References and Notes

1. J. D. Jennings and E. Norbeck, *Amer. Antiquity* **21**, 1 (1955).
2. C. W. Meighan, *ibid.* **24**, 289 (1959).
3. ———, *Nevada State Museum Anthropol. Papers*, 78 (1963).
4. W. J. Wallace, *Southwestern J. Anthropol.* **2**, 214 (1955).
5. C. N. Warren and D. L. True, *Univ. Calif. Arch. Surv. Ann. Rpt., 1960–1961*, 246 (1961).
6. M. J. Rogers, *San Diego Museum Paper*, 1 (1939); C. W. Meighan, in *The Quaternary of the United States*, H. E. Wright, Jr., and D. G. Frey, Eds. (Princeton Univ. Press, Princeton, N.J., 1965), p. 709. The Seventh Congress of the International Association for Quaternary Research volume in 1965 contains the most definitive and up-to-date review of Pacific Coast archaeology. This paper, by Meighan, is much too long to detail here. It is, however, an extremely fine summary and marks a point of origin for this study. Our archaeological knowledge of California has reached the stage where we are now able to direct our attention along those lines of research which are likely to lead us to conclusions that will have far greater validity than ever before.
7. J. R. Moriarty, *Can. J. Anthropol.* **4**, 20 (1966).
8. C. L. Hubbs, G. S. Bien, H. E. Suess, *Amer. J. Sci. Radiocarbon Suppl.* **4**, 204 (1962); *ibid.* **5**, 254 (1963).
9. ———, *ibid.* **7**, 109 (1964).
10. J. R. Moriarty, G. Shumway, C. N. Warren, *Univ. Calif. Arch. Surv. Ann. Rpt., 1958–1959*, 185 (1959).
11. D. L. True, *Amer. Antiquity* **23**, 255 (1958).
12. J. R. Curray in *The Quaternary of the United States*, H. E. Wright, Jr., and D. G. Frey, Eds. (Princeton Univ. Press, Princeton, N.J., 1965), p. 723.
13. J. R. Moriarty and N. F. Marshall, *Pacific Discovery* **17**, 1 (1964).

21 December 1966

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Venus: Atmospheric Evolution

Abstract. *Because of the high temperatures prevailing in the lower atmosphere of Venus, its chemistry is dominated by the tendency toward thermodynamic equilibrium. From the atomic composition deduced spectroscopically, the thermodynamic equilibrium composition of the atmosphere of Venus is computed, and the following conclusions drawn. (i) There can be no free carbon, hydrocarbons, formaldehyde, or any other organic molecule present in more than trace amounts. (ii) The original atomic composition of the atmosphere must have included much larger quantities of hydrogen and a carbon/oxygen ratio* ≤ 0.5. *(This ratio is now almost precisely 0.5.) (iii) The present atomic proportions of the atmosphere of Venus are so unique that an evolutionary mechanism involving two independent processes seems necessary, as follows. Water, originally present in large quantities, has been photodissociated in the upper atmosphere, and the resulting atomic hydrogen has been lost in space. The resulting excess oxygen has been very effectively bound to the surface materials. (iv) There must be some weathering process, for example, violent wind erosion, to disturb and expose a sufficient quantity of reduced surface material to react with the oxygen produced by photodissociation.*

The bulk of contemporary evidence indicates that the surface of Venus, and the greater part of its atmosphere, are at high temperatures (*1–4*). Chemical reactions must occur with such rapidity that thermodynamic equilibrium should be approximated closely. Beneath the clouds of Venus, endothermic reactions, energized, for example, by solar radiation or electrical discharge, should be rare; in any case the products of such reactions will be rapidly degraded. We have described elsewhere (*5*) a computer program appropriate to these circumstances. It assumes an ideal gas of known temperature, pressure, and atomic composition, and computes, by minimizing the free energy of the system, the molecular distribution which obtains at thermodynamic equilibrium. There are only a small number of well-known compounds which comprise the bulk of such equilibrium mixtures. Any other compound of interest may be included in such computations, but no significant error results from its omission. Our calculation method does not depend explicitly on the equilibrium constants of specific reactions. Only the free energy of each compound at the temperature considered need be known, provided there exists at least one reversible reaction pathway between each of the compounds and the major constituents. If no such pathway exists (as may happen in special cases), the compound is prohibited from entering the calculation by omitting it from the input data.

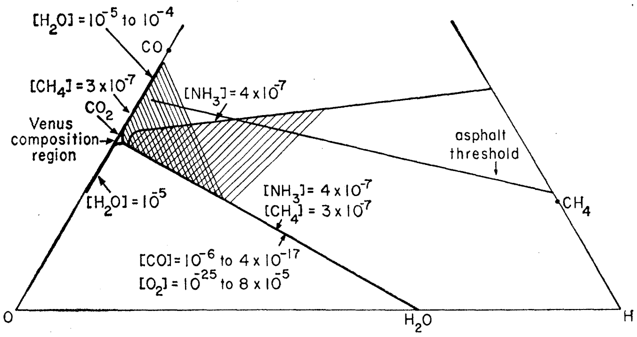
Our initial intent in applying this program to the atmosphere of Venus was to test whether the atmosphere is close to thermodynamic equilibrium, to determine whether certain materials hypothesized for Venus are thermodynamically plausible, and to predict the presence in significant quantities of molecules not yet detected spectroscopically. In the course of the calculations, however, some unexpected results emerged which are relevant to the evolution of the atmosphere of Venus.

All possible atomic proportions of the elements C, H, and O can be exhibited in an equilateral ternary diagram (Fig. 1). Any nitrogen abundance can be represented as a projection on this diagram, since under Cytherean conditions it remains almost entirely N_2 and does not significantly influence the proportions of C, H, and O. The surface pressure used in these calculations is 50 atm; the temperature, 700°K (*2, 3, 6*). The atomic composition is derived from molecular spectroscopy.

Volume mixing ratios adopted include $[CO_2]$, a few percent (*7*); $[H_2O]$, between 10^{-4} and 10^{-6}, the larger value probably prevailing in the lower atmosphere (*8*); and $[N_2] \cong 0.95$. A measurement of $[CO] \sim 10^{-6}$ (*9*) has been reported, and upper limits on O_2, NO_2, N_2O, NH_3, CH_4, C_2H_4, C_2H_6, and HCHO have been established (*10*). The calculations show that equilibrium is rather insensitive to changes in these abundances, and variations by an order of magnitude would have little influence on the conclusions.

Given the temperature and pressure, an estimate of the abundance of a compound defines a closed curve or one intersecting the axes on the ternary diagram; an upper limit on abundance necessarily excludes an area of the diagram. On Venus (Fig. 1) the amount of water limits the overall composition to a narrow band along the C—O border. Upper limits on $[NH_3]$ and $[CH_4]$ exclude the greater part of the reducing regions, and the upper limit on $[O_2]$ eliminates almost all of the oxidizing regions. If the value for $[CO] \sim 10^{-6}$ is accepted as characteristic for the atmosphere as a whole, the equilibrium atmospheric composition lies at a point on the ternary diagram which can be distinguished from the CO_2 point only when the diagram is magnified ten thousandfold.

It is possible that much of the CO reported spectroscopically arises from CO_2 photodissociation in the upper atmosphere of Venus (*9, 11*). If any major fraction of the reported CO is a constituent of the lower equilibrium atmosphere, there can be no free oxygen on Venus ($[O_2] < 10^{-25}$). If all the reported CO is produced by photodissociation, or if this difficult observation has given a spuriously high CO abundance, there may be a trace of free oxygen on Venus ($[O_2] \leq 8 \times 10^{-5}$).



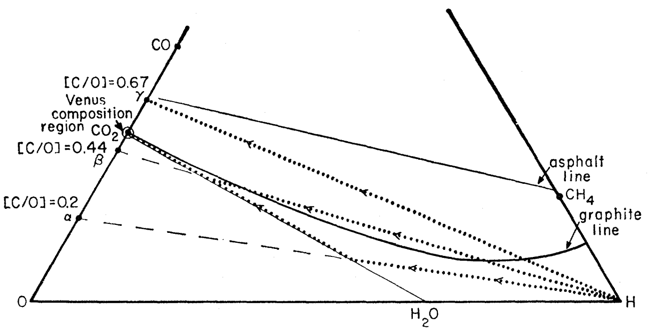


Fig. 1 (left). Equilateral ternary C—H—O diagram for the atmosphere of Venus. The carbon point is at the apex not shown. The shaded regions are excluded at thermodynamic equilibrium by the observational upper limits on [CH_4] and [NH_3]. For clarity the shading has not been extended through the entire excluded region. The adopted values of [H_2O] and the observed upper limits on [CO] and [O_2] are denoted by lines. On this scale, the Venus composition point cannot be distinguished from the CO_2 point. Fig. 2 (right). Evolution of the atmosphere of Venus. Initial conditions assume three [C/O] abundance ratios. Whatever the original proportion of hydrogen, loss of hydrogen 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 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].

In either case, there can be no free carbon or organic molecules at equilibrium in contact with the atmosphere; otherwise, an easily detectable abundance, [CO] $\sim 10^{-3}$, would be produced. This result provides evidence against petroleum oceans (*12*), hydrocarbon (*13*) or formaldehyde polymer (*14*) clouds, or large quantities of unspecified atmospheric organic molecules (*15*) on Venus. Similar conclusions have been reached previously for a much smaller array of compounds (*16*). The absence of hydrocarbons from the surface is consistent both with passive observations of the microwave phase effect, and with active radar observations of Venus (*2*). Small amounts of formaldehyde and other simple organic compounds may be produced by nonequilibrium processes, such as electrical discharges in the clouds (*17*). The most abundant organic compound expected at equilibrium is formic acid with a volume mixing ratio $\sim 10^{-15}$. Other molecules expected in very small quantities at equilibrium are tabulated elsewhere (*18*).

None of the abundances or abundance upper limits are mutually exclusive in an equilibrium atmosphere. This is consistent with our expectations that the atmosphere of Venus is close to that expected under thermodynamic equilibrium. It should be emphasized that the finding that the predicted thermodynamic equilibrium is consistent with the available observations is not trivial. Whatever the given molecular species used to define a particular atomic composition of the atmosphere, the computed equilibrium molecular proportions would be the same. Neither can one predict a priori which of the major compounds would be present, given a particular elemental composition. Consider the following example. The proportions 1C : 2H : 2O give the empirical formula of formic acid, but this compound would be only a minor component of the equilibrium mixture. The same proportions apply to an equimolar mixture of CO and H_2O. However, a gas composed of these two compounds is not the correct answer, either. The equilibrium result is a mixture of H_2O, CH_4, and CO_2—unless the computation had been for a higher temperature, in which case there would also have been appreciable amounts of CO and H_2.

A disagreement between predicted and observed results can occur in two ways. First, a definite observed species may be unobtainable at equilibrium. If 1 percent of HCN had also been observed on Venus, we would have found no C : H : O proportions for which this large amount would be predicted. Such an observation would have been inconsistent with the hypothesis of thermodynamic equilibrium on Venus.

Second, all systems consistent with the observed concentrations might be computed to contain observable quantities of compounds which were not in fact observed. Such inconsistencies were sought, but not found. We therefore conclude that the results are consistent with general thermodynamic equilibrium on Venus; only a very limited fraction of the atmosphere is being produced by special processes, such as electrical discharge, ultraviolet photoreactions, or vulcanism.

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 (see Fig. 2), if the atmosphere was originally derived from a solar nebula. If it was derived from outgassing, the composition would have been somewhere in the central portion of the ternary diagram where H_2 is in excess over O_2, and the following considerations would apply just as well.

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 (*19*). Any differential escape is correspondingly unlikely. The track along which the atmospheric composition of Venus evolved 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 (*20*), while Cameron (*21*) has suggested a value of 0.44, and more recently (*22*), 0.67. Since both oxygen and carbon have probably been depleted during the formation of Venus, there is no guarantee that cosmic abundance ratios were actually the initial Venus abundance ratios. For purposes of illustration we consider initial Venus [C/O] ratios of 0.20, 0.44, and 0.67. For a ratio of 0.20 or 0.44, the evolution would proceed along the lines ending at α or β (Fig. 2), 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 an amount 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 to a considerable depth. Accordingly, there must have been some active weathering agent, such as extensive wind erosion, to disturb and expose a sufficient volume of surface material to allow for efficient reactions with oxygen. An independent argument for the presence of extensive oxygen sinks on the surface of Venus has been offered by Sagan *(19)*, in an attempt to explain the differential abundance of water on Venus and on Earth by differential rates of water photodissociation.

Typical evolutionary tracks would then have resembled those illustrated by the arrows in Fig. 2. Owing 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 near 0.44, the initial evolutionary track due to the loss of hydrogen would twice intersect the graphite threshold (see Fig. 2). 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. If it did, it would react and disappear at the high temperature of Venus as the system lost more hydrogen. Such a track would follow the line marked H-β in Fig. 2 until it intersected the oxidation threshold, whereupon it would turn and proceed toward the CO_2 point.

If the initial [C/O] ratio had been perceptibly above 0.5, as, for example, 0.67, the evolutionary track would follow the line marked H-γ in Fig. 2. 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 would have to exist for the removal of carbon from the atmosphere or the addition of oxygen to it. 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 by the precipitation of graphite, the atmosphere would then evolve along the graphite line. As the C—O line was approached, any such exposed, precipitated graphite would undergo equilibrium reactions with the atmosphere and disappear. The composition would end significantly above the actual composition point, where the CO concentration would be 10^{-3}. This is in conflict with the spectroscopic observations. While the outgassing of water, photodissociation, and hydrogen escape could conceivably increase the O_2 abundance over a surface which was *not* highly reducing, the addition of precisely enough O_2 to bring the atmosphere to its present unique composition very close to the CO_2 point is highly implausible. It is interesting to note that if the temperature of Venus were much lower, for example, 500°K, graphite could exist in equilibrium with the observed atmosphere, if a mechanism were available for its formation. However, no complex organic compounds would be stable even under these conditions.

Thus, it is probable that Venus began its evolutionary history with $[C/O] \leq 0.5$ 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.

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References and Notes

1. C. H. Mayer, T. P. McCullough, R. M. Sloanaker, *Astrophys. J.* **124**, 399 (1956).
2. J. B. Pollack and C. Sagan, *Icarus* **4**, 62 (1965).
3. ———, *Astrophys. J.* **141**, 1161 (1965).
4. B. G. Clark and A. D. Kuz'min, *ibid.* **142**, 23 (1965).
5. M. O. Dayhoff, E. R. Lippincott, R. V. Eck, *Science* **146**, 1461 (1964).
6. C. Sagan, *Icarus* **1**, 151 (1962).
7. H. Spinrad, *Publ. Astron. Soc. Pacific* **74**, 156 (1962); J. W. Chamberlain, *Astrophys. J.* **136**, 582 (1965).
8. M. Bottema, W. Plummer, J. Strong, *Astrophys. J.* **139**, 1021 (1964); H. Spinrad, *Icarus* **1**, 266 (1962); A. Dollfus, *Compt. Rend.* **256**, 3250 (1963); M. J. S. Belton and D. M. Hunten, *Astrophys. J.* **146**, 307 (1966); H. Spinrad and S. J. Shawl, *ibid.* **146**, 328 (1966); C. Sagan and J. B. Pollack, in preparation.
9. V. I. Moroz, *Soviet Astron. A.J. English Trans.* **8**, 566 (1965).
10. G. P. Kuiper, "Planetary atmospheres and their origins," in *The Atmospheres of the Earth and Planets*, G. P. Kuiper, Ed. (Univ. of Chicago Press, Chicago, 1952), p. 306; H. Spinrad and E. H. Richardson, *Astrophys. J.* **141**, 282 (1965).
11. M. Shimizu, *Planetary Space Sci.* **11**, 269 (1963).
12. F. Hoyle, *Frontiers of Astronomy* (Harper, New York, 1955).
13. L. D. Kaplan, *J. Quant. Spectr. Radiative Transfer* **3**, 537 (1963).
14. R. Wildt, *Astrophys. J.* **86**, 321 (1937); see also *ibid.* **92**, 247 (1940).
15. A. D. Kuz'min, *Astron. Zh.* **42**, No. 6 (1965); ———, in *Proceedings of the Caltech—JPL Lunar and Planetary Conference*, H. Brown *et al.*, Eds. (California Inst. of Technology, Pasadena, 1966), p. 184.
16. R. R. Mueller, *Icarus* **3**, 285 (1964).
17. C. Sagan and S. L. Miller, *Astrophys. J.* **65**, 499 (1960).
18. E. R. Lippincott, R. V. Eck, M. O. Dayhoff, C. Sagan, *Astrophys. J.*, in press.
19. C. Sagan, "Origins of the atmospheres of the earth and planets," in *International Dictionary of Geophysics*, S. K. Runcorn, Ed. (Pergamon Press, London, in press).
20. H. E. Suess and H. C. Urey, *Rev. Mod. Phys.* **28**, 53 (1956).
21. A. G. W. Cameron, *Astrophys. J.* **129**, 676 (1959).
22. ———, unpublished.
23. Supported in part by NASA contract No. 21-003-002 with the National Biomedical Research Foundation, in part by NASA grant No. 21-002-059 to the University of Maryland, and in part by NASA grant No. NGR 09-015-023 with the Smithsonian Astrophysical Observatory. The computations were made at the University of Maryland Computer Science Center.

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Weight Loss in Men in Space

Abstract. *Men returning from orbital flights have lost from 2 to 6 percent of their body weights. Similar losses occur during simulated weightlessness; blood normally pooled in dependent parts returns to the circulation, increasing central blood volume and causing excretion of water which is not replaced during flight.*

Astronauts lose weight during orbital flights. All medical data reported from the United States and Soviet manned flights tell of loss ranging from 2 to 6 percent of initial body weight (Table 1). Such loss is independent of the