Reports

Stability of the Martian Atmosphere

Abstract. *A detailed chemical dynamic model is presented for a moist martian atmosphere. Recombination of carbon dioxide is catalyzed by trace amounts of water. The abundances of carbon monoxide and molecular oxygen should vary in response to changes in atmospheric water and atmospheric mixing.*

Carbon dioxide is the major gaseous component in the atmospheres of Mars and Venus, and it is difficult to understand its apparent stability. The gas is readily dissociated by sunlight at wavelengths less than 2000 Å. However, recombination of CO_2 by the elementary reaction 1 (see Table 1) proceeds at a rate which is negligibly slow (*1*) compared with that of the competing reaction 2. It would appear, therefore, that the atmospheres of Mars and Venus should contain large amounts of O_2 and CO, and yet both atmospheres are remarkably deficient in dissociation products, such as CO, O_2, O_3, and O.

We shall argue here that recombination occurs predominantly between CO and O and proceeds catalytically by the sequence of reactions 3 to 5. Photolysis of H_2O provides the source of hydrogen radicals (*2*). This sequence readily accounts for the removal of oxygen atoms below about 25 km. At higher altitudes the HO_2 concentration is vanishingly small, a consequence of the strong dependence on altitude of the three-body reaction 3. The alternate scheme, reaction 6, followed by reaction 5 plays some role at higher altitudes, where O_3 is produced mainly by reaction 7 and removed by photolysis (reaction 8) in the Hartley continuum, 2000 to 3000 Å.

A viable photochemical model must also account for a chemical balance in O_2. Molecular oxygen is formed by reactions 2 and 9, both of which provide large potential sources of O_2 above 20 km. Molecular oxygen diffuses downward and is removed by photolysis (reaction 10) in the Herzberg continuum, below 2400 Å, followed by reactions 3 to 5, with some additional removal associated with the sequence of reactions 12 and 13 (*3*), followed by reaction 5. However, the bulk of the recombination is due to reactions 3 to 5. This is a consequence of the rapid downward transport of oxygen atoms, which suppresses the formation of O_2.

An alternate scheme (*2, 4*) for the recombination of CO and O_2 involves reaction 3 followed by reactions 11 and 5. We shall argue that reaction 11 is too slow to play a role for Mars.

The importance of H_2O in the martian atmosphere was emphasized earlier in another context (*5*). The recombination of $O_2{}^+$ in the martian exosphere leads to the production of energetic O atoms, and a significant number of O atoms escape to interplanetary space. The estimated escape rate for O is approximately equal to half the observed escape rate for H. The H atoms are supplied to the upper atmosphere by upward diffusion of H_2 formed as a by-product of H_2O chemistry in the near-surface region. The primary source of H_2 is reaction 14, and the net production of H_2 is determined by the magnitude of the escape rate for O atoms. It was argued that the relative concentrations of CO and O_2 in the lower atmosphere would be moderated as a result of oxygen escape so as to supply the required upward flux of H_2. The escape of oxygen acts, therefore, to determine the magnitude of the integral I:

$$I = \int_0^\infty k_{14}[\mathrm{H}][\mathrm{HO_2}]dz \qquad (1)$$

where [H] and $[HO_2]$ are the number densities of H and HO_2 at height z, and k_{14} is the rate constant for reaction 14. Using the analyses by Hunten and McElroy (*2*), and McElroy (*5*), we estimate that I is equal to 3.5×10^8 cm^{-2} sec^{-1} with a probable uncertainty of about a factor of 2. An acceptable chemical model for Mars is constrained therefore to provide the appropriate value for I (*6*).

Detailed numerical studies of martian photochemistry are simplified by a number of factors. First, O_2 and CO may be assumed to be in diffusive equilibrium over an extensive altitude regime. The relevant photochemical time constants are long compared to any conceivable transport times. We may therefore assume that the abundances of CO and O_2 are known and adopt the observed mixing ratios of 8×10^{-4} (*7*) and 1.3×10^{-3} (*8*), respectively. Second, the concentration of odd hydrogen, $[H] + [HO_2] + [OH]$, should also be well mixed in view of the relatively long time constants for radical removal. The principal paths for radical loss are reactions 14 and 15. The dominant radical below 25 km is HO_2. Atomic hydrogen dominates at higher altitudes, and the mixing ratio of odd hydrogen, for particular O_2 and CO concentrations, is specified by the conservation condition (Eq. 1). With the model employed here we find a mixing ratio for odd hydrogen equal to 5.0×10^{-10}.

The detailed chemical model is summarized in Table 1. The important rate constants are moderately well known, with two exceptions. Reaction 11 is currently in some dispute. Clark (*1*) noted that an extrapolation of the high-temperature data obtained by Baldwin *et al.* (*9*) implied a rate constant at martian temperatures of the order of 10^{-30} cm^3 sec^{-1}. Davis (*10*) determined an upper limit for the reaction at room temperature equal to 10^{-18} cm^3 sec^{-1}. On the other hand, Westenberg and DeHaas (*11*) concluded that the reaction was fast at room temperature, with a rate constant equal to approximately 0.06 times that of reaction 14. The choice of rate constant in Table 1, $k_{11} < 10^{-16}$ cm^3 sec^{-1}, reflects a careful study of the available data. We note, for example, that Westenberg and DeHaas (*11*) did not allow for the fast reaction 15 as a mechanism for loss of OH. On the basis of our current understanding of Mars it would be difficult to accept a value of k_{11} much larger than the upper limit adopted here (*12*).

Some uncertainty is also associated with k_{14}. Kaufman (*13*) concluded that k_{14} should exceed 3×10^{-12} cm^3 sec^{-1} at room temperature, and the choice indicated here, 10^{-11} cm^3 sec^{-1}, reflects a recent analysis of the available data by McConnell (*14*). A smaller

Table 1. Relevant reactions with their rate constants (*1*, *13*). For two-body reactions the units are cm³ sec⁻¹, and for three-body reactions the units are cm⁶ sec⁻¹.

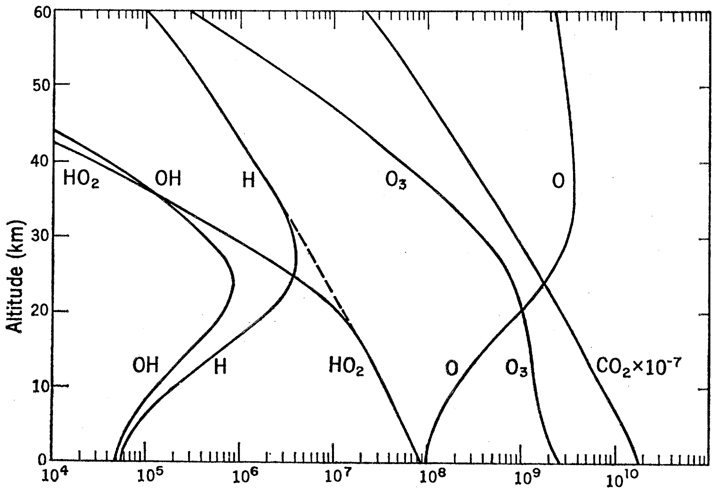
Reaction number	Reaction	Rate constant	Reference
1	$CO + O + CO_2 \rightarrow CO_2 + CO_2$	$k_1 = 2 \times 10^{-37}$	(*21,22*)
2	$O + O + CO_2 \rightarrow O_2 + CO_2$	$k_2 = 3 \times 10^{-33} (T/300)^{-2.9}$	
3	$H + O_2 + CO_2 \rightarrow HO_2 + CO_2$	$k_3 = 2 \times 10^{-31} (T/273)^{-1.3}$	(*23*)
4	$O + HO_2 \rightarrow OH + O_2$	$k_4 = 7 \times 10^{-11}$	(*24*)
5	$CO + OH \rightarrow CO_2 + H$	$k_5 = 9 \times 10^{-13} \exp(-500/T)$	
6	$H + O_3 \rightarrow OH + O_2$	$k_6 = 2.6 \times 10^{-11}$	
7	$O + O_2 + CO_2 \rightarrow O_3 + CO_2$	$k_7 = 1.4 \times 10^{-33} (T/300)^{-2.5}$	(*25*)
8	$O_3 + h\nu \rightarrow O_2 + O$	$J_8 = 4.2 \times 10^{-3}$ sec⁻¹	
9	$O + OH \rightarrow O_2 + H$	$k_9 = 5 \times 10^{-11}$	
10	$O_2 + h\nu \rightarrow O + O$	$J_{10} = 5.8 \times 10^{-10}$ sec⁻¹	
11	$CO + HO_2 \rightarrow CO_2 + OH$	$k_{11} = < 10^{-16}$	
12	$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$	$k_{12} = 9.5 \times 10^{-12}$	
13	$H_2O_2 + h\nu \rightarrow OH + OH$	$J_{13} = 5.2 \times 10^{-5}$ sec⁻¹	(*26*)
14	$H + HO_2 \rightarrow H_2 + O_2$	$k_{14} = 1 \times 10^{-11}$	
15	$OH + HO_2 \rightarrow H_2O + O_2$	$k_{15} = 2 \times 10^{-10}$	(*24*)

value for k_{14} would imply somewhat larger mixing ratios for odd hydrogen and lower values for the eddy mixing coefficient near 30 km, but it should not significantly alter the general characteristics of the photochemical model. In particular, recombination of O and CO would continue to occur primarily by reactions 3 to 5, although photolysis of H_2O_2 would be relatively more important as a sink for O_2.

Concentrations of odd oxygen were obtained by numerical solution of the coupled diffusion and continuity equations. Odd oxygen, mainly O and O_3, is produced by photolysis of CO_2 and O_2. We used the data of Widing *et al.* (*15*) to compute dissociation rates. Their fluxes are somewhat lower than the values employed in earlier calculations (*16*), and the photolysis rates are similarly reduced. The net production of O in the present model is equal to 1.8×10^{12} cm⁻² sec⁻¹. Loss of odd oxygen is primarily by reaction 5, with some contribution from reactions 2 and 9. The results for the principal constituents are shown in Fig. 1. This model corresponds to a vertical eddy diffusion coefficient of 1.5×10^8 cm² sec⁻¹ and is most sensitive to the diffusion coefficient in the vicinity of 30 km. The value of the diffusion coefficient derived here is similar to values discussed by Gierasch and Goody (*17*) in their study of energy transfer in the martian troposphere. According to calculations by McElroy and McConnell (*16*), somewhat larger eddy coefficients, about 10^9 cm² sec⁻¹, are required at higher elevations (above 60 km) in order to account for upper atmospheric data on O and CO.

The relative importance of various source and sink terms is illustrated in Fig. 2. The difference between the CO_2 photolysis rate and the total recombination rate reflects the contribution of flow to the local O production rate. Evidently recombination of CO and O occurs mainly below 25 km, and the sequence of reactions 3 to 5 is the dominant path for recombination. Formation of O_2 occurs in a restricted altitude regime, between 25 km and 30 km, and reaction 9 dominates. The rate of reaction 15 obtained from Fig. 1 implies an average rate for photolysis of H_2O equal to 2.7×10^9 cm⁻² sec⁻¹, in agreement with earlier estimates (*2*) of the mean photolysis rate based on observed H_2O concentrations (*18*). The model predicts an O_3 abundance of 1.4×10^{-4} cm atm, in satisfactory agreement with limits set by the ultraviolet experiments on Mariner 6, Mariner 7, and Mariner 9 (*19*). Ozone is normally a minor source of ultraviolet opacity in the martian atmosphere, although strong absorption is occasionally detected. High O_3 concentrations are apparently correlated with unusually cold atmospheric conditions (*19*) and may be a natural consequence of the chemical model discussed here. One would expect lower concentrations of H_2O and consequently OH, HO_2, and H in colder regions of the martian atmosphere. Wet chemistry is less effective and odd oxygen concentrations should be consequently higher.

The response of the martian atmo-



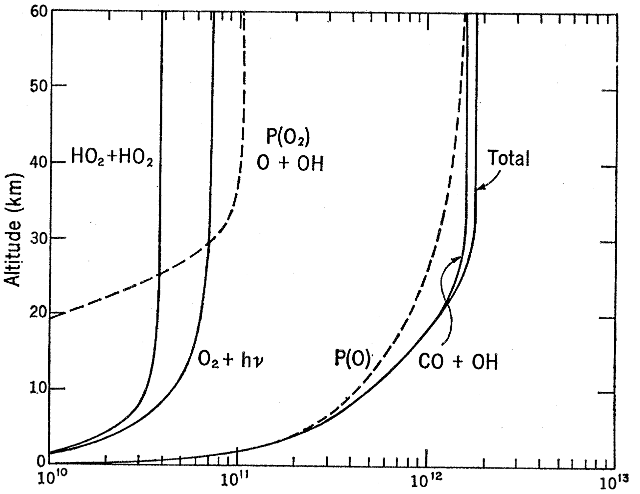


Fig. 1 (left). Concentrations of principal constituents in the martian atmosphere. The surface temperature is 220°K. The eddy diffusion coefficient is 1.5×10^8 cm² sec⁻¹. The curve for odd hydrogen, shown as a broken line between the portions labeled HO_2 and H, is plotted for a density of odd hydrogen 5×10^{-10} times the CO_2 density. The O_2 and CO densities are, respectively, 1.3×10^{-3} and 8×10^{-4} times the CO_2 density. Fig. 2 (right). Integrated rates of reactions important in CO_2 and O_2 formation and loss. The rates are integrated from the martian surface to height z. The curve labeled $P(O)$ is the integrated photolysis rate for CO_2. The contribution from $O + O + CO_2$ is only 2.3×10^9 cm² sec⁻¹ and is not shown.

sphere to a change in the concentration of H_2O is of interest. For modest changes, the atmosphere readily adjusts to a new equilibrium state with a different CO/O_2 mixing ratio. To first order, the concentration of OH is proportional to the concentration of H_2O, and the concentrations of O, H, and HO_2 in the lower atmosphere remain constant. Only the CO concentration changes, and the change is inversely proportional to the change in H_2O concentration. To a higher level of approximation, however, consequent changes in the production of O_2 must be considered. By numerical experimentation we found that if the H_2O concentration were arbitrarily reduced by a factor of 2, the CO concentration would increase by a similar factor and the O_2 concentration would decrease by about 50 percent, if the eddy mixing coefficient remained constant.

It is also of interest to consider the atmospheric response to a change in the eddy mixing coefficient near 30 km. A reduction (or increase) in the eddy mixing coefficient at 30 km leads to an increase (or decrease) in O_2 formation. The chemical equilibrium in the lower atmosphere is altered with a consequent increase (or decrease) in the abundance of CO and O_2. The CO/O_2 mixing ratio remains relatively constant. It has been suggested that the O_2 concentration varied with time in the late stages of the recent planetwide dust storm (*8*). This may reflect in part a change in the dynamic state of the atmosphere, in part a change in the atmospheric H_2O concentration. It is difficult to draw more quantitative conclusions. A complete analysis should allow for heterogeneous chemistry on atmospheric dust, and there are reasons to suspect that martian dust may play some role in the chemistry of atmospheric oxygen (*20*).

Finally, we note the central importance in the present analysis of the conservation condition (Eq. 1). The relative abundance of various forms of odd hydrogen, and the mixing ratio of odd hydrogen, are controlled by this relation in the present scheme. An increase (or decrease) in O escape—associated, for example, with increased (or decreased) solar activity—will result in an increase (or decrease) in the amount of atmospheric CO. The concentration of HO in the lower amtosphere will change. For a fixed H_2O concentration, the concentration of HO_2 will increase (or decrease) with an increase (or decrease) in O escape. The production of H_2 and escape of H will alter accordingly. The present model provides a plausible explanation of the observed relation between H and O escape and supports conclusions derived earlier (*5*) regarding the evolutionary history of martian H_2O (*21*).

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6. Molecular hydrogen is formed mainly by reaction 14 and removed by reactions with $O(^1D)$ and CO_2^+. A lower bound for I may be specified on the basis of the observed H escape rate. In addition, we can derive an upper limit to the mixing ratio of H_2 if we assume that the bulk of the escaping H is provided by the reaction between CO_2^+ and H_2. This limit, 5×10^{-5}, can then be employed to estimate an upper bound for I, if the O_3 concentration is known. We find $8 \times 10^7 < I < 2 \times 10^{-7} N$, where N is the column density of O_3 in reciprocal square centimeters (*19*). With the present chemical model, N is approximately 3×10^{15} cm^{-2}, close to the upper limit derived from Mariner 9 observations. Our choice for I reflects these considerations. In a more elaborate calculation the coupled flows of odd hydrogen and odd oxygen should be considered, and the value of I would be specified accordingly. We were unable to find additional important sinks for H_2. For example, the rate of loss of H_2 by reaction with OH is less than 5×10^7 cm^{-2} sec^{-1} at martian temperatures.
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Detection of Molecular Oxygen on Mars

Abstract. *Molecular oxygen was detected in martian spectra near 7635 angstroms and its abundance measured both during and after the 1971 dust storm. Its column abundance in the clear martian atmosphere is about 10.4 ± 1.0 centimeters amagat, giving a mixing ratio of molecular oxygen to carbon dioxide of 1.3×10^{-3}. The mixing ratio of molecular oxygen to carbon monoxide (1.4 ± 0.3) is quite different from the value of 0.5 that would result from the photolysis of a pure carbon dioxide atmosphere, which indicates that there is or was a net source of oxygen relative to carbon (probably water) in the martian atmosphere.*

The atmospheric composition of Mars has been known (*1*) for several years now to be primarily CO_2, with trace amounts of CO (0.08 percent) and water vapor (approximately 0.2 percent). Upper limits have also been placed on the amounts of ozone ($< 3 \times 10^{-6}$ percent), N_2 (< 5 percent), and O_2 [< 0.26 percent (*2*) and < 0.19 percent (*3*)]. The measurements we report here yield 0.13 percent for the O_2 abundance.

Knowledge of the O_2 abundance, in addition to its intrinsic interest, provides us with another clue to a puzzle concerning the photochemistry of CO_2 atmospheres. A number of investigators (*4, 5*) have noted that in a period of about 2000 years most of the CO_2 on Mars should be decomposed by sunlight (at wavelengths below 2270 Å) into CO and O_2, according to laboratory measurements of the rates of the reactions $CO_2 + h\nu \rightarrow CO + O$, $O + O + M \rightarrow O_2 + M$, and $O + CO + M \rightarrow CO_2 + M$, where M is a third body. By including transport terms in the rate equations, McElroy and McConnell (*4*) were able to account for the small amounts of