Reports

Atmosphere of Mars

Abstract. *The Martian ionospheric observations made by Mariner IV are interpreted in terms of an atmospheric model. The ion peak is identified as an F2 peak, that is, as a maximum whose profile is controlled by ambipolar diffusion. The principal features of the resulting atmospheric model are that the atmosphere consists mainly of carbon dioxide, the temperature is very low, and there is no thermosphere. Surface temperature is 210°K. The tropopause occurs at an altitude of 14 kilometers and has a temperature of 140°K. Above the tropopause, the temperature decreases with altitude at the rate of 0.64°C* km^{-1}, *following the solid carbon dioxide vapor-pressure curve up to 100 km, where the temperature is 85°K; at higher altitudes the temperature is isothermal.*

Mariner IV provided substantial new information regarding the atmosphere of Mars (*1*). Certain aspects of the measurements may be interpreted, leading to a fairly complete model of the Martian atmosphere; although these interpretations will be controversial, they have substantial support.

I discuss particularly the peak ionization observed at an altitude of 120 km by Mariner IV, the scale height of about 25 km for the decrease of ionization well beyond the peak, and the low surface pressure of about 5 mb. In addition to the Mariner data, there are spectral data for the weak carbon dioxide absorption lines near 8700 Å, indicating that the path through the atmosphere is 55 m when the latter is reduced to standard pressure and temperature (*2*); this amount of carbon dioxide would contribute about 4 mb to the surface pressure. Additional information comes from the strong bands near 2 μ (*3*); taken along with the weak-line data, the pressure broadening in the strong bands indicates a total pressure at the surface (*2*) of about 25 mb. However, the spectral data for weak and strong bands are interrelated in such a way that the best value for the total carbon dioxide has to be greater if the surface pressure is less (*4*), that is, if other gases are not sufficiently abundant to bring the surface pressure up to 25 mb.

If the atmosphere were essentially all carbon dioxide, the spectral data would fit best with an amount of carbon dioxide about twice that which I have indicated. Since the Mariner IV radio signals were probably occulted by a somewhat-elevated portion of the Martian surface, a pressure of 8 mb may be more typical of conditions at the surface than the 5 mb indicated by Mariner; this would be in better agreement with the spectroscopic observations. In any case, the low density observed by Mariner near the surface indicates that the atmosphere consists almost entirely of carbon dioxide.

The principal identification to be made in the Mariner data relates to the peak ionization that is observed near 120 km. By analogy with Earth's ionosphere, it seems necessary to identify this as an F2 peak, which means that it occurs at a level at which ambipolar diffusion has become sufficiently slow (compared to that at higher altitudes) that the ion distribution must pass through a maximum in order to maintain the gradients that are required to produce the necessary downward flux of ions into the region where most of the recombination occurs. If the electron-loss process at the peak is linear and characterized by a rate constant β, the peak ionization occurs where $\beta = D/H^2$, where D is the ambipolar diffusion coefficient and H is the scale height of the neutral constituent that limits the ambipolar diffusion (*5, 6*). There is not much latitude in assigning the particle concentration at the altitude where this occurs; almost certainly it must fall within a factor of about 2 of 2×10^9 particles per cubic centimeter.

The low particle concentration associated with the identification of the peak ionization as an F2 peak requires that the atmosphere be very cold. Mariner observations indicate a gas density near the surface of about 1.5×10^{-5} g cm^{-3}. Thus, a decrease in concentration by a factor of about 10^8 within 120 km is indicated, or an average scale height of about 6.5 km; even with a gas as heavy as CO_2, the average temperature therefore could be no higher than 130°C.

In addition to the surprisingly low altitude for the ionization peak, there is a correspondingly low-scale height for the decrease in ionization above the peak. One is tempted to suggest that a rather heavy ion is implicated, so that a very low temperature would not be required. It seems impossible, however, to avoid the conclusion that the carbon dioxide is partially photodissociated and that some atomic oxygen is therefore present. Atomic oxygen is so much lighter than carbon dioxide that it will rapidly dominate carbon dioxide in the outer portion of the atmosphere, where diffusive separation in the gravitational field can occur. In fact, diffusion proceeds so rapidly in the rarefied atmospheric regions where a substantial degree of ionization can persist that atomic oxygen can be reasonably expected to be the principal atmospheric constituent near the ionization peak. Further, atomic oxygen ions will surely have lifetimes far exceeding those of carbon dioxide, since the latter can undergo dissociative recombination—a relatively rapid process—while atomic oxygen ions must become involved in an ion-atom interchange reaction before recombining—a considerably slower process. Thus it seems necessary to conclude that the ions at and above the observed ionization peak are primarily atomic oxygen. If so, they are very cold indeed; a temperature of about 85°K is required to produce the observed scale height.

If one accepts the temperature and concentration that I have mentioned, there is not much latitude in selecting a temperature distribution that avoids precipitation of carbon dioxide as dry-ice crystals. It is in fact necessary to run along the dry-ice vapor-pressure line through most of the atmosphere. Figure 1 shows the probable temperature distribution, in which the air temperature near the surface is 210°C and the convective layer is 14 km thick, with a temperature of 140°C at its top. The fall in temperature with altitude in

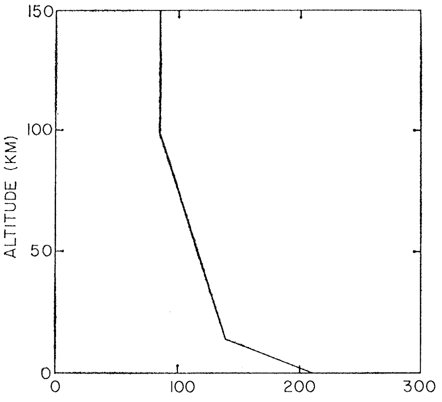

Fig. 1. Probable temperature distribution through the Martian atmosphere; late afternoon, late winter, 55°S latitude.

the convective layer should be adiabatic, which is about 5°C km^{-1} for an atmosphere consisting mainly of carbon dioxide. From the top of the convective layer up to 100 km, the temperature approximately follows the vapor-pressure curve for dry ice; above 100 km, the temperature is constant at 85°K to provide the observed ionization scale height. An air temperature of 210°C near the surface is colder than is usually suggested, but a much higher temperature is irreconcilable with the required low particle concentration at 120 km. The model presented by me applies, of course, to the time and place of the Mariner IV observations: late afternoon in late winter at 55°S latitude; thus significantly warmer temperatures should be expected near the equator or in the summer hemisphere during the afternoon.

A molecular weight of 44 has been assumed in the calculations, and it is impossible to reach the desired concentration at 120 km with an appreciably lighter average molecular weight; a correspondingly lower temperature would be required and this would lead to precipitation of the carbon dioxide. For the pressure distribution through the atmosphere (Fig. 2), surface pressure has been taken to be 8 mb, which is judged to be in best overall agreement with the spectroscopic and the Mariner IV data, assuming the atmosphere to consist almost entirely of CO_2.

The temperature distribution indicated in Fig. 1 is not consistent with the spectroscopic determination of water vapor on Mars. Kaplan, Munch, and Spinrad (*2*) state that the water-vapor content of the Martian atmosphere is $(14 \pm 7) \times 10^{-4}$ g cm^{-2}. If the atmosphere were saturated, with the temperature distribution shown in Fig. 1, the total water-vapor content would be 9×10^{-4} g cm^{-2}. Although this falls within the stated limit of error of the spectroscopic determination, such a moist atmosphere would contain extensive clouds of sufficient opacity to be unmistakable, the total ice content through the cloud being of the order of 5×10^{-3} g cm^{-2}. For the clouds to be thin enough to appear as haze, the total ice content would have to be much lower—of the order of 10^{-5} g cm^{-2} or less. If the atmosphere were dried by exposure to surface temperatures in the vicinity of 175°K near the polar caps, the total water-vapor content of the atmosphere would be about 0.3×10^{-4} g cm^{-2}. With deep convective clouds, the cloud bases would be near 8 km and the maximum ice content of the clouds would be about 0.5×10^{-5} g cm^{-2}; these would not be recognizable as clouds, but rather would have the appearance of patches of haze. With so little water in the atmosphere, the polar caps would consist of no more than a thin layer of hoar frost. So that the evaporation of the polar caps should not too seriously increase the water-vapor content of the atmosphere and produce thick clouds, the total water content of a polar cap (extending in latitude down to 65°) should not exceed the atmospheric water content by any substantial factor. If the total water content of the polar caps were twice that of the atmosphere, the water content per unit area would be about 10^{-3} g cm^{-2}; if the density of hoar frost were 0.01, its thickness would therefore be about 1 mm, sufficient to give a white appearance to the polar cap.

This model has important implications relating to the geologic history of Mars. The atmosphere is very cold, and escape at a significant rate cannot now occur, although the situation may have been different earlier. It seems reasonable to assume that the principal gases released from a planet such as Mars (or Earth) are carbon dioxide and water vapor. The release of carbon dioxide and water vapor from Earth has far exceeded that of all other gases, being of the order of 3×10^5 g cm^{-2} for water and 3×10^4 g cm^{-2} for carbon dioxide (*7*); the water vapor went mainly into the oceans and the carbon dioxide into geologic deposits; the minor constituent, nitrogen, being inert, is the main constituent remaining in Earth's atmosphere. Mars is so cold that the water vapor released into its atmosphere has mainly collected as ice at the surface, leaving the carbon dioxide in the atmosphere; the ice deposits, of course, are covered with dust and cannot be seen. Without liquid water, the carbon dioxide has simply accumulated in the atmosphere to its present concentration without significant loss to geologic deposits. Since any other gases released from the planet were probably rare by comparison, it seems reasonable to assume that impurities do not amount to more than a few percent of the atmosphere at most.

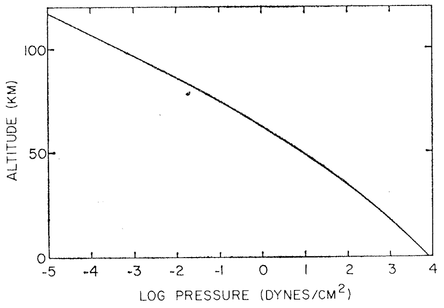

Fig. 2. Pressure distribution through the Martian atmosphere.

Nitrogen released into Earth's atmosphere amounts to only about 3 percent of the carbon dioxide released, and argon amounts to only about 1 percent of the nitrogen. These ratios may apply also on Mars, and curves indicating these proportions have been included in Fig. 3, which gives the composition of the Martian atmosphere as a function of altitude. From the standpoint of internal consistency of the atmospheric model, argon could equal carbon dioxide in concentration, since its molecular weight nearly equals that of carbon dioxide. The model could not accommodate a nitrogen concentration as great as that of carbon dioxide; it would lower the molecular weight too much and would require a corresponding decrease in temperature in order to match the ionospheric requirements. However, the geologic evidence favors relative concentrations about as indicated in Fig. 3.

The atomic oxygen concentrations (Fig. 3) are about the lowest, still having atomic oxygen as the major constituent at 120 km, that can be selected; this is not an absolute requirement of the model, but it appears reasonable when one makes appropriate comparison with Earth's atmosphere. If small-scale eddy mixing proceeds in the Martian atmosphere at about the same rate as on Earth, diffusion equilibrium should apply down to an altitude of about 70 km; it is assumed that the turbopause occurs near this altitude. The base of the exosphere lies at an altitude of 150 km.

The carbon monoxide distribution (Fig. 3) corresponds to a total content equal to the total atomic-oxygen content. No molecular-oxygen curve is indicated in Fig. 3 because its concentration is very uncertain—probably not exceeding that of nitrogen and perhaps much less.

The importance of the low temperature in freezing-out the water vapor in the atmosphere is clearly shown in Fig. 3: in the lowest 8 km, a constant mixing ratio is indicated, and at higher altitudes the saturation concentration is shown; the less-rapid decrease above 14 km is, of course, due to the slower decrease in temperature above that altitude.

A ledge of ionization is evident on the Mariner ionization profile at 90 km, and one is tempted to identify this as an F1 ledge. This identification a priori is less certain than that of the F2 maximum at 120 km, but this model indicates that this is indeed the correct identification. The concentration at 90 km indicated in Fig. 3 is 3 × 10^{11} particles per cubic centimeter, and the scale height is about 4 km, indicating 1.2 × 10^{17} particles per square centimeter above that altitude. The number of particles above the F1 ledge on earth is about 10^{17}, and the average absorption cross sections for the two atmospheres are probably about the same for wavelengths in the 200- to 700-Å spectral region that produces the F region.

The amount of carbon dioxide that has been released on Mars is very small compared with the release on Earth, the ratio being of the order of 10^3. Since gases from Earth's interior have been released mainly by volcanic activity, it is reasonable to conclude that volcanic activity on Mars has been much less than on Earth, about 1:1000.

This model is much at variance with earlier predictions. One important point emerges that might have been foreseen. For more than a year it has been known that carbon dioxide is at least a major constituent of the Martian atmosphere. Under these conditions, a high-temperature thermosphere cannot be expected. Earth has a thermosphere because atomic oxygen and molecular nitrogen are the principal atmospheric constituents in the altitude range where the F region is produced; these constituents are not effective in removing the ionospheric heat by radiation, and the regions become warm enough so that the heat is removed mainly by downward conduction; thus a thermosphere is developed. Mars has a relatively large amount of carbon dioxide at the altitude at which the ionospheric heat is released, and the heat is readily radiated away by the carbon dioxide; thus no thermosphere develops. Carbon dioxide above 70 km on Earth is about the same as the quantity above 90 km on Mars (about 10^{-2} cm, standard temperature and pressure), but 90-km altitude on Mars corresponds to the F1 region, the region of maximum ionospheric heating, which lies near 150 km above Earth. Heat absorbed in the F1 region is much less than absorption above the mesopause on Earth, so it is easy to recognize in a qualitative way that the Mars ionosphere should be cold and that there should be no thermosphere. The abundance of triatomic and heteronuclear-diatomic molecular species in the Martian ionosphere is probably responsible for keeping the electron temperature essentially equal to the neutral-particle temperature, something that does not happen in the F region on Earth, where there are not enough appropriately placed energy levels to aid the removal of energy from the electron gas when its temperature somewhat exceeds the neutral-particle temperature. If the electron temperature on Mars exceeded the neutral-particle temperature, the latter would have to be correspondingly lower than is indicated in Fig. 1, which seems very unlikely.

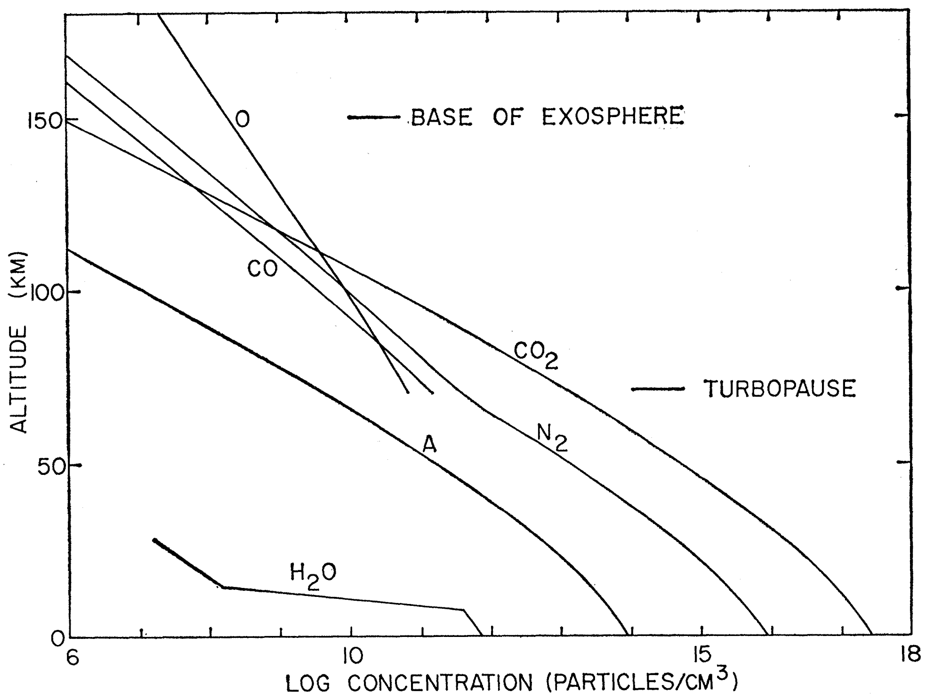

Fig. 3. Composition of the Martian atmosphere as a function of altitude; levels of the turbopause and the base of the exosphere are indicated.

If my model is correct, there must be a physical reason why the temperature curve follows the carbon dioxide condensation line. Although this appears to be analogous to the moist adiabatic temperature distribution on Earth when condensation of water occurs, it appears more likely that radiation effects are responsible for controlling the temperature distribution above 14 km on Mars. If the equilibrium radiation temperatures were lower than are indicated in Fig. 1 for the altitude region from 14 to 100 km, the atmosphere should cool until sublimation starts to occur. As soon as agglomerates of molecules began to form, it would seem that their infrared-radiative properties would lead to additional radiative heating of the atmosphere, thus stopping the cooling process at that point.

Although the temperature of the

Martian outer atmosphere is too low to permit any significant thermal escape, the possibility remains that the solar wind might sweep away some of the atmospheric gases. The observational evidence seems to oppose this. The outermost portion of the atmosphere must be atomic oxygen, and it would be mainly atomic oxygen that would be swept away by contact with the solar wind, leaving corresponding quantities of carbon monoxide in the atmosphere.

The failure to find spectroscopic evidence of carbon monoxide therefore indicates that the solar wind has not swept away any significant portion of the outer atmosphere. It is difficult to imagine any mechanism other than magnetic field that could protect the atmosphere from being partially swept away; this suggests that Mars may have a weak magnetic field, sufficient to divert the solar wind at some altitude exceeding a few hundred kilometers but not strong enough for detection by the magnetometers in Mariner IV. Alternatively, the magnetic field within the solar wind may be diverted by the Martian ionosphere, and this diversion may divert the solar wind and prevent any sweeping away of the Martian atmosphere.

The arguments for my model rest heavily on the spectroscopic evidence that carbon monoxide is not a prominent constituent of the Martian atmosphere. This factor indicates that atomic oxygen, formed by photodissociation of carbon dioxide, is not continually being swept away by the solar wind, carbon monoxide thus being permitted to accumulate. If the atomic oxygen is not rapidly removed, it must be a principal constituent of the Martian upper atmosphere, and its ions almost certainly must produce the principal band of ionization that was observed by Mariner IV.

F. S. JOHNSON

Earth and Planetary Sciences Laboratory, Southwest Center for Advanced Studies, Dallas, Texas

References and Notes

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Electron Density and Electronic Properties in Noble-Metal Transition Elements

Abstract. *It is shown empirically that the superconducting transition temperature as well as the magnetic susceptibility and the electronic specific heat of noble-metal transition elements and alloys can be described reasonably well as universal functions of the valence electron density, that is, the number of valence electrons per cubic centimeter.*

We have found that one can describe the electronic and magnetic behavior of all the noble-metal transition elements surprisingly well in terms of a single parameter—the electron density, that is, the number of valence electrons per cubic centimeter. This is quite a different concept from that of using valence electrons per atom as has previously been done (*1, 2*). In both cases the valence electrons are considered to be all those electrons outside the last filled shell. By plotting the superconducting transition temperature, the magnetic susceptibility, and the electronic specific heat against the electron density, we find universal functions of these properties for alloys both among the 4*d* and 5*d* elements as well as between them. Thus the difference between 4*d* and 5*d* alloys that otherwise showed up in similar plots in the past when the number of valence electrons per atom were used as a parameter can be accounted for by the difference in atomic volume.

Desorbo (*3*) had proposed a modification of the valence-electrons-per-atom rules (*1*) which took into account the difference in atomic volume of alloys with the same number of valence electrons per atom. He introduced an effective electron-per-atom ratio ($N_{\text{eff.}}$), which depended on the ratio of the atomic volumes of solute and solvent atoms. For alloys with the same solvent atom, his $N_{\text{eff.}}$ is also proportional to the electron density; his concept is, however, different from ours in that the constant of proportionality still depends on the volume of the solvent atom.

We have made a rather detailed investigation on the occurrence of superconductivity in alloys of noble-metal transition elements [Ir-rich alloys of the face-centered-cubic (fcc) phase] from 1.0 to 0.012°K. Our data are summarized in Fig. 1, in which we represent binary and ternary alloys in a two-dimensional way. The dashed lines indicate the various alloy systems which we have studied, namely the systems Os-Ir, Ir-Pt, Ir-Rh, Ir-Pd, Ir-Ru, $Ir_{0.8}Re_{0.2}$-Rh, $Ir_{0.7}Os_{0.3}$-Rh, and $Ir_{0.5}Rh_{0.5}$-Os. The scale on the *x*-axis in Fig. 1 represents the number of valence electrons per atom, namely 8 for Os and Ru, 9 for Ir and Rh, and 10 for Pt and Pd. Alloys with roughly equal transition temperatures are shown by a given symbol. The labeled solid lines are the approximate lines of constant transition temperature. In Fig. 2 we indicate in a similar plot

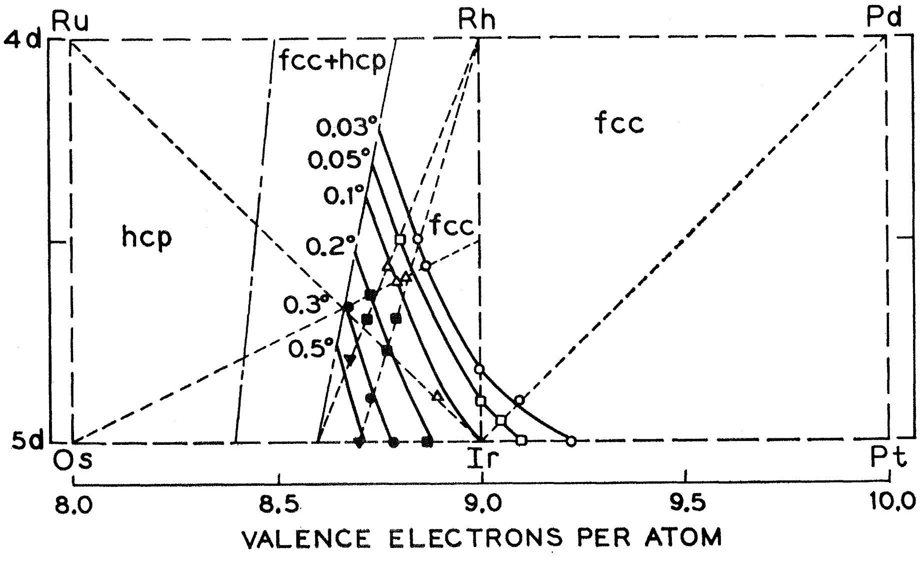

Fig. 1. Superconductivity in alloy systems of noble metals and transition elements. The dashed lines indicate the alloy systems investigated. The superconducting transition temperature of each alloy, represented by a point on a dashed line, is indicated roughly by the kind of symbol used for the point, namely 0.5° (▼), 0.3° (●), 0.2° (**X**), 0.1° (△), 0.05° (□), and 0.03° (○). The labeled solid lines are the approximate lines of constant transition temperature; *hcp*, hexagonal-close-packed; *fcc*, face-centered-cubic.