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Salt Water Plasma Model of the Venus Atmosphere

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SALT WATER PLASMA MODEL
II.
OF THE VENUS ATMOSPHERE

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ABSTRACT

A model of a planetary atmosphere is developed for a planet whose surface temperature exceeds the critical temperature for water. If the planet has enough water, so the water's partial pressure at the surface is in the range of 100 atmospheres or more, the dielectric constant of the vapor will be high enough to make it an excellent solvent. Under these circumstances, the lower atmosphere becomes a plasma, with a plasma frequency characteristically in the far infrared. Thus, visible light will pass through it but infrared radiation will be strongly absorbed and the greenhouse effect will be enhanced. This model is applied to the early Venus atmosphere and is shown to modify substantially the previously reported pictures of this atmosphere.

SALT WATER PLASMA MODEL

OF THE VENUS ATMOSPHERE

I. INTRODUCTION

A new mechanism is examined that will influence chemical and physical phenomena of planetary atmospheres, e.g. enhance the greenhouse effect, once their surface temperatures rise above the critical point for water. This mechanism depends on the fact that high pressure water vapor, or steam, above 100 atmospheres has a dielectric constant large enough to make it an excellent solvent. Salts dissolved in this solvent will turn the atmosphere into an ionic plasma, with plasma frequencies typically in the infrared. Thus the plasma will absorb radiation in the infrared and at lower frequencies, but it will be transparent to visible light. Given these circumstances the greenhouse effect will be enhanced over that due to molecular absorption. All sorts of chemical equilibria will be affected and there will undoubtedly be interesting interactions between the currents from the solar wind and the conducting atmosphere. Since the surface temperature of Venus lies above the critical temperature for water, and because of other reasons to be discussed presently, we shall use parameters appropriate to Venus in our model.

While we shall discuss this problem in the context of Venus, we have not developed a complete realistic model of its early atmosphere. Our aim in this present work is much more limited. We only wish to establish the importance of the salt water atmospheric plasma. To do so the greenhouse enhancement will be calculated.

Venus, the Veiled Planet, has been called the twin of our Earth because of the similarity of some of their geophysical features, (1)

i.e., the gravitational acceleration (888 cm/sec) is ~90%, the mean radius (6050 km) is ~95%, and the mass is ~82% that of Earth. The two planets were probably formed from the same mix of gas and dust ~4.5 billion years ago. Like most twins, their differences are as striking as their similarities. Their atmospheres and surface conditions differ markedly. The Venus atmosphere is about 100 times more dense than the Earth's, and its composition is more than 90% carbon dioxide, a gas that constitutes only 0.03% of the Earth's atmosphere. The surface temperature is 700°K. Although the surface temperature is well above the critical temperature [2] (~650°K) where all water on the surface turns to steam, there is little water vapor in the Venus atmosphere, about 10^4 times less than on the Earth. Barring some undiscovered mechanism that binds water to the surface, or something that caused Venus to form without water, one must conclude that the water left the planet or converted to another less volatile chemical species.

The principal cause of the difference between the Venus and Earth atmospheres is that Venus is 30% closer to the Sun. Consequently, the solar energy reaching Venus is ~90% greater than that reaching Earth. The Sun's temperature is gradually increasing. Because Venus lies closer to the Sun than the Earth, its surface temperature exceeded the critical temperature for water some time ago. [3] The Earth will eventually suffer the same fate.

There are two other features of Venus that will enter our discussion. Venus rotates very slowly on its axis, the period is 243.16 days. This affects the atmospheric heat budget. Second, Venus has no magnetic field so the solar wind passes through its atmosphere rather than deflecting around it. This could have some interesting

consequences on a conducting atmosphere.

The planetary parameters inserted into the model will be those of Venus over 4 billion years ago when the Sun's luminosity was 30% lower[3] and Venus began developing an atmosphere. Shortly thereafter, it became supercritical with respect to water.[1][3] We shall assume that water was then as abundant on Venus as it is on Earth today. Before the atmosphere began to evolve Rasool and De Bergh[1] estimate the planetary albedo would have been $\sim 7\%$, and the surface temperature for the slowly rotating planet would be 390°K. By the time the atmosphere reached a pressure of 0.1 atmospheres the surface temperature rose to 410°K, well above the boiling point of water but still below the critical point of 650°K.[2] From there the pressure and temperature rise rapidly and Pollack[2] has shown that even including the likely increase in cloud cover as steam enters the atmosphere the critical point will be reached and all the water will evaporate.

Hoyle[4] suggested that the water might photodissociate, with the hydrogen then escaping from the planet and the oxygen reacting with surface material. Sagan[5] and Gold[6] argued, based on a model where water is a minor constituent, that the amount of water available for photodissociation in the stratosphere would be too small to account for the loss of the water from Venus. Ingersoll[7] showed that a gas, like water in the early Venus atmosphere that is a major constituent, would be abundant at all levels. He concludes that photodissociation could account for the present lack of water on Venus. Smith and Gross[8] calculated exospheric temperatures from a steady-state model that includes the photochemistry of important products in the upper atmosphere. They find temperatures for the exosphere of $\sim 100,000$°K and

conclude that atomic hydrogen would be thermally ejected from the atmosphere, but little oxygen or CO_2 would be lost. Rasool and De Bergh[1] showed that reactions with surface constituents like $CaSiO_3$ could account for the present amount of CO_2 in the atmosphere if water is not present. They also estimate that the CO_2 alone could cause a greenhouse effect almost strong enough to account for the current 700°K surface temperature. Pollack[9] needs 0.5% water vapor in the atmosphere to account for the observed surface temperature.

None of the authors cited above who treated the early Venus atmosphere included the plasma in their considerations, so their work should be reviewed with it in mind.

II. EQUATIONS FOR THE MODEL

In normal atmospheres the temperature decreases from the surface of the planet to the bottom of the stratosphere. However, we have assumed for simplicity an isothermal atmospheric model, so the equation of state[10] is

$$n(x,T) = n_0 \exp\left(-\frac{x}{H}\right) \qquad (1)$$

where $n(x,T)$ is the density of water at height x and temperature T, n_0 is the density of water at the surface, $H = kT/mg$ is the scale height, m is the mass of a water molecule, k is Boltzmann's constant, and $g = 888$ cm/sec^2 is the acceleration of gravity at the surface of Venus.

The dielectric constant ϵ for the water is calculated from the Onsager relation[11]

$$\frac{(\epsilon(x,T) - \epsilon_\infty)(2\epsilon(x,T) + \epsilon_\infty)}{\epsilon(x,T)(\epsilon_\infty + 2)^2} = \frac{4\pi n(x,T)\mu^2}{9kT} \qquad (2)$$

where ϵ_∞ is the high frequency dielectric constant, and μ is the dipole moment of water. Note that $\epsilon(x,T)$ is a decreasing function of both x and T. Water molecules have a dipole moment of $\mu = 1.87 \times 10^{-18}$ e.s.u. However, when this value is inserted into the Onsager equation, it gives too low a dielectric constant for liquid water at room temperature. We have chosen an effective μ so that Eq. (2) fits the characteristics of liquid water with the parameters $\epsilon = 80$, $\epsilon_\infty = 2.0$, $T = 300°K$, $n = 3.3 \times 10^{22}$ cm^{-3}. This procedure yields a $\mu_{eff} =$

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3.0 x 10^{-18} e.s.u.

As the ions dissolve in the steam they become a plasma and so shield charges from one another, i.e. increase the effective dielectric constant of the medium. This provides a positive feedback, that tends to make it easier for still more ions to enter the solution. This effect can be calculated from the Bjerrum modification of the Debye-Huckel theory[11]. According to that theory in a reaction of the form AB $\Longleftrightarrow$ A$^+$ + B$^-$, the probability of finding an ion of type A$^+$ at a place where the average potential is U(r) is given by a Boltzmann factor $e^{-eU(r)/kT}$ where e is the charge of a proton. U can be expressed in terms of the ion concentration, and the Poisson equation is solved self consistently to obtain a binding energy E for the AB pair

$$E = \frac{e^2}{\epsilon(1+Ka)a} \tag{3}$$

where a is the internuclear separation between the ions A$^+$ and B$^-$ in the AB molecule, and

$$K = \left(\frac{8\pi e^2 n^+}{\epsilon kT}\right)^{1/2} \tag{4}$$

is the reciprocal of the Debye screening length, with n$^+$ being the positive ion density. The water molecules do not ionize easily because their internuclear separation is quite small, $a \simeq 0.9$ Å. If the AB molecule is a part of the solid surface of an ionic salt then Eq. (3) must be modified by addition of the surface Madelung constant α [12],

$$E = \frac{1}{\epsilon(1+Ka)} \frac{\alpha e^2}{a} \tag{5}$$

The surface Madelung constant is about 1.38 for a NaCl structure.

The ion concentration can be computed from a sublimation model

for the solubility of the steam. The surface ions are supposed to
sublime in pairs into the steam with an energy per pair given by Eq. (5).
The positive ion concentration n^+ ($= n^-$) in the steam can be calculated
from a slight generalization of the usual sublimation theory[13] to the
case where ions sublime in pairs, to give

$$n^+ = \left[\frac{2\pi (M^+ M^-)^{1/2} kT}{h^2} \cdot 2 \sinh \left(\frac{\hbar \omega_b}{2kT} \right) \right]^{3/2} e^{-\frac{E}{2kT}} \qquad (6)$$

where M^+, M^- are the masses of the ions, and ω_b is the vibrational
frequency of the molecules. Since E is a function of n^+ (see equations
(4) and (5)), equation (6) is an implicit equation for n^+ that depends
sensitively on the internuclear spacing of the A and B atoms in the
solid, and on the dielectric constant at the planet's surface $\epsilon (0, T)$.

The absorption constant η of a plasma in the limit where the
radiation frequency ω is small compared to the relaxation frequency
$1/\tau$; i.e. $\omega \tau \gg 1$ is given by the expression[14]

$$\eta = \frac{1}{4\pi^2 c} \frac{\omega_p^2}{\omega^2 \tau} \qquad (7)$$

where c is the velocity of light, and ω_p is the plasma frequency.
The plasma frequency can be approximated by

$$\omega_p \approx \sqrt{\frac{4\pi n^+ e^2}{M_0}} \qquad (8)$$

where M_0 is the reduced mass of M^+, M^-, $M_0^{-1} = (M^+)^{-1} + (M^-)^{-1}$. In
the limit $Ka \ll 1$, an expression for the collision time τ has been
found from a fairly sophisticated plasma calculation by Montgomery[15]
to be

(a)
$$\tau = \frac{M^2 \bar{v}^3 \left(\frac{e_n - 1}{e_n} \right)^2}{8\pi n^+ e^4 \ln (1/Ka)} ; \qquad Ka \ll 1 \qquad (9)$$

where $\overline{U}$ is the r.m.s. thermal speed of the ions, $e_n = 2.718 \ldots$, and a is the characteristic distance of closest approach of ions in a collision. Because of its dependence on n^+ and K, τ is a function of both x and T. τ is fastest at the surface where the density is greatest. Note also that in this region η depends on $M_o^{-3/2}$, so lighter ions have a lower mobility and will absorb most strongly. In the other limit where $K a \geq 1$ the shielding is so strong that the ions scatter like hard core potentials, so $\tau = 1 / \sigma \, n^+ \, \overline{v^2}^{1/2}$ where the cross section σ is $\sigma = \dfrac{\pi}{K^2}$. Substituting K^2 from Eq. (4) and $\overline{v^2} = \dfrac{3 k T}{M}$ yields

$$\tau = \frac{8}{3^{1/2}} \frac{e^2 M^{1/2}}{\epsilon (k T)^{3/2}} \tag{10}$$

The Eddington approximation[1] can be used for the greenhouse temperature T_g,

$$T_g = T_e \left(1 + \frac{3}{4} \Lambda (T_g) \right)^{1/4} \tag{11}$$

where T_e (= 390°K) is the surface temperature in the absence of a greenhouse effect, and $\Lambda (T_g)$ is called the optical thickness. The optical thickness is given by

$$\Lambda (T_g) = \int_o^\infty \overline{\eta} (x, T_g) \, dx \tag{12}$$

where $\overline{\eta}$ is the absorption coefficient averaged over a black body distribution at temperature T_g,

$$\overline{\eta} = \frac{1}{\pi} \frac{e^2 \hbar^2}{M c k^2} \frac{n^+}{\tau T_g^2} \tag{13}$$

To find T_g, Eqs. (1)-(13) must be solved self consistently.

When equations (1)-(13) are solved numerically using parameters

appropriate to common salts, e.g. NaCl, the answers are quite revealing, though taken literally they are completely unphysical. Equation (6) for n^+ assumes that the number of salt ions in the vapor phase is small compared to that in the solid. However, the solutions to the equations yield ion densities near the surface of about 10^{25}cm^{-3}, and greenhouse temperatures in the thousands of degrees range. Clearly the supply of salt will be exhausted from the planet long before densities this high could be reached. Thus, the model must be modified to have a finite amount of salt. Before we do that it is instructive to examine two other features of the numerical solutions.

First, the ion density exhibits an abrupt transition, a first order phase change, as a function of height above the planet's surface. The phase change is a consequence of the positive feedback that the ion shielding has on n^+. The greater the ion density, the shorter the screening length, and the easier it is for still more ions to form. All this depends on the background dielectric constant of the steam. As the height above the planet increases, the water density decreases to a point where the feedback ceases to function. At a critical height X, the ion concentration drops abruptly, in our numerical results by a factor of 10^{10}.

Second, at the elevated temperatures reached, the dielectric constant due to the water is nearly one. The dielectric response of the medium is dominated by the conducting ions. The whole process cannot start without some background dielectric, but once it does the temperature rises to a point where this dielectric constant goes to unity.

The numerical results cited above provide us with hints that

lead the way to an analytical solution to the problem. To a good approximation, all the salt from the planet's surface will ionize and go into solution. It will almost all be in a layer adjacent to the surface that is below the critical level X where the phase transition occurs. If we suppose that Venus was like Earth, and practically all the salt is in the ocean, then the ratio of salt to water molecules[16] is about 1/200. Under these circumstances the height of the ion layer X will be small compared to the radius of the planet R. Since we are using an isothermal model--in view of the phase transition a terrible approximation--the ion density will be almost constant to height X, and negligible above height X. The ion density n^+ below X is

$$n^+ = \frac{N^+}{4\pi R^2 X} \tag{14}$$

where $N^+ = 10^{45}$ is the total number of salt molecules on the planet. Then from equations (12), (13), (10), the optical thickness is simply

$$\Lambda(T_g) = \bar{\eta} X = \frac{3^{1/2}}{32\pi^2} \frac{\hbar^2 N^+}{M^{3/2} c\, k^{1/2}} \frac{1}{R^2 T_g^{1/2}} \tag{15}$$

Equation (15) has the interesting feature that it is independent of X, i.e., the product $n^+ X$ and τ are both independent of X. Since $T_g^4 \gg T_e^4$ is found, we can substitute equation (15) into (11) to find

$$T_g = T_e^{8/9}\left(\frac{3^{3/2}}{128\pi^2} \frac{\hbar^2 N^+}{M^{3/2} c\, k^{1/2} R^2}\right)^{2/9} \tag{16}$$

For $T_e = 390\,°K$, $N^+ = 10^{45}$, R = 6000 km, and M = 2 x 10^{-23} gm., the greenhouse temperature is $T_g = 1300\,°K$.

If one inserts regular molecular absorption into the problem by taking a $\Lambda_T = \Lambda + \Lambda_M$, where Λ_M is the optical thickness due to molecular absorption, then T_g can again be found from equation (11).

We have arbitrarily chosen $\Lambda_M = 290$, a value that in the absence of the plasma effect would correspond to $T_{gM} = 1500\,°K$. Then the combined effects of the plasma plus the molecular absorption gives a temperature of $1700\,°K$.

Finally, the height of the ion layer can be estimated from equation (6) by supposing that below X, $n^+ = \dfrac{N^+}{4\pi R^2 X}$ and above X, n^+ is zero. Then taking the logarithm of both sides of equation (6) one can solve for the product Ka,

$$Ka = \frac{\alpha e^2}{2\beta k T_g\, a} - 1 \tag{17}$$

where

$$\beta \equiv \ln\left\{ \frac{4\pi R^2 X}{N^+}\left[\frac{2\pi(M^+ M^-)^{1/2}}{h^2}\, k T_g \cdot 2\sinh\frac{\hbar\omega_b}{2 k T_g}\right]^{3/2}\right\} \tag{18}$$

β is a slowly varying function of X so it can be accurately estimated even though X is not well known. Substituting equation (4) for K into equation (17) allows us to solve for n^+ or X,

$$n^+ = \frac{k T_g}{8\pi e^2 a^2}\left(\frac{\alpha e^2}{2\beta k T_g\, a} - 1 \right)^2 \tag{19}$$

Substituting the collection of parameters quoted earlier with $T_g = 1300\,°K$, produces the results $\beta = 13$, $n^+ = 2.8 \times 10^{20}\,cm^{-3}$, $X = 7.9\ km.$, $K = 9.5 \times 10^7\,cm^{-1}$, $\omega_p = 6 \times 10^{12}$, and $\tau = 6 \times 10^{-11}$ sec.

III. CONCLUSIONS

While the effects we have displayed in the previous section are strong and important in the heat budget of a planet that exceeds the critical temperature for water, it is still not the whole story. As we mentioned earlier, H_2O doesn't dissociate into ions easily because the effective separation between an H^+ and the OH^- is small in the molecule. However, in the layer that contains the plasma the shielding from the salt is so great, $K \cong 9.5 \times 10^7 cm^{-1}$, that the water will also dissociate in this layer. This will then dominate everything and our simple isothermal grey atmosphere model is woefully inadequate to deal with this situation. The main conclusion we wish to draw is that any realistic model of the early Venus atmosphere (or of later stages of the Earth's atmosphere) must include a treatment of the phenomena discussed here.

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