively—and hence have only a small effect on the surface energy balance. On a much larger scale, the dust layers thought to have been ejected into the atmosphere by giant impacts (such as the terminal Cretaceous event) and smoke produced in a major nuclear exchange also produce antigreenhouse effects (14).

On Titan, the antigreenhouse effect is dominated by the haze, which absorbs much of the incident sunlight, with an additional antigreenhouse effect resulting from the strong absorption bands in the near infrared of the stratospheric CH_4 . The haze on Titan is optically thick in visible wavelengths and is believed to be composed of organic ma-

terial similar to the “tholin” material produced in laboratory simulations (5, 15). The haze is visible to altitudes of 500 km and probably extends down to the level of CH₄ condensation (16). Our recent model (5) suggests that the haze production rate is $\sim 1 \times 10^{-14} \text{ g cm}^{-2} \text{ s}^{-1}$ and that the production rate is the primary factor controlling the opacity of the haze layer. To illustrate the effect of the haze layer on the surface temperature, we have calculated the surface temperature for haze production values ranging from 0 to three times the present value (Fig. 3). As expected, the temperature increases with decreasing haze production, reaching a value of 105 K for zero haze production. Even without haze production, there is still a small antigreenhouse effect due to stratospheric CH₄. This is evidenced by the fact that in the stratosphere temperatures are still about 140 K with no haze present. We have also performed calculations in which we bypassed the antigreenhouse effect by depositing all of the absorbed solar radiation (equivalent to an effective temperature of 82 K) at the surface. This results in a 33 K greenhouse effect and represents the upper limit of the greenhouse effect on Titan.

We can estimate the magnitude of the actual greenhouse and antigreenhouse effects on Titan’s atmosphere by considering

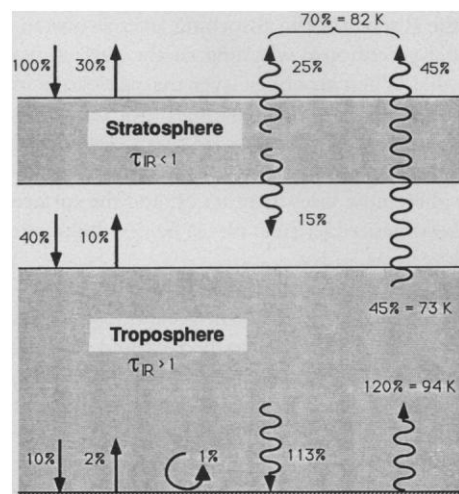


Fig. 4. Diagram of the energy balance of the stratosphere and troposphere on Titan; τ_{IR} , optical depth in the infrared. Straight lines denote the solar radiation and the wavy lines the thermal infrared radiation. The flux units are the percent of the globally averaged solar radiation at the top of Titan’s atmosphere. The troposphere emission temperature (near the tropopause) is determined by the antigreenhouse effect and is 9 K cooler than the effective temperature. The increase in temperature from the tropopause to the surface is due to a greenhouse effect of 21 K resulting from thermal infrared radiation (113%) emitted from the lower atmosphere and warming the surface. The surface is not in radiative balance because convective motions account for an energy flux of 1%.

the energy balance of the combined troposphere and surface:

$$\epsilon \sigma T^4 = F^- - F^+ + IR_s \quad (1)$$

where ϵ and T are the emissivity and emission temperature of the combined troposphere and surface, respectively, σ is the Stefan-Boltzmann constant, F^- is the downwelling solar flux at the base of the stratosphere, F^+ is the upwelling solar flux at the top of the troposphere, and IR_s is the thermal infrared radiation emitted downward by the stratosphere (neglecting reflection in the thermal infrared). The energy input, the right side of Eq. 1, is the solar energy absorbed by the troposphere and surface plus that fraction of the solar energy absorbed in the stratosphere and reradiated as thermal infrared to the troposphere.

These fluxes total about 45% of the incident solar flux (Fig. 4). The downwelling infrared flux from the stratosphere is not equal to its upwelling flux to space because the stratosphere is not isothermal and is optically thick in the gaseous spectral lines, which slightly adds to the antigreenhouse effect. A flux of 70% corresponds to the effective temperature of emission to space so a flux of 45% corresponds to a temperature of $\sim 73 \text{ K}$ [$(T = 82(0.45/0.7)^{1/4} \text{ K})$, close to the observed temperature of the upper tropopause of 71 K. Because the tropopause is nearly isothermal, the effective temperature of the troposphere is expected to be only slightly warmer than the temperature at its top (17). Thus the troposphere emits at a temperature equal to the effective temperature less a decrement due to the antigreenhouse effect.

The fluxes of visible and thermal radiation in Titan’s atmosphere are illustrated graphically in Fig. 4. Both reflection and absorption must be considered together to understand the greenhouse or antigreenhouse effects (1, 5). The surface emits at a temperature warmer than the top of the troposphere because of the greenhouse effect discussed above. Thus, we conclude that on Titan there is a -9 K ($73 - 82 \text{ K}$) antigreenhouse effect and a $+21 \text{ K}$ greenhouse effect ($94 - 73 \text{ K}$), resulting in a net increase of surface temperature of $+12 \text{ K}$ over the effective temperature. We can state these effects in terms of energy balance as well: the antigreenhouse effect robs the lower atmosphere (troposphere and surface) of 25% of the incident solar energy (holding the albedo constant) while the greenhouse effect contributes a thermal infrared flux to the surface energy balance equivalent to 113% of the incident solar energy. This thermal radiation is emitted by the atmospheric layers in the troposphere.

If the haze layer were removed, the anti-greenhouse effect would be greatly reduced with only the residual effect of CH₄ absorption left. The increased solar flux reaching the surface would strengthen the tropospheric greenhouse effect, and the net effect would be that the surface temperature would rise to over 105 K (Fig. 3). In the opposite limit, that of a perfect isothermal antigreenhouse layer—no solar transmission through the upper layer and a very low infrared optical depth—the tropopause temperature on Titan would reach a value of 69 K, $(1/2)^{1/4}$ times the effective temperature of Titan (13). In this case there would be no transmitted solar radiation and the lower atmosphere would become isothermal. The surface would not benefit from any greenhouse effect and the surface temperature would equal the troposphere’s constant temperature. Model simulations with very high haze opacities show that this limit is approached.

The H₂-greenhouse and the haze-anti-greenhouse are actually coupled in that both the haze production rate and the concentration of H₂ should scale approximately linearly with the CH₄ photolysis rate. If we compute the surface temperature for a range of photolysis rates from 0 to ten times the current level (see Fig. 5), we find that the H₂-greenhouse and the haze-anti-greenhouse tend to compensate for each other and the variation in the surface temperature is less than with either effect taken alone. However, there is a small tendency toward surface cooling with increasing haze production; that is, the antigreenhouse dominates slightly. CH₄ also has both a greenhouse effect (due to CH₄-N₂ and CH₄-CH₄ absorption) and an antigreenhouse effect (due to solar absorption in the stratosphere). The former is more significant because of the key spectral

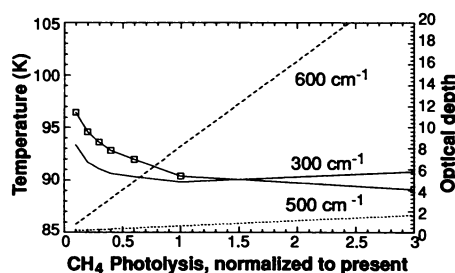


Fig. 5. Temperature (curve with square symbols) and opacity at 300, 500, and 600 cm^{-1} as both the H₂ concentration and the haze production rate are varied together; both are assumed to depend on the photolysis of CH₄. The antigreenhouse effect of the haze (Fig. 3) roughly balances the greenhouse effect of H₂ (Fig. 2), and the surface temperature is buffered against change. The haze production factor is in units of $3.5 \times 10^{-14} \text{ g cm}^{-2} \text{ s}^{-1}$ (5).

regions of the $\text{CH}_4\text{-N}_2$ and $\text{CH}_4\text{-CH}_4$ absorption.

Comparative planetology has appropriately focused on understanding the relation between the so-called terrestrial planets: Venus, Earth, and Mars. The large planets in the outer solar systems seem to represent a different type of object, not akin to Earth from an atmospheric science point of view. However, Titan does have an atmosphere of Earth-like composition and pressure. Preliminary studies of the data returned from the Voyager 1 flyby of Titan have allowed us to explore first the greenhouse effect of atmospheric gases other than CO_2 and H_2O and now the antigreenhouse effect due to organic haze particles. Further investigation of Titan in the upcoming NASA-European Space Agency Cassini Orbiter and Huygens Probe mission should give us more understanding of Titan's atmosphere, one that is both strange and yet similar to our own.

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5. C. P. McKay, J. B. Pollack, R. Courtin, *ibid.* **80**, 23 (1989).
6. Toon *et al.* (2) have determined that the cloud opacity is less than 2 at 200 cm^{-1} and that the particles of the cloud are probably larger than tens of micrometers. This implies that the visible optical depth is also about 2. McKay *et al.* (5) have shown that only large particles and optically thin clouds are consistent with both the Voyager data and the surface energy balance.
7. The existence of an ocean on Titan was suggested by J. I. Lunine, D. J. Stevenson, and Y. L. Yung [*Science* **222**, 1229 (1983)] on the basis of the CH_4 photochemistry. However, recent radar data suggest that only small lakes may exist on Titan [D. O. Muhleman, A. W. Grossman, B. J. Butler, M. A. Slade, *ibid.* **248**, 975 (1990)]. In either case atmospheric CH_4 is determined by equilibrium with this liquid reservoir.
8. Our model is described in McKay *et al.* (5); the parameters in the current best-fit model are as those listed in table III of McKay *et al.* under the no-cloud model except that: pressure $P_0 = 10^{-4}$ mbar (correcting the misprint in McKay *et al.*), relative humidity RH_{CH_4} is taken to be 66% following Lellouch *et al.* (4), and the haze asymmetry scaling factor $\langle \theta \rangle_h$ is 1.05. This model comes close to reproducing the temperature profile of Titan's atmosphere. The computed surface temperature is 93.67 K compared to the reported value of 93.9 K (4).
9. R. E. Samuelson, *Icarus* **53**, 364 (1983).
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11. We assume that in this idealized antigreenhouse the layer is isothermal because this simplifies the analysis. Isothermal conditions could be maintained by adiabatic motions if the layer were physically thin. However, in general the layer would not be isothermal and the emissions from the bottom of the layer would depend on the temperature at that point. This temperature would be determined by the internal greenhouse and antigreenhouse effects within the layer itself.

12. The effective temperature is the temperature at which a blackbody would emit the same total thermal infrared radiation as the surface and atmosphere of Titan. This must balance the total solar radiation absorbed by the surface and atmosphere. In our model calculations, the effective temperature of Titan is 82 K (5).
13. The factor $(1/2)^{1/4}$ in temperature arises as follows: the idealized isothermal (11) antigreenhouse layer absorbs all the incoming solar radiation and emits half back to space and half to the surface. Thus, the flux reaching the surface is reduced by a factor of $1/2$. Temperature is proportional to the fourth root of the flux.
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16. Below the tropopause it is likely that the haze particles are coated with condensing hydrocarbons, principally CH_4 , and are thereby swept from the atmosphere. See (2); C. F. Frère, thesis, University of Paris XII (1989).
17. The troposphere does not emit as a graybody but the opacity of $\text{N}_2\text{-N}_2$ dominates the spectrum (Fig. 1), and an optical depth of unity at the peak of the Planck function occurs near the tropopause. At 130 cm^{-1} , near the emission peak for 73 K, an optical depth of unity occurs at an altitude of 25 km and a temperature of 73 K, in agreement with our simple estimation.
18. We thank R. E. Samuelson for a careful and incisive review that considerably improved the final paper. This work was supported by NASA's Planetary Atmospheres Program.

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Reversible Decrease of Gel-Solvent Friction

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The friction between water and the polymer network of a gel is found to decrease reversibly by three orders of magnitude and appears to diminish as the gel approaches a certain temperature at constant volume and network structure.

WHEN WATER PASSES THROUGH A polymer network, a frictional resistance arises between the water and the network. For a permanently cross-linked network, the friction, normalized by the viscosity of water, was expected to be independent of temperature. It was found, however, that the friction decreases reversibly by three orders of magnitude and appears to diminish as the gel approaches a certain temperature. This phenomenon occurs in spite of the fact that the network structure and the total volume of the gel, and thus the network density, are unchanged.

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The configuration for measuring the friction coefficient of a gel is schematically shown in Fig. 1. Water is pushed through a gel slab of thickness d by a small pressure p . The proportionality between the velocity of the water v and the pressure determines the friction coefficient:

$$f = \frac{p}{dv} \quad (1)$$

To avoid any leak of water and to maintain constant gel volume, most of the gel surfaces were chemically attached to the surfaces of a pair of gel bonding plastics (Bio-Rad) by covalent bonding, except the small circular portions left open for the water flow. The open portion was mechanically pressed by rigid paper filters to prevent swelling. Small shrinkage should have oc-

Fig. 1. Schematic illustration of the measurements of the friction coefficient between a polymer network and water. In order to avoid any leak of water and to fix the gel volume, most of the gel surfaces (diameter 10 mm) were chemically attached to the surfaces of a pair of gel bonding films (Bio-Rad) by covalent bonding, except the small circular portions left open for the water flow. The small open portion (diameter 2 mm) was mechanically pressed by rigid paper filters to prevent swelling.

