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Title: INVESTIGATION OF THERMODYNAMIC MECHANISMS FOR THE PRODUCTION
OF COMPLEX COMPOUNDS ESSENTIAL FOR THE ORIGIN OF LIFE

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The paper "Thermodynamic Equilibria in Planetary Atmospheres" was completed and submitted to the Astrophysical Society Journal.

The computer programs to produce the booklet "Thermodynamic Equilibria in Atmospheres Containing Elements C H O N S P Cl" are completed. The programs have been translated into Fortran IV using double precision numbers. Extensive print out routines for tables of free energies and compound concentrations have been added. The free energy data for the booklet is almost in order.

Programming has begun to treat systems containing solid and liquid phases in addition to the ideal gas.

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Abstract

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From present information on the composition, pressures, and temperatures of planetary atmospheres, we have calculated the expected thermodynamic equilibrium composition of the atmospheres of the Earth, Venus, Mars, and Jupiter. Departures from thermodynamic equilibrium must be attributed to special mechanisms, including, on the Earth, biological activity. The major constituents of the terrestrial atmosphere are found to be in approximate thermodynamic equilibrium; while many minor constituents have abundances exceeding their equilibrium values, there is a marked tendency for equilibrium to be restored. It appears that the atmosphere of Venus is in thermodynamic equilibrium, while that of Jupiter is not. The evidence for Mars is less conclusive, although not inconsistent with thermodynamic equilibrium. For none of these planets is there a molecular species with a large predicted equilibrium abundance and spectroscopically accessible absorption features which has not been already identified. The predicted equilibrium abundances of oxides of nitrogen are extremely low on all planets. The measured upper limits on the abundances of Cytherean CH_4, NH_3, and CO are all inconsistent with the possibility of elemental carbon or organic molecules in contact with the atmosphere of Venus either on the surface or as clouds. The possibility of small quantities of oxygen on Mars is not excluded. We suggest that the colored materials at the Jovian clouds are organic molecules, produced by non-equilibrium processes in a reducing environment.

If the Cytherean atmosphere evolved from an original gas mixture much more reducing than the present mixture, two processes are required to achieve the unique contemporary composition: the loss of hydrogen to space, and the efficient reaction of atmospheric oxygen with reduced surface materials. In addition, Venus must have begun its evolutionary history with a [C/O] abundance ratio ≤ 0.5, a value consistent with several cosmic abundance estimates.

Author

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1. Introduction

It is not known how closely the gross chemical composition of planetary atmospheres is approximated by thermodynamic equilibrium of the constituents. In the upper reaches of planetary atmospheres, where the optical depth at ultraviolet frequencies is small, relative molecular abundance may be dominated by photodissociation and recombination. In the lower portions of the atmospheres, which are shielded from photodissociating ultraviolet radiation, a closer approximation to thermodynamic equilibrium can be expected. Especially where surface temperatures are high or when catalysts such as water are present, there will be a strong tendency for the degradation of molecules to the lowest energy state. Even in the presence of special mechanisms which favor the production of specific compounds -- mechanisms such as ultraviolet radiation or lightning -- the thermodynamic equilibrium distribution of reaction products should be a useful first-order approximation. Since the equilibrium state is independent of particular reaction mechanisms and reaction rates, and since the computations of equilibrium states are quite straightforward, studies of thermodynamic equilibrium chemistry would appear prerequisite to considerations of non-equilibrium processes.

One of the earliest examples of a fruitful argument from thermodynamic equilibrium in planetary atmospheres was provided by Wildt (1937), who pointed out that the absence of detectable amounts of higher hydrocarbons, both saturated and unsaturated, in the atmospheres of the Jovian planets was an argument for the presence of a great excess of molecular hydrogen, a gas which had not been detected at that time. Further indirect evidence for the presence of low-mass constituents in the Jovian atmosphere was provided by observations of the occultation of σ Arietus, by Baum and Code (1953); but not until fairly

recently were the quadrupole lines of H_2 observed directly in the photographic infrared (Kiess, Corliss, and Kiess, 1960). Urey (1959) has argued from the large abundance of carbon dioxide on Venus that substantial quantities of CH_4, NH_3, H_2, N_2O, and other oxides of nitrogen would not be expected on that planet. A very low upper limit on the allowed abundance of oxides of nitrogen in the Martian atmosphere was set by Sagan, Hanst and Young (1965) in a discussion of combined photochemical and thermodynamic equilibria. Wildt (1937) and Urey (1952), while performing thermodynamic equilibrium calculations in a planetary atmospheres context, stressed the possibility of significant departures from thermodynamic equilibrium.

Some more recent studies have suggested that thermodynamic equilibrium calculations may, under certain circumstances, be a useful approximation to reality. Thermodynamic equilibrium calculations by Dayhoff, Lippincott, and Eck (1964) for the relative abundances of a large number of compounds of biological interest have been performed under a wide variety of assumed conditions of temperature, pressure, and elemental composition. These machine computations have revealed a possible mechanism for the abiological formation of polycyclic aromatic hydrocarbons (asphaltic tars) and have shown the existence of an oxidation threshold where free oxygen appears and at which all but the simplest organic compounds disappear. Studier, Hayatsu, and Anders (1965) have recently called attention to a remarkable agreement between the distribution of organic compounds observed in the carbonaceous chondrites, and as we predicted from thermodynamic equilibrium calculations in the range of elemental abundances where asphaltic tars are expected. This success has encouraged us to extend thermodynamic equilibrium calculations to planetary atmospheres.

2. Methods of Calculation

Our computational procedures have been described previously (Dayhoff, Lippincott, and Eck, 1964) following a well-known method (White, Johnson, and Dantzig, 1958) which minimizes the free energy of the system, simultaneously satisfying the equilibrium constants of all possible reactions. The calculations were performed on an IBM 7094 computer.

At thermodynamic equilibrium, the distribution of molecular species is independent of the specific reaction pathways by which equilibrium is attained. The molecular balance depends upon the relative elemental abundances, pressure, temperature, and the standard free energies of formation of the compounds. All compounds present in significant concentrations must be included in order to arrive at the correct molecular distribution. Fortunately, there are only a small number of these major compounds; they are simple in structure and well-known to chemists. For a real system to approach equilibrium, there need be only one reversible reaction pathway which leads from the major constituents to the other compounds.

In our computations on planetary atmospheres, we explored the entire range of possible relative atomic compositions using a large number of molecular species in order to locate any specific ranges of atomic abundances which would be simultaneously compatible with all the existing estimates of molecular abundances or their upper limits. The results are presented in ternary diagrams which cover all possible proportions of the elements C, H, and O. Compounds of nitrogen can also be represented as a projection on this diagram. The astronomical observation of a specific relative abundance for a given molecular species will, in general, define a line on the ternary diagram. An upper or lower concentration limit will exclude a certain area. The application of several such constraints may operate in a mutually inconsistent manner, so that no point on the diagram simultaneously satisfies all observations. In such a case, we would conclude that thermodynamic equilibrium is not attained in this atmosphere. On the other hand, if the application of several such constraints can be performed in a consistent manner, yielding a region of the ternary diagram simultaneously compatible with all constraints, we might tentatively conclude that thermodynamic equilibrium is a useful first approximation to the atmosphere in question. Each point in the allowed region of the diagram would then correspond to a possible elemental composition in the planetary atmosphere. The calculations would place some upper and lower limits on the allowable relative abundances of other possible constituents of the atmosphere.

3. Observational Uncertainties

The initial conditions for these computations are based upon the results of astronomical spectroscopy. It is not a trivial matter to derive relative abundances from such observations. The conversion of equivalent widths to absolute abundances requires careful laboratory calibrations. Intercomparisons of abundances derived for the same molecule at different wavelengths must allow for the possibility that the effective reflecting atmospheric level is a function of wavelength. Existing observational discrepancies on, for example, the abundance of water vapor in the atmosphere of Venus (see, e.g., the discussion by Sagan and Kellogg, 1963) underscore the uncertainties of such reductions. Intercomparisons of the relative abundances of different molecular species is even more uncertain. Determinations of absolute abundances is complicated by the possibility of multiple scattering (see Chamberlain, 1962; 1965). Observations of very weak lines of a given molecular species may refer to substantial depths in the planetary atmosphere, where ultraviolet photodissociation is not a dominant process. Observations of strong lines may refer to high altitudes alone, where the relative distribution of molecular species may be far from that predicted by thermodynamic equilibrium. However, the species must be derivable from some compounds present extensively in the atmosphere.

Bearing these cautions in mind, we now proceed to a discussion of thermodynamic equilibrium in the atmospheres of the planets Earth, Venus, Mars, and Jupiter. In general, the conclusions we will draw will not be sensitively dependent on the exact values of the adopted mixing ratios of minor constituents; and variations in these mixing ratios even by several orders of magnitude will leave most of the results unchanged. Thus, despite the uncertainties in the observational material, it will nevertheless be possible to draw conclusions of some significance.

4. The Earth

As a test of our computation procedures, we first consider thermodynamic equilibrium in the terrestrial atmosphere. In addition to its major components, the atmosphere of the Earth contains a variety of compounds of diverse origins: methane and smaller amounts of other hydrocarbons from natural gas, petroleum, and asphalt; sulfur dioxide, hydrogen sulfide, carbon monoxide and nitrogen oxides from vulcanism; terpenes and other volatile organics from vegetation; methane, N_2O, and hydrogen sulfide from the metabolic processes of microorganisms; ozone and nitrogen oxides from lightning and solar radiation, etc. Table 1 shows the amounts of some of these compounds which have been detected in the open air.

With the relative atomic composition and physical parameters implied by Table 1 we have calculated the chemical composition which the Earth's atmosphere should have in thermodynamic equilibrium. The results are displayed in Table 2. We see that the relative abundances of major constituents in the terrestrial atmosphere are completely compatible with thermodynamic equilibrium. The minor constituents, however, cannot exist at thermodynamic equilibrium in the presence of excess oxygen. At equilibrium, any carbon in the atmosphere would occur as CO_2, and any sulfur as SO_3. Since there is no reason to think that less oxidized materials are presently accumulating in the atmosphere, they must be in approximate dynamic equilibrium, being removed or destroyed as fast as they are being added. That is, even at the prevailing low temperatures there is a definite tendency for the Earth's atmosphere to approach thermodynamic equilibrium. Such reactions are no doubt catalyzed by solar radiation and by dust particles and droplets suspended in the air. This constitutes a specific example of our general contention that, even in the presence of special mechanisms which favor the production of certain specific compounds, the overall tendency will be for a planetary atmosphere to approach thermodynamic equilibrium. If the major components of the atmosphere were methane, hydrogen, water, and nitrogen (or ammonia) instead of the present composition, the details of the radiation-coupled reactions would be different, but the overall trend to thermodynamic equilibrium would still be present. It is not obvious at what

relative rates unstable prebiological compounds such as amino acids would be produced by nonequilibrium processes and degraded by the environment and by their interaction with each other.

The observation of complex, very energetic compounds such as terpenes in the contemporary atmosphere of the Earth would lead an extra-terrestrial observer to suspect the existence of life here. The lack of any obvious simple mechanism to form terpenes, either by thermodynamic equilibrium at some plausible combination of elemental composition, temperature, and pressure, or by photochemical reactions or other physical processes, would indicate the presence of biological activity on the Earth -- even in the absence of any other signs of life. Even the presence in the observed large amounts of much simpler, but highly reduced, compounds such as methane in our oxidizing atmosphere would be suggestive of life on Earth.

5. Venus

The adopted initial atmospheric composition of Venus is given in Table 3, constructed from the references there given. Some comments should be made on the values adopted for $[CO_2]^*$, $[H_2O]$, and $[CO]$. The 5% volume mixing ratio of carbon dioxide adopted in our analysis is a fairly conventional one, derived from Spinrad's (1962a) observations, and dependent upon the assumption that the near infrared CO_2 bands are formed by single scattering. Chamberlain (1965) has recently shown that the introduction of multiple scattering might reduce the CO_2 mixing ratio by as much as an order of magnitude. The precise reduction factor is at the present time unknown. However, similar correction factors for multiple scattering will be applicable to all other abundances and abundance upper limits of Table 3, and relative abundances of all minor constituents should be approximately those of Table 3, whether single or multiple scattering is assumed. The relative abundance of the major atmospheric constituents -- probably N_2, with some admixture of noble gases -- would then vary from 95% to larger values. Such variations have no significant effects on our conclusions.

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* In the following discussion square brackets denote volume mixing ratios.

Reported observations of water vapor in the spectrum of Venus have been
made by Dollfus (1964) and by Bottema Plummer, and Strong (1964). The derived
values of the water vapor mixing ratio depend on the scattering mechanism and
the total atmospheric pressure at the effective level of band formation. The
range of derived mixing ratio values shown in Table 3 is consistent (Sagan and
Kellogg, 1963; Chamberlain, 1965) with a previous upper abundance limit on
water vapor established by Spinrad (1962b). However, the water vapor which is
observed by infrared spectroscopy is primarily in the region of the clouds.
Since there is now fairly convincing evidence that the clouds are condensed
water (Bottema, Plummer, Stong, and Zander, 1964; Sagan and Pollack, 1965),
it is in general invalid to assume that the water vapor mixing ratio in the
vicinity of the clouds applies to the lower Cytherean atmosphere. The amount
of condensed water in the clouds required to explain the near infrared reflec-
tion spectrum of Bottema, Plummer, Strong, and Zander (1964), and also to ex-
plain the millimeter attenuation of the surface thermal microwave emission, is
1 gm cm^{-2} or less convective atmospheres which can maintain such clouds at the
observed pressures and temperatures must have volume mixing ratios of water
vapor in their lower reaches of a few times 10^{-4} (Sagan and Pollack, 1965).
The water vapor mixing ratio may therefore range from a few time 10^{-6} in the
vicinity of the clouds and above, to a few times 10^{-4} near the Cytherean
surface.

The quantities of carbon monoxide in the spectrum of Venus observed by
Moroz (1965), if related to a 1 atm pressure level near the cloudtops, give a
volume mixing ratio $\sim 10^{-6}$. However, CO is a principal carbon dioxide photo-
dissociation product, and amounts of carbon monoxide almost comparable to
those reported by Moroz may arise from photodissociation (Moroz, 1965; Shimiu, 1963).
If the observed carbon monoxide abundance is significantly in excess of that
expected from photochemical equilibrium, then a CO mixing ratio of 10^{-6} may be
extended down to the lower Cytherean atmosphere. If, on the other hand, the
observed carbon monoxide is due principally to photochemical processes, then
the carbon monoxide abundance in the lower Cytherean atmosphere will be substan-
tially less.

We adopt a Venus surface temperature of $700^\circ K$, and a surface pressure of 50 atm (Sagan, 1962; Pollack and Sagan, 1965). Moderately large departures from these values will not alter our conclusions significantly. In particular, the calculations performed at such pressures and temperatures should, because of the relative pressure and temperature insensitivity of the reaction thresholds and because of atmospheric convection, be applicable to a major fraction of the total mass of the Cytherean atmosphere.

A C-H-O ternary diagram is presented in Figure 1. The corners of the triangle represent pure carbon, pure hydrogen, and pure oxygen. The positions of pure carbon dioxide and pure water are also indicated. The line connecting the CO_2 and H_2O points is an oxidation threshold, which divides the diagram into an upper, reducing, portion in which sizeable numbers of different species of organic molecules may be expected at thermodynamic equilibrium, and a lower, oxidizing, portion, in which such molecules are unstable, and in which free oxygen exists. Also indicated in Figure 1 is the asphaltic tar threshold. Above this line, polycyclic aromatic hydrocarbons occur at thermodynamic equilibrium (in the absence of a mechanism to form graphite); below it, they are excluded.

The ammonia upper abundance limit of 4×10^{-7} restricts the atmosphere at thermodynamic equilibrium to the region below the line marked NH_3 in Figure 1. This line lies in the reducing region of the diagram, slightly above the oxidation threshold, and curves away from the carbon dioxide point, as illustrated. This one spectroscopic upper limit therefore excludes most of the reducing portion of the ternary diagram. The concentration of ammonia varies so rapidly in the region of the illustrated line that the width of this line represents several orders of magnitude in concentration -- an example of the insensitivity of these calculations to exact relative abundances.

. · We next consider the upper abundance limit on methane. This concentration yields a curve which closely follows the C-O edge until the CO_2 point is reached, whereupon it swings away and follows the oxidation threshold. The CH_4 curve is even more constraining than the NH_3 curve, and excludes almost the entire reducing portion of the diagram.

We now consider the constraints imposed by the water vapor mixing ratio. Figure 1 shows a line for $[H_2O] = 10^{-5}$, which, in the oxidizing region of the diagram, lies very close to the C-O edge. The curves for mixing ratios an order of magnitude larger would lie very close to the curve shown. Thus, the searches for methane, ammonia, and water have restricted the equilibrium chemistry of the Cytherean atmosphere to a very narrow region of the ternary diagram, hugging the C-O edge throughout the oxidizing region, and extending very slightly into the reducing region.

In Figure 2, where the Venus ternary diagram has been magnified 100 times, the line corresponding to a carbon monoxide volume mixing ratio of $[CO] = 10^{-6}$ is indicated. Since part of the observed carbon monoxide may be due to CO_2 photodissociation, the fraction of carbon monoxide relevant for thermodynamic equilibrium calculations will be somewhat less than 10^{-6}. The observations therefore further restrict the ternary diagram to the area below the line $[CO] = 10^{-6}$. We see that this line closely parallels the oxidation threshold. As with the NH_3 and CH_4 lines, the width of the $[CO] = 10^{-6}$ line actually corresponds to many orders of magnitude in the mixing ratio. The lower side of this line corresponds to the oxygen upper abundance limit, 8×10^{-5}. If observations can establish any detectable amount ($> 10^{-16}$) of CO in the lower atmosphere, the amount of O_2 must be extremely small. Conversely, if $[O_2] \geq 8 \times 10^{-5}$, then $[CO] \leq 4 \times 10^{-17}$. At any rate the upper limits on Cytherean [CO] and $[O_2]$ restrict the thermodynamic equilibrium composition to the thickness of the thick slant line in Figures 1 and 2.

In Figure 2 is displayed a line above which a solid phase of graphite might form. The composition of the atmosphere is clearly incompatible with solid carbon in equilibrium in the atmosphere or on the surface. Similarly, any equilibrium accumulation of polycyclic aromatics, or any other hydrocarbons, is forbidden, a conclusion reached for a much smaller array of compounds by

Mueller (1964). The asphalt threshold seen in Figure 1 lies well into the region excluded by the unsuccessful searches for CH_4 and NH_3. This conclusion is separately confirmed by the CO upper abundance limits, and is independent of the quantity of water present. This exclusion of hydrocarbons is relevant to some models of the Venus atmosphere which invoke hydrocarbon clouds (Kaplan, 1963). The absence of polycyclic aromatic hydrocarbons from the surface is consistent both with passive observations of the microwave phase effect and with active radar observations of Venus (Pollack and Sagan, 1965).

Table 4 shows the chemical composition of the atmosphere of Venus, at two extremes of CO and O_2 concentration, predicted from thermodynamic equilibrium. If the measured value of CO depends entirely on photodissociation, then there may be as much as $[O_2] = 8 \times 10^{-5}$. We emphasize again that any error in the relative abundance of nitrogen would cause negligible deviation in the relative abundance of carbon compounds, and indeed, would have very little effect on the calculated ammonia abundance. A smaller amount of nitrogen would only make the ammonia concentration a less severe restriction on the actual composition (cf. Figure 1). The constituents shown at the bottom of the table would be formed if 0.0001% sulfur were added to the atmosphere.

Formaldehyde was once suspected in the atmosphere of Venus (Wildt, 1940) but at thermodynamic equilibrium with the detected amounts of water and the observational upper limit on methane, the concentration of formaldehyde would be negligible. Non-equilibrium reactions in simulated Cytherean atmospheres are known, however, to produce formaldehyde (Sagan and Miller, 1960).

We now explore some other consequences of the foregoing abundances. Possible atmospheric compositions are limited to a segment of the $[CO] = 10^{-6}$ curve near $[H_2O] = 10^{-4}$, as shown in Figure 2. The composition of Venus is then specified by a segment of one thick line in the ternary diagram, near the CO_2 composition point, and slightly on the reducing side of the oxidation threshold. This conclusion is consistent with all abundance determinations and upper limits. The fact that none of the observations are mutually

inconsistent suggests that the atmosphere of Venus is, on the whole, close to that predicted by thermodynamic equilibrium.

In this case some remarks can be made on the original composition and subsequent evolution of the Cytherean atmosphere. From cosmic abundance considerations, it is clear that the atmosphere must originally have had a composition putting it in the extreme right-hand corner of the ternary diagram (cf. Figure 3). The chemical evolution of the atmosphere occurs initially through the escape of atomic hydrogen from the Cytherean exosphere. Escape of significant quantities of carbon or oxygen from Venus during geological time seems quite unlikely (see, e.g., Sagan, 1966). Any differential escape is correspondingly unlikely. The track along which the atmospheric composition of Venus evolves depends then on the initial carbon-to-oxygen abundance ratio. The cosmic [C/O] abundance ratio has been assigned a value of 0.20 by Suess and Urey (1956), while Cameron (1959) has suggested a value of 0.44 and more recently (1963), 0.67. For a ratio of 0.20 or 0.44, the evolution would proceed along the lines ending at α or β (Figure 3), in a region where free oxygen exists. For an initial [C/O] ratio of 0.67, the evolutionary track ends at γ, in the reducing portion of the diagram. The actual present atmosphere of Venus appears to have a [C/O] ratio that differs from that of CO_2 by a factor of 10^{-5} or less. If the initial atmosphere had a C/O ratio anywhere between 0.2 and 0.7, the probability that the present ratio would be as close to CO_2 as it appears to be, through no other process but the loss of hydrogen, would then be about 4×10^{-5}. This seems quite unlikely. However, if oxygen were also depleted from the atmosphere, then over a wide range of initial [C/O] ratios the atmosphere would finally settle at the CO_2 point. Since it seems unlikely that oxygen has escaped from Venus, the depletion of atmospheric oxygen must be attributed to chemical reactions, and the surface material of Venus, initially reducing, must now be partially oxidized. An independent argument for the presence of extensive oxygen sinks on the surface of Venus has been offered by Sagan (1966), in an attempt to explain the differential abundance of water on Venus and on Earth by differential rates of hydrogen escape.

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Typical evolutionary tracks would then have resembled those illustrated by the arrows in Figure 3. Due to loss of hydrogen, the atmosphere evolves away from the hydrogen corner of the ternary diagram until it intersects the oxidation threshold. As soon as free oxygen is produced, it combines with surface material and the evolutionary track turns abruptly upward, following the oxidation threshold toward the CO_2 point.

If the initial [C/O] ratio were 0.44, the initial evolutionary track due to the loss of hydrogen would twice intersect the graphite threshold (cf. Figure 3). There would then be an interlude in the evolutionary history of Venus in which graphite might be present. However, the activation energy for the formation of graphite is so great that it would very likely never precipitate directly. Such a track would follow the line marked H-β until it intersected the oxidation threshold, whereupon it would turn and proceed towards the CO_2 point.

If the initial [C/O] ratio were 0.67, the evolutionary track would follow the line marked H-γ in Figure 3. This line intersects the graphite threshold once, and never crosses the oxidation threshold. The atmosphere would then always remain in the reducing portion of the diagram. In order to end at the CO_2 point, some mechanism must exist for the removal of carbon from the atmosphere. The asphalt threshold is not intersected, so no formation of polycyclic aromatics would be expected. If the removal of carbon from the atmosphere were possible -- for example, by the precipitation of graphite or other organic material -- the atmosphere would then evolve along the graphite line in Figure 2. The composition would end significantly above the actual composition point, in conflict with the spectroscopic observations.

Thus, it is probable that Venus began its evolutionary history with a [C/O] abundance ratio ≤ 0.5 and that its evolutionary track in the ternary diagram was directed towards the CO_2 point by the simultaneous loss of hydrogen to space and oxygen to the surface.

6. Mars

Because of the low temperature and relative ultraviolet transparency of the Martian atmosphere, the applicability of thermodynamic equilibrium calculations should be more limited than in the case of Venus. The character of the equilibrium state is nevertheless of interest. A surface temperature of $240^\circ K$ and a surface pressure of 50 mb was assumed for the Martian atmosphere (Kaplan, Munch, and Spinrad, 1964; Hanst and Swan, 1965). Our remarks on the insensitivity of the calculations to the precise values of pressures and temperatures apply again to this case and a surface pressure of 10 mb would not appreciably alter the results. The assumed atmospheric composition is shown in Table 5. The atmosphere is assumed to be approximately 90% molecular nitrogen and noble gases. The remainder of the atmosphere is expected to be compounds of carbon, oxygen, nitrogen, and hydrogen. The anticipated CO_2 mixing ratio is not known at the present time. Its value is tied closely to the value of the absolute surface pressure (Kaplan, Munch, and Spinrad, 1964; Hanst and Swan, 1965; Chamberlain and Hunten, 1965). The values of Table 5 correspond to the range of suggested values at the time of writing. As in the case of Venus, the absolute value of the CO_2 mixing ratio is not critical in computations of the relative values of the mixing ratios of minor constituents.

The ammonia upper abundance limit excludes the highly reducing portion of the ternary diagram, as shown in Figure 4. The upper limit on the methane mixing ratio imposes a more significant boundary condition, restricting the range of possible atmospheric compositions essentially to the portion below the oxidation threshold, with the exception of a small section of the reducing part of the diagram along the C-O axis. The carbon monoxide upper limit places no new constraint on the diagram; the upper limits on oxygen and ozone eliminate a region near the oxygen corner of the ternary diagram. The estimate for the abundance of water vapor in the Martian atmosphere places the equilibrium composition along a curve which crosses the oxidation threshold not far from the CO_2 composition point, quite analogous to the situation for Venus. This line quickly enters the region forbidden by the methane abundance upper limits.

The composition of the Martian atmosphere is therefore restricted to the solid portion of the water line of Figure 4, encompassing a small region of the oxidizing part of the diagram, and a very small segment, near CO_2, in the reducing region.

It has been suggested that various oxides of nitrogen are produced by non-equilibrium processes in the atmosphere of Mars, and that these oxides of nitrogen play a major role in the total chemistry of the atmosphere and surface of Mars (Kiess, Karrer, and Kiess, 1960; 1963). In Table 6, we present some calculations of the equilibrium abundance of various compounds in the Martian atmosphere at representative points in Figure 4. Even in the favorable case where oxygen is present as a major constituent, we see that the resulting abundances of the oxides of nitrogen are extraordinarily small. These conclusions are consistent with those of Sagan, Hanst, and Young (1965), who used a much smaller array of equilibrium reactions than are implicitly included here and considered also photochemical production and breakdown of these oxides. The present results place the equilibrium upper limit on NO_2 several orders of magnitude below the previous calculated values (Sagan, Hanst, and Young, 1964); and below the most recent observational upper limits (Marshall, 1964) by the same factor.

Further conclusions on the nature of the Martian atmosphere in thermodynamic equilibrium could be drawn if reliable estimates were performed of the abundances of such molecules as CO, CH_4, H_2S, SO_3, or O_2. The limited data available are consistent with the existence of thermodynamic equilibrium, but do not demonstrate thermodynamic equilibrium. As in the case of the atmosphere of Venus, the escape of hydrogen, plus the depletion of atmospheric oxygen (here, either by reaction with the crust or by escape from the planetary exosphere) could have led to an evolutionary track in the ternary diagram approximately along the oxidation threshold. The present information is consistent with a small proportion of molecular oxygen in the atmosphere, although the atmosphere could also be slightly reducing. The possibility of an equilibrium abundance of organic molecules on the Martian surface depends in part

on this question of which side of the oxidation threshold the total atmospheric composition lies. The long-term stability of organic molecules on the Martian surface also depends on the rate of ultraviolet photodissociation, if the atmosphere is transparent in the near ultraviolet (see Sagan and Kellogg, 1963).

7. Jupiter

The assumed composition of the Jovian atmosphere is shown in Table 7. Because there is no way for water to escape from Jupiter, it must be present in significant amounts below the visible clouds. At the clouds it is forzen out because of the low temperatures. We have arbitrarily assumed that the H_2O mixing ratio below the clouds is comparable to that of methane and ammonia. In the clouds it is fixed by the vapor pressure of ice. The thermodynamic equilibrium calculations were carried out for two sets of pressures and temperatures -- in the first case, for a pressure of 1 atm and a temperature of $200^{\circ}K$, corresponding approximately to the region of the clouds (Spinrad and Trafton, 1962; Owen, 1965); and in the second case, for a pressure of 1000 atm and a temperature of $350^{\circ}K$. This point corresponds to the level of the hypothesized water droplet clouds, predicted by Gallet (1963; see also Wildt, Smith, Salpeter, and Cameron, 1963). The concentrations of the major resulting constituents of the Jovian atmosphere at thermodynamic equilibrium are presented in Table 8. The addition of 10^{-6} sulfur, would give the other constituents shown. As first pointed out by Wildt (1937), the large excess of molecular hydrogen works to greatly reduce the concentration of even simple organic molecules at thermodynamic equilibrium. Essentially all carbon is present as methane, all oxygen as water, and all nitrogen as ammonia. The total atmospheric composition gives a point very near the H corner of the ternary diagram. The relative abundance of molecular nitrogen increases fairly rapidly with temperature, but even at $350^{\circ}K$, it is still a very minor atmospheric constituent.

Despite the extremely low computed mixing ratios of even the simplest organic molecules, there is nevertheless reason to believe that organic molecules may be present in the atmosphere of Jupiter. The bright and contrasting colors of the bands, belts, and spots -- particularly, the Great Red Spot -- surely betoken differences in molecular composition in the vicinity of the Jovian clouds. While some small concentration of minerals may be expected in this region, due to micrometeoritic infall, it seems unlikely that such materials are differentially distributed over the Jovian clouds; a more reasonable source of chromophores would appear to arise from the major atmospheric constituents, and therefore, be organic materials (see e.g., Urey, 1952; Sagan, 1963). Experiments attempting to simulate the Jovian atmosphere, in which a mixture of the major gases is supplied with energy from a corona discharge, have succeeded in producing such simple organic molecules as HCN, CH_3CN, C_2H_2, C_2H_4, and C_2H_6 (Sagan and Miller, 1960). Their interaction products may be brightly colored. Indeed, in experiments relevant to the origin of life on Earth, mixtures of materials which are in effect simulated Jovian environments have been subjected to a wide array of energy sources, and organic molecules have been consistently produced in high yield, provided only that the over-all conditions were reducing (see, e.g., Fox, 1965). Electric discharges and solar ultraviolet light -- both to be expected in the vicinity of the Jovian clouds -- will lead to the production of organic molecules in abundances far greater than those expected from thermodynamic equilibrium considerations.

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H

CH$_4$

asphalt threshold

[H$_2$O] = 10^{-5} to 10^{-4}

CO

[CH$_4$] = 3 × 10^{-7}

CO$_2$

[NH$_3$] = 4 × 10^{-7}

Venus composition region

[H$_2$O] = 10^{-5}

[NH$_3$] = 4 × 10^{-7}
[CH$_4$] = 3 × 10^{-7}

[CO] = 10^{-6} to 4 × 10^{-17}
[O$_2$] = 10^{-25} to 8 × 10^{-5}

H$_2$O

O
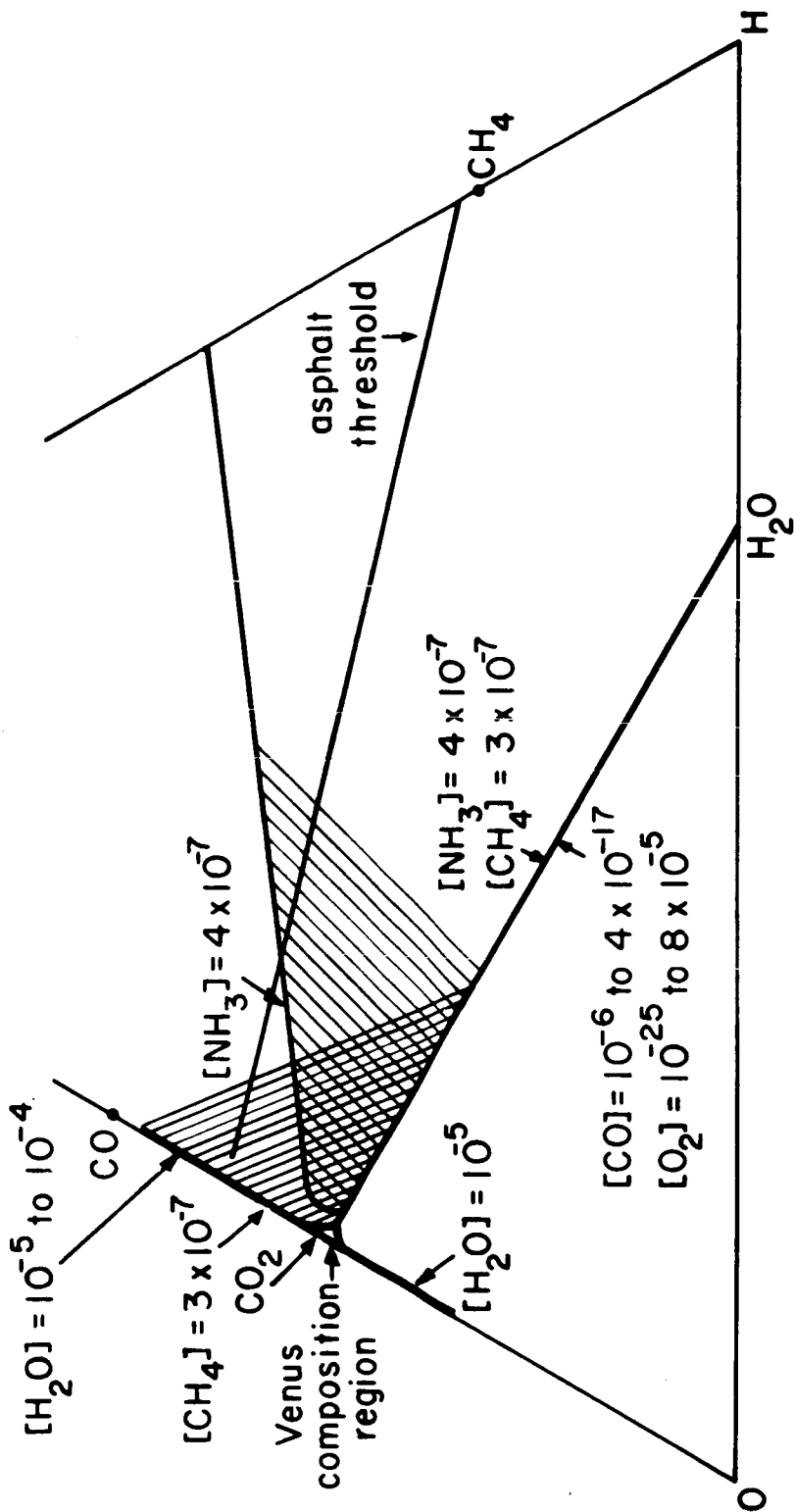
Fig. 1.—C-H-O ternary diagram for the Cytherean atmosphere. The shaded regions are excluded at thermodynamic equilibrium by the observational upper limits on [CH$_4$] and [NH$_3$]. For clarity the shading has not been extended through the entire excluded region. The adopted values of [H$_2$O] and the observed upper limits on [CO] and [O$_2$] are denoted by lines.

-19-
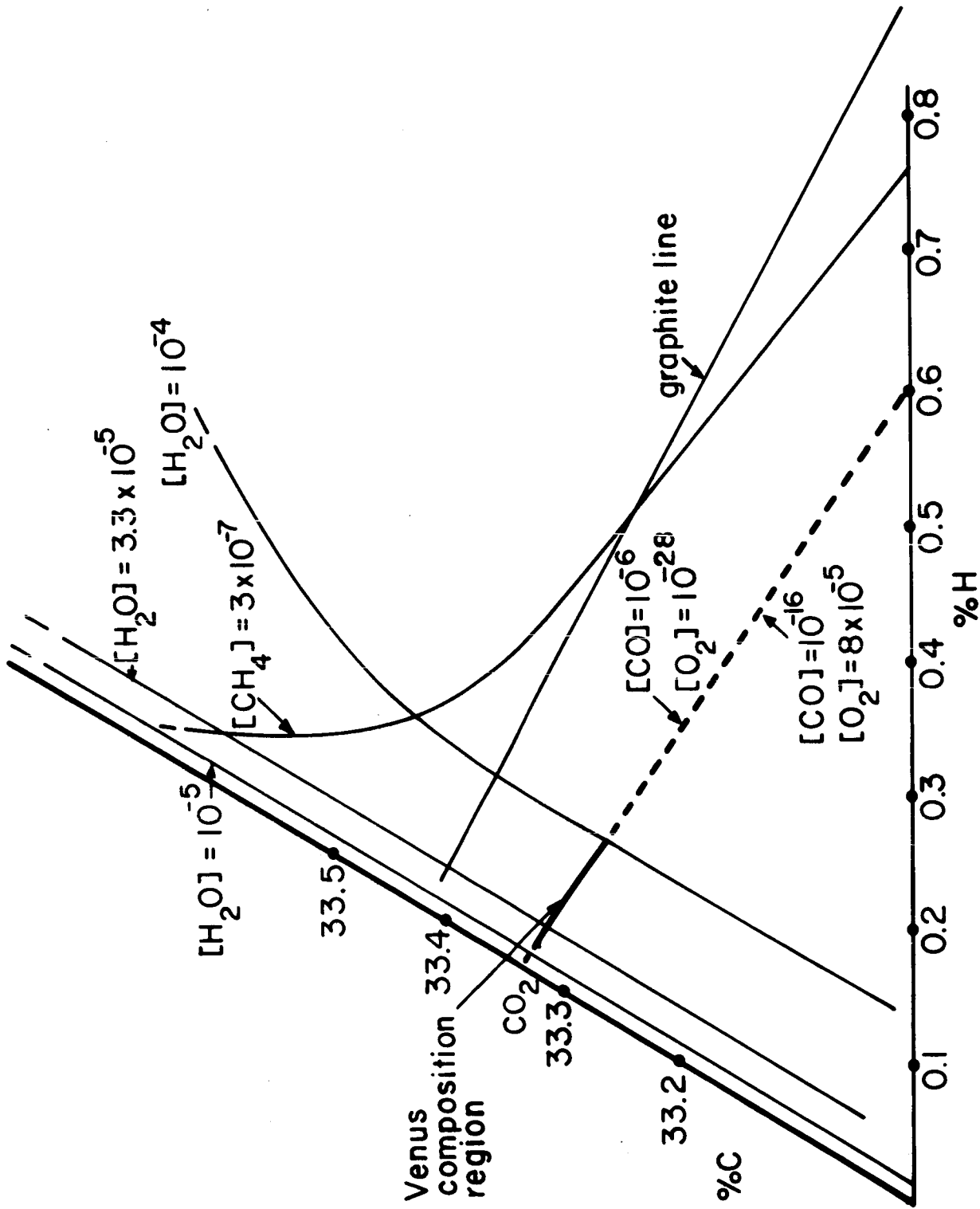
Fig. 2.—C-H-O ternary diagram of Figure 1, here enlarged one hundred-fold.
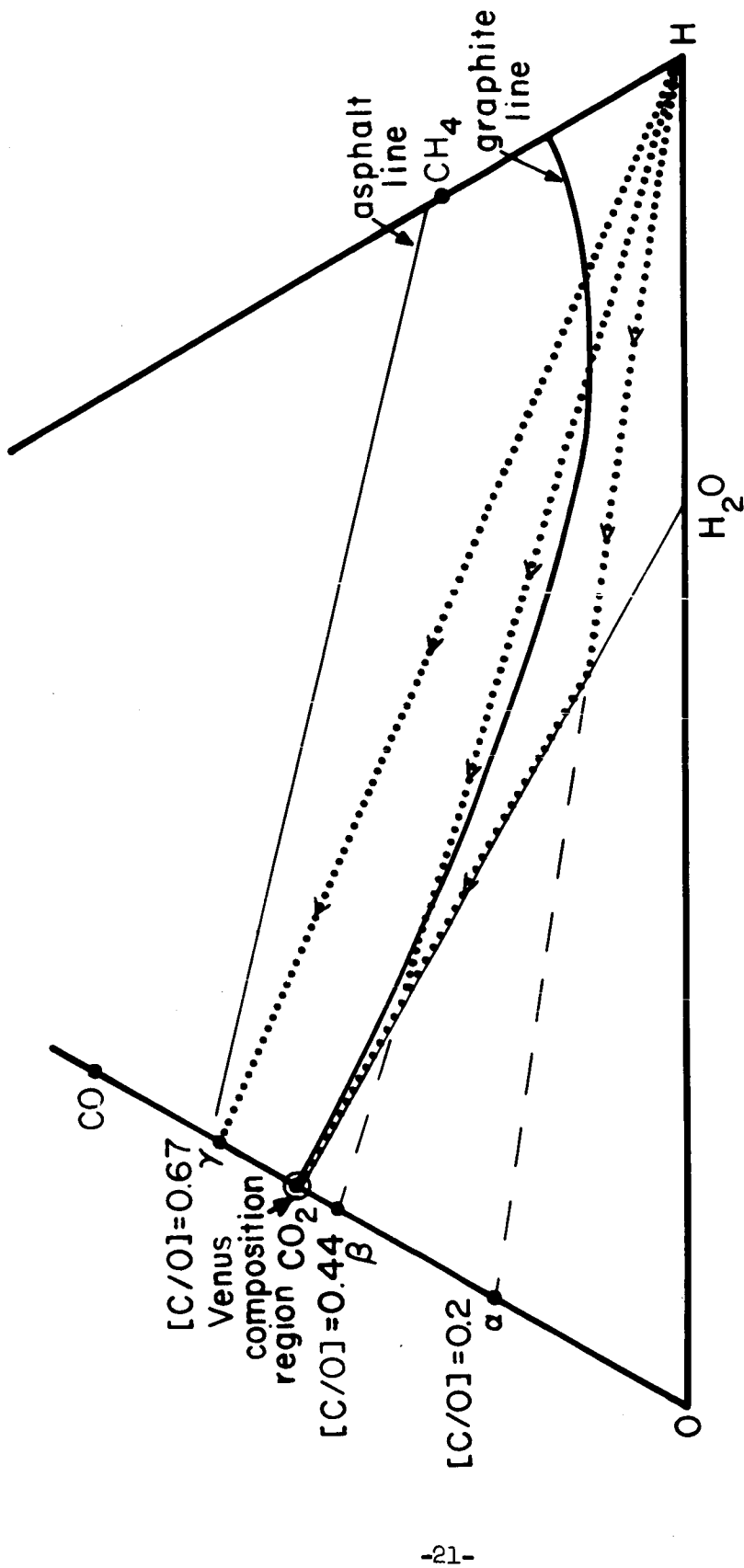
Fig. 3.—Evolution of the atmosphere of Venus. Initial conditions assumed include a large excess of H_2, and three [C/O] abundance ratios. Loss of hydrogen alone causes evolution along the tracks H-α, H-β, and H-γ. Additional loss of oxygen would tend to deflect the lower two evolutionary tracks along the oxidation threshold, the line CO_2 - H_2O. Tracks with initial [C/O] > 0.5 must lose carbon to arrive at the present composition; but the precipitation of graphite or polycyclic aromatics would not lead to the contemporary value of [C/O].

-21-
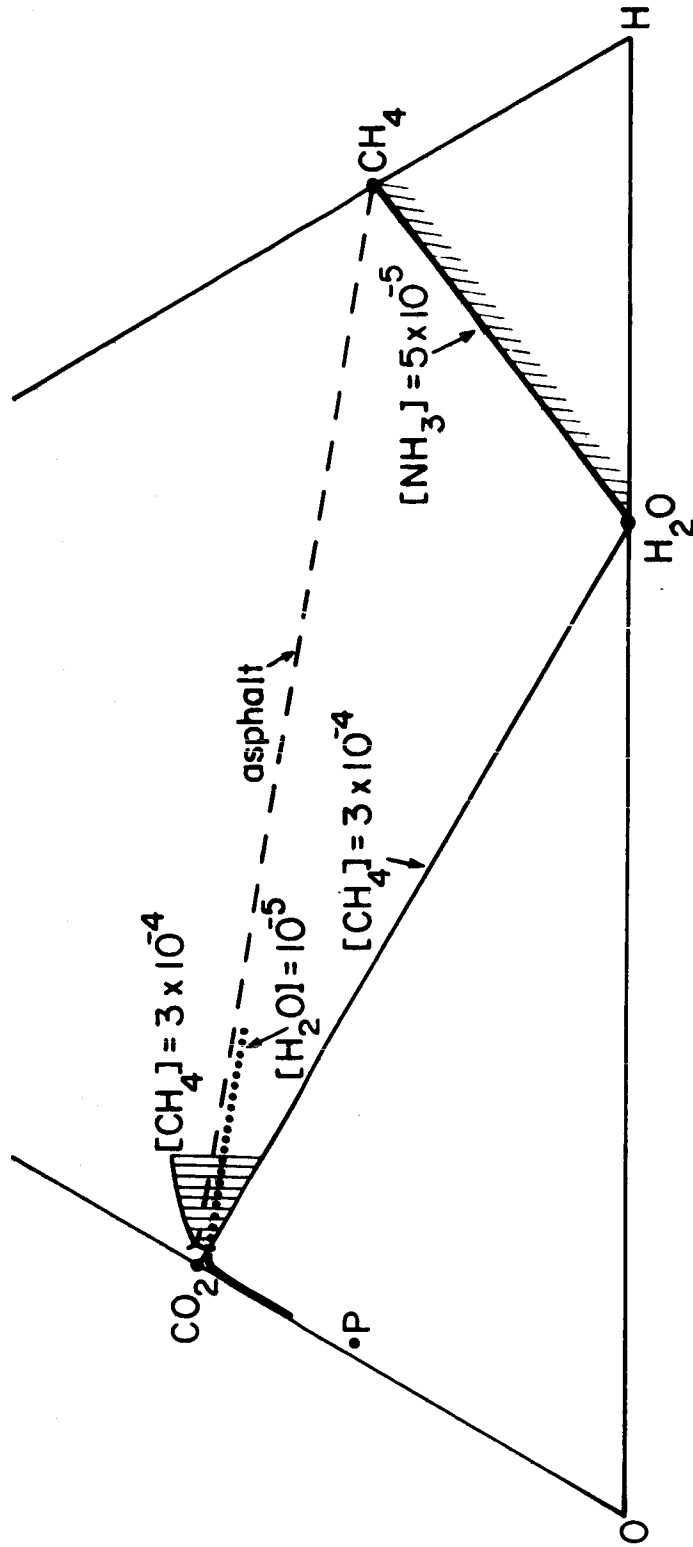
Fig. 4.--C-H-O ternary diagram for the Martian atmosphere. Areas not excluded by observation are localized about the solid portion of the water line, near the CO_2 point. One additional abundance determination can specify the thermodynamic equilibrium composition.

TABLE 1

ADOPTED CHEMICAL COMPOSITION AND PHYSICAL PARAMETERS OF THE
TERRESTRIAL ATMOSPHERE (VOLUME MIXING RATIOS ARE DISPLAYED)

O_2	0.2095
O_3	10^{-8} to 10^{-7}
H_2	5×10^{-7}
H_2O	1×10^{-3} to 2.8×10^{-2}
N_2	0.7808
NO_2	5×10^{-10} to 2×10^{-8}
N_2O	5×10^{-7}
NH_3	1.7×10^{-8}
SO_2	1×10^{-6}
CO_2	3.30×10^{-4}
CH_4	1.5×10^{-6}
A	1×10^{-2}
He	5.2×10^{-6}
Ne	1.8×10^{-5}
Pressure	1.0 atm
Temperature	$280^\circ K$

(References: Allen 1963; Hutchinson 1954)

TABLE 2

THERMODYNAMIC EQUILIBRIUM COMPOSITION OF THE TERRESTRIAL

ATMOSPHERE, COMPUTED FROM THE TOTAL ELEMENTAL COMPOSITION OF TABLE 1[*]

N_2	0.78	H_2S	0
O_2	0.21	CO	0
A	0.01	H_2	0
H_2O	1.0×10^{-3}	CS_2	0
CO_2	3.33×10^{-4}	CH_4	0
SO_3	1×10^{-6}	CH_3SH	0
HNO_3	5.1×10^{-10}	COS	0
NO_2	6.2×10^{-11}	Benzene	0
NO	2.9×10^{-17}	Formic acid	0
H_2SO_4	4.1×10^{-18}	HCN	0
SO_2	8.6×10^{-20}	NH_3	0
N_2O	3.8×10^{-20}	Formaldehyde	0
Ozone	6.6×10^{-32}	Methenol	0

[*] A mixing ratio of zero is an abbreviation for a value $< 10^{-35}$.

TABLE 3

ADOPTED CHEMICAL COMPOSITION OF THE CYTHEREAN ATMOSPHERE
(VOLUME MIXING RATIOS ARE DISPLAYED)

O_2	$< 8 \times 10^{-5}$
H_2O	1×10^{-6} to 1×10^{-4}
N_2	~ 0.95
NO_2	$< 1 \times 10^{-6}$
N_2O	$< 4 \times 10^{-7}$
NH_3	$< 4 \times 10^{-7}$
CO_2	$\sim 5 \times 10^{-2}$
CO	$\leq 1 \times 10^{-6}$
CH_4	$< 3 \times 10^{-7}$
C_2H_4	$< 2 \times 10^{-7}$
C_2H_6	$< 1 \times 10^{-7}$
$HCHO$	$< 3 \times 10^{-8}$
Pressure	~ 50 atm
Temperature	$700^\circ K$

(References: Kuiper 1952; Spinrad 1962a, 1962b; Sinrad and Richardson, 1965; Bottema, Plummer, and Stron 1964; Dollfus 1964; Sagan and Pollack 1965)

TABLE 4

THERMODYNAMIC EQUILIBRIUM COMPOSITION OF THE CYTHEREAN ATMOSPHERE, COMPUTED FROM TOTAL ELEMENTAL COMPOSITION OF TABLE 2[*]

Compound	Oxidizing Limit	Reducing Limit
O_2	8×10^{-5}	1×10^{-25}
CO	4×10^{-17}	1×10^{-6}
CO_2	5×10^{-2}	5×10^{-2}
H_2O	1×10^{-5}	1×10^{-5}
N_2	0.95	0.95
H_2	2×10^{-19}	5×10^{-9}
NH_3	1×10^{-29}	4×10^{-14}
HCN	0	1×10^{-18}
NO	3×10^{-9}	1×10^{-19}
NO_2	2×10^{-10}	3×10^{-31}
N_2O	2×10^{-12}	6×10^{-23}
HNO_3	2×10^{-15}	0
O_3	5×10^{-21}	0
Methane	0	7×10^{-21}
Ethane	0	0
Formic Acid	7×10^{-26}	2×10^{-15}
Formaldehyde	0	4×10^{-19}
Methanol	0	6×10^{-26}
Acetic Acid	0	5×10^{-23}
Methyl Amine	0	5×10^{-33}
Acetylene	0	8×10^{-34}
Benzene	0	0
Asphalt	0	0
SO_2	2×10^{-7}	1×10^{-6}
SO_3	8×10^{-7}	1×10^{-16}

TABLE 4 (Cont.)

Compound	Oxidizing Limit	Reducing Limit
COS	0	3×10^{-8}
H_2S	0	1×10^{-9}
CH_3SH	0	1×10^{-26}
H_2SO_4	2×10^{-17}	3×10^{-27}

*Two extreme systems, $[CO] = 10^{-6}$, $[O_2] = 10^{-25}$ and $[CO] = 4 \times 10^{-17}$, $[O_2] = 8 \times 10^{-5}$ are shown. The hypothesized sulfur mixing ratio of 10^{-6} has a negligible effect except on compounds containing sulfur.

TABLE 5

ADOPTED CHEMICAL COMPOSITION OF THE MARTIAN ATMOSPHERE
(VOLUME MIXING RATIOS ARE DISPLAYED)

O_3	$< 1.3 \times 10^{-6}$
H_2O	$\sim 10^{-5}$
N_2	~ 0.9
NO_2	$< 3 \times 10^{-7}$
N_2O	$< 5 \times 10^{-3}$
NH_3	$< 5 \times 10^{-5}$
SO_2	$< 1 \times 10^{-7}$
H_2S	$< 2 \times 10^{-4}$
COS	$< 5 \times 10^{-5}$
CO_2	$\sim 1 \times 10^{-1}$
CH_4	$< 3 \times 10^{-4}$
C_2H_4	$< 5 \times 10^{-5}$
C_2H_6	$< 3 \times 10^{-5}$
$HCHO$	$< 1 \times 10^{-5}$
Pressure	~ 0.05 atm
Temperature	$240°K$

(References: Kaplan, Munch, and Spinrad 1964; Owen and Kuiper 1964; Hanst and Swan 1965; Chamberlain and Hunten 1965; Marshall 1965)

TABLE 6

THERMODYNAMIC EQUILIBRIUM COMPOSITION OF THE MARTIAN ATMOSPHERE, COMPUTED FROM THE ELEMENTAL COMPOSITION OF TABLE 5[*]

	Oxidizing Case	Slightly Reducing Case
N_2	0.82	0.90
CO_2	0.09	0.10
CO	0	3×10^{-13}
O_2	0.09	0
H_2O	1×10^{-5}	1×10^{-5}
CH_4	0	1×10^{-6}
C_2H_6	0	5×10^{-18}
C_6H_6	0	0
H_2	0	1×10^{-10}
$HCHO$	0	3×10^{-28}
$HCOOH$	0	3×10^{-21}
CH_3COOH	0	9×10^{-19}
CH_3OH	0	4×10^{-27}
NH_3	0	7×10^{-12}
HNO_3	1×10^{-12}	0
NO_2	6×10^{-13}	0
NO	3×10^{-20}	0
N_2O_4	4×10^{-23}	0
N_2O	2×10^{-23}	0
NO_3	4×10^{-27}	0
N_2O_5	2×10^{-29}	0

TABLE 6 (Cont.)

	Oxidizing Case	Slightly Reducing Case
N_2O_3	6×10^{-32}	0
HCN	0	2×10^{-29}
SO_3	1×10^{-6}	0
SO_2	6×10^{-22}	1×10^{-27}
COS	0	6×10^{-10}
H_2S	0	1×10^{-6}
$(CH_3)_2SO$	0	3×10^{-12}
CS_2	0	8×10^{-19}
CH_3SH	0	4×10^{-19}
H_2SO_4	8×10^{-22}	

[*]Two extreme systems, one with $[O_2] = 0$, the other with $[O_2] = 0.09$ -- corresponding to the point P in Figure 4 -- are displayed. The more highly oxidizing conditions favor the presence of oxides of nitrogen, but even then their predicted equilibrium abundances are miniscule.

TABLE 7

ADOPTED CHEMICAL COMPOSITION OF THE JOVIAN ATMOSPHERE
(VOLUME MIXING RATIOS ARE DISPLAYED)

	High	Deep
H_2	0.60	0.60
H_2O	$\sim 1 \times 10^{-6}$	$\sim 1 \times 10^{-4}$
NO_2	$< 3 \times 10^{-6}$	$< 3 \times 10^{-6}$
NH_3	2×10^{-4}	2×10^{-4}
CH_4	5×10^{-3}	5×10^{-3}
C_2H_6	$< 1.2 \times 10^{-4}$	$< 1.2 \times 10^{-4}$
CH_3NH_2	$< 3 \times 10^{-4}$	$< 3 \times 10^{-4}$
C_2H_2	$< 6 \times 10^{-5}$	$< 6 \times 10^{-5}$
He	0.36	0.36
Ne	0.03	0.03
Pressure	1 atm	1000 atm
Temperature	$200°K$	$350°K$

(References: Kuiper 1952; Spinrad and Trafton 1963; Owen 1965)

TABLE 8

THERMODYNAMIC EQUILIBRIUM COMPOSITION OF THE MAJOR CONSTITUENTS OF THE JOVIAN
ATMOSPHERE, COMPUTED FROM THE ELEMENTAL COMPOSITION OF TABLE 7[*]

	High	Deep
H_2	0.60	0.60
He	0.36	0.36
Ne	0.03	0.03
CH_4	5×10^{-3}	5×10^{-3}
NH_3	2×10^{-4}	2×10^{-4}
H_2O	1×10^{-4}	1×10^{-4}
H_2S	1×10^{-6}	1×10^{-6}
C_2H_6	3×10^{-23}	1×10^{-15}
N_2	6×10^{-22}	1×10^{-16}
CH_3SH	2×10^{-28}	7×10^{-20}
CH_3NH_2	2×10^{-31}	8×10^{-21}
CH_3OH	0	3×10^{-24}
$(CH_3)_2SO$	0	2×10^{-29}
CO_2	0	1×10^{-31}
CO	0	9×10^{-32}
HCHO	0	2×10^{-33}
HCOOH	0	0
HCN	0	0
COS	0	0

[*]For the sulfur compounds, addition of $[S] = 10^{-6}$ was assumed.