

HDO in the Martian Atmosphere: Implications for the Abundance of Crustal Water¹

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The physical and chemical processes that lead to the preferential escape of hydrogen over deuterium in the Martian atmosphere are studied in detail using a one-dimensional photochemical model. Comparison of our theory with recent observations of HDO suggests that, averaged over the planet, Mars contains 0.2 m of crustal water that is exchangeable with the atmosphere. Our estimate is considerably lower than recent estimates of subsurface water on Mars based on geomorphological analysis of Viking images. The estimate can be reconciled if only a small fraction of crustal water can exchange with the atmosphere. © 1988 Academic Press, Inc.

INTRODUCTION

Recently Owen *et al.* (1987) reported the detection of several lines in the Q-branch of the ν_1 band of HDO in the Martian atmosphere. Preliminary analysis indicates that the D/H ratio on Mars may be enhanced by about a factor of 6 relative to the terrestrial standard value of 1.6×10^{-4} (Craig 1961).

If we assume that the D/H ratio of juvenile water on Mars is the same as that for the Earth, the observed enhancement must be explained by a divergent history of atmospheric evolution. It is known that hydrogen escapes from the present Martian atmosphere (Anderson and Hord 1971, Mc-

Elroy 1972, see also recent review by Barth 1985). Preferential escape of the light isotope could lead to the enrichment of the heavy isotope. In this paper we examine this mechanism in some detail, using the approach that has been developed for understanding the isotopic enrichment of nitrogen and oxygen on Mars (McElroy *et al.* 1976b, McElroy and Yung 1976), the origin of HDO on Venus (McElroy *et al.* 1982, Donahue *et al.* 1982), and the origin of deuterated species in the primitive solar nebula (Yung *et al.* 1988).

The present Martian atmosphere holds at most, during summer at the North Pole, 100 precipitable μm of H_2O . For comparison, the atmosphere of Venus contains about 2 cm of H_2O , and the Earth's oceans are equivalent to an average of 3 km of H_2O . Due to the lower temperature on Mars, the bulk of water is believed to reside beneath the surface. Part of this paper also addresses the question of the interaction between the atmosphere and the surface reservoir, and constraints on the abundance of crustal water (see review by Squyres 1984).

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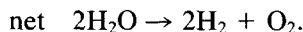
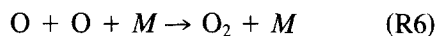
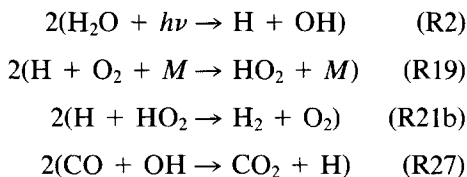
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PHOTOCHEMISTRY AND MECHANICS OF HYDROGEN ESCAPE

A complete list of reactions essential for understanding the photochemistry of the Martian atmosphere is given in Table Ia. The corresponding chemistry of deuterated species is included in Table Ib. The major reservoir of hydrogen in the Martian atmosphere is H₂O, concentrated primarily in the lower atmosphere. Therefore, the first step in the escape of hydrogen is the conversion of H₂O to H₂ and O₂ via the reactions



This takes place within the lowest 30 km of the atmosphere, and as much as 10% of H₂O dissociation results in the production of H₂. Since H₂ is fairly unreactive, it acts as a carrier of hydrogen from the lower atmosphere to the upper atmosphere.

In the Martian ionosphere (~140 km), H₂ is decomposed into H mainly by the ionic reactions

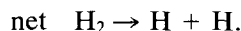
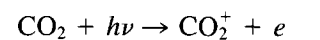
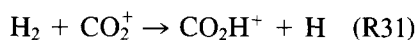


TABLE Ia

LIST OF ESSENTIAL REACTIONS FOR THE ATMOSPHERE OF MARS WITH THEIR PREFERRED RATE COEFFICIENTS

	Reaction	Rate coefficient	Reference
R1a	CO ₂ + hν → CO + O	2.8 × 10 ⁻⁷	a
R1b	→ CO + O(¹ D)	1.0 × 10 ⁻⁷	a
R2	H ₂ O + hν → H + OH	1.9 × 10 ⁻⁶	b
R3a	O ₂ + hν → 2O	2.3 × 10 ⁻⁹	c
R3b	→ O + O(¹ D)	5.5 × 10 ⁻⁷	c
R4a	O ₃ + hν → O ₂ + O	2.0 × 10 ⁻⁴	d
R4b	→ O ₂ + O(¹ D)	1.6 × 10 ⁻³	d
R5	H ₂ O ₂ + hν → 2OH	2.2 × 10 ⁻⁵	e
R6	2O + M → O ₂ + M	5.2 × 10 ⁻³⁵ e ^{900/T}	f
R7	O + O ₂ + M → O ₃ + M	2.99 × 10 ⁻²⁸ T ^{-2.3}	g
R8	O + O ₃ → 2O ₂	8.0 × 10 ⁻¹² e ^{-2060/T}	g
R9	O + OH → O ₂ + H	2.2 × 10 ⁻¹¹ e ^{117/T}	g
R10	O + HO ₂ → OH + O ₂	3.0 × 10 ⁻¹¹ e ^{200/T}	g
R11	O + H ₂ O ₂ → OH + HO ₂	1.4 × 10 ⁻¹² e ^{-2000/T}	g
R12	O + CO + M → CO ₂ + M	6.5 × 10 ⁻³³ e ^{-2184/T}	h
R13	O(¹ D) + O ₂ → O + O ₂	3.2 × 10 ⁻¹¹ e ^{67/T}	g
R14a	O(¹ D) + O ₃ → 2O ₂	1.2 × 10 ⁻¹⁰	g
R14b	→ O ₂ + 2O	1.2 × 10 ⁻¹⁰	g
R15	O(¹ D) + H ₂ → H + OH	1.0 × 10 ⁻¹⁰	g
R16	O(¹ D) + CO ₂ → O + CO ₂	7.4 × 10 ⁻¹¹ e ^{117/T}	g
R17	O(¹ D) + H ₂ O → 2OH	2.2 × 10 ⁻¹⁰	g
R18	2H + M → H ₂ + M	1.5 × 10 ⁻²⁹ T ^{-1.3}	f
R19	H + O ₂ + M → HO ₂ + M	k ₀ = 5.5 × 10 ⁻³² (300/T) ^{1.6} k _∞ = 7.5 × 10 ⁻¹¹	g
R20	H + O ₃ → OH + O ₂	1.4 × 10 ⁻¹⁰ e ^{-470/T}	g
R21a	H + HO ₂ → 2OH	6.8 × 10 ⁻¹¹	i
R21b	H + HO ₂ → H ₂ + O ₂	2.8 × 10 ⁻¹²	i

TABLE Ia—Continued

	Reaction	Rate coefficient	Reference
R21c	$H + HO_2 \rightarrow H_2O + O$	1.4×10^{-12}	<i>i</i>
R22	$2OH \rightarrow H_2O + O$	$4.2 \times 10^{-12} e^{-242/T}$	<i>g</i>
R23	$2OH + M \rightarrow H_2O_2 + M$	$k_o = 6.9 \times 10^{-31} (300/T)^{0.8}$ $k_\infty = 1.0 \times 10^{-11} (300/T)$	<i>g</i> <i>g</i>
R24	$OH + O_3 \rightarrow HO_2 + O_2$	$1.6 \times 10^{-12} e^{-940/T}$	<i>g</i>
R25	$OH + H_2 \rightarrow H_2O + H$	$6.1 \times 10^{-12} e^{-2030/T}$	<i>g</i>
R26	$OH + HO_2 \rightarrow H_2O + O_2$	$4.6 \times 10^{-11} e^{230/T}$	<i>j</i>
R27	$OH + CO \rightarrow CO_2 + H$	$1.5 \times 10^{-13} (1 + 0.6P_{atm})$	<i>g</i>
R28	$OH + H_2O_2 \rightarrow H_2O + HO_2$	$3.1 \times 10^{-12} e^{-187/T}$	<i>g</i>
R29	$2HO_2 \rightarrow H_2O_2 + O_2$	$2.3 \times 10^{-13} e^{590/T}$	<i>g</i>
R30	$HO_2 + O_3 \rightarrow OH + 2O_2$	$1.4 \times 10^{-14} e^{-580/T}$	<i>g</i>
R31	$CO_2^- + H_2 \rightarrow CO_2H^+ + H$	5.8×10^{-10}	<i>k</i>
R32	$CO_2H^+ + e \rightarrow CO_2 + H$	3.0×10^{-7}	<i>l</i>

Note. The units for mean photolysis rates (J) and two-body and three-body reactions (k) are sec^{-1} , $\text{cm}^3 \text{sec}^{-1}$, and $\text{cm}^6 \text{sec}^{-1}$, respectively. The numerical values for photolysis refer to the optically thin region. Reactions for deuterated species are included in Table Ib.

^a Henry and McElroy (1968); Hitchcock and Brion (1980); Lewis and Carver (1983); Shemansky (1972); Nakata *et al.* (1965); Okabe (1978); Slinger and Black (1978); Lawrence (1972a,b).

^b Watanabe and Zelikoff (1953); Thompson *et al.* (1963); Kley (1984); Lee and Suto (1986); Haddad and Samson (1986); Slinger and Black (1982); Stief *et al.* (1975); Wu and Judge (1981).

^c Kirby *et al.* (1979); Watanabe (1958); Ackerman (1971); Kley (1984); Hudson (1974); WMO (1985); Hudson and Reed (1979); Hudson and Mahle (1972); Prather (1981); Herman and Mentall (1982); Shardanand and Rao (1977); Carver *et al.* (1977).

^d Ackerman (1971); WMO (1985); DeMore *et al.* (1985).

^e Schügers and Welge (1968); CIAP (1975); DeMore *et al.* (1985).

^f Tsang and Hampson (1986).

^g DeMore *et al.* (1985).

^h Baulch *et al.* (1976).

ⁱ Keyser (1986).

^j DeMore (1987), private communication.

^k Karpas *et al.* (1979).

^l Kong and McElroy (1977).

Both H and H₂ diffuse upward to the exobase (~240 km) and can escape to space via the Jeans (thermal) mechanism. The escape of hydrogen derived from H₂O would leave the atmosphere enriched in oxygen. However, it is known that oxygen can also escape from Mars. Indeed, McElroy (1972) showed that the rates of hydrogen and oxygen escape are self-regulated such that $\phi_O = \frac{1}{2}\phi_H$, where ϕ_i is the escape flux of species *i*. Consequently the escape of hydrogen will not lead to a net change of the oxidation state of the atmosphere.

It is clear from the above discussion that

the escape of hydrogen from Mars involves four steps:

- (a) photochemical production of H₂,
- (b) transport of H₂ to the upper atmosphere,
- (c) dissociation of H₂ into H, and
- (d) thermal escape of H and H₂.

Each of these steps is well understood for hydrogen. However, there has been no previous study of these processes for the corresponding deuterated species. Each of these four steps is expected to differentiate

TABLE Ib

LIST OF ESSENTIAL REACTIONS FOR DEUTERATED COMPOUNDS

	Reaction	Rate coefficient	Reference
R33a	HDO + $h\nu$ → H + OD	$\frac{1}{2}J_2$	<i>a</i>
R33b	→ D + OH	$\frac{1}{2}J_2$	<i>a</i>
R34	HDO ₂ + $h\nu$ → OH + OD	J_5	<i>a</i>
R35	O + OD → O ₂ + D	k_9	<i>a</i>
R36	O + DO ₂ → OD + O ₂	k_{10}	<i>a</i>
R37a	O + HDO ₂ → OD + HO ₂	$\frac{1}{2}k_{11}$	<i>b</i>
R37b	→ OH + DO ₂	$\frac{1}{2}k_{11}$	<i>b</i>
R38a	O(¹ D) + HD → H + OD	0.41(k_{15})	<i>b</i>
R38b	→ D + OH	0.41(k_{15})	<i>b</i>
R39	O(¹ D) + HDO → OD + OH	k_{17}	<i>a</i>
R40	H + D + <i>M</i> → HD + <i>M</i>	k_{18}	<i>a</i>
R41	D + O ₂ + <i>M</i> → DO ₂ + <i>M</i>	k_{19}	<i>a</i>
R42	D + O ₃ → OD + O ₂	0.71(k_{20})	<i>b</i>
R43a	D + HO ₂ → OH + OD	0.71(k_{21a})	<i>b</i>
R43b	→ HD + O ₂	0.71(k_{21b})	<i>b</i>
R43c	→ HDO + O	0.71(k_{21c})	<i>b</i>
R44a	H + DO ₂ → OH + OD	k_{21a}	<i>a</i>
R44b	→ HD + O ₂	k_{21b}	<i>a</i>
R44c	→ HDO + O	k_{21c}	<i>a</i>
R45	OD + OH → HDO + O	k_{22}	<i>a</i>
R46	OD + OH + <i>M</i> → HDO ₂ + <i>M</i>	k_{23}	<i>a</i>
R47	OD + O ₃ → DO ₂ + O ₂	k_{24}	<i>a</i>
R48a	OD + H ₂ → HDO + H	k_{25}	<i>b</i>
R48b	→ H ₂ O + D	0	<i>b</i>
R49a	OH + HD → HDO + H	$\frac{2}{3}k_{25}$	<i>c</i>
R49b	→ H ₂ O + D	$\frac{2}{3}k_{25}$	<i>c</i>
R50	OH + D → OD + H	$3.3 \times 10^{-9}T^{-0.63}$	See text
R51	OD + H → OH + D	k_{50}/K_1	See text
R52	OD + HO ₂ → HDO + O ₂	k_{26}	<i>a</i>
R53	OH + DO ₂ → HDO + O ₂	k_{26}	<i>a</i>
R54	OD + CO → CO ₂ + D	k_{27}	<i>a</i>
R55a	OD + H ₂ O ₂ → HDO + HO ₂	k_{28}	<i>b</i>
R55b	→ H ₂ O + DO ₂	0	<i>b</i>
R56a	OH + HDO ₂ → HDO + HO ₂	$\frac{1}{2}k_{28}$	<i>a</i>
R56b	→ H ₂ O + DO ₂	$\frac{1}{2}k_{28}$	<i>a</i>
R57	DO ₂ + HO ₂ → HDO ₂ + O ₂	k_{29}	<i>a</i>
R58	DO ₂ + O ₃ → OD + 2O ₂	k_{30}	<i>a</i>
R59	D + HO ₂ → DO ₂ + H	1.0×10^{-10}	<i>b</i>
R60	H + DO ₂ → HO ₂ + D	k_{59}/K_2	See text
R61a	CO ₂ ⁺ + HD → CO ₂ H ⁺ + D	$\frac{2}{3}k_{31}$	<i>d</i>
R61b	→ CO ₂ D ⁺ + H	$\frac{2}{3}k_{31}$	<i>d</i>
R62	CO ₂ D ⁺ + <i>e</i> → CO ₂ + D	k_{32}	<i>b</i>

^a Kasting and Pollack (1983).

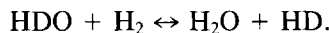
^b Assumed

^c Estimate based on Ravishankara *et al.* (1981).

^d Estimate based on Karpas *et al.* (1979).

between H and D species and is discussed separately.

(a) Given two primary reservoirs of deuterium, HDO and HD, the partitioning of deuterium between HDO and HD is kinetically controlled by the rates of formation and destruction of these compounds. But it is illuminating to consider the partitioning based on thermodynamics,

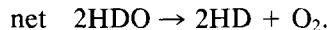
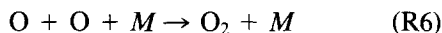
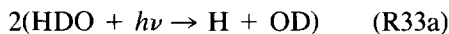
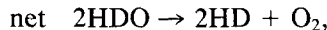
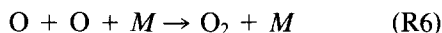
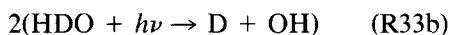


The equilibrium constant,

$$K = \frac{[\text{HD}][\text{H}_2\text{O}]}{[\text{H}_2][\text{HDO}]} = \frac{[\text{HD}]/[\text{H}_2]}{[\text{HDO}]/[\text{H}_2\text{O}]},$$

has been computed by Hubbard and MacFarlane (1980) and is about 1/7 at 200°K. Thus for a given D/H ratio in water, the corresponding D/H ratio of molecular hydrogen in thermochemical equilibrium with water would be significantly less. Of course, at 200°K these exchange reactions are too slow, and the correct fractionation must be computed on the basis of kinetic modeling.

Consider the following schemes:



These schemes are obvious analogs of the scheme for converting H₂O to H₂ and O₂. However, the isotopic exchange is also affected by other reactions not included in the above schemes, such as



The rate coefficient for R50 has been measured by Margitan *et al.* (1975) at room temperature, and by Howard and Smith (1982) at temperatures between 300 and

515°K. At room temperature the measured values differ by a factor of 2.5. In this work we adopt a value for k_{50} that is intermediate between these measurements. The reverse reaction,



has not been measured, but can be estimated by

$$k_{51} = \frac{k_{50}}{K_1},$$

where K_1 is the equilibrium constant for the equilibrium reactions

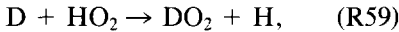


The value of K_1 has been computed using standard thermodynamic techniques, and the result is

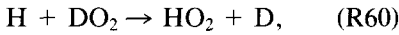
$$K_1 = 0.72e^{717/T}$$

(Yung *et al.* 1988).

The exchange of isotopes between D and HO_2 ,



should be fast. This reaction has not been measured, but is expected to proceed at the gas kinetic rate. The reverse reaction,



can be estimated using the equilibrium reaction,



The equilibrium constant has been computed by a straightforward method and is given by

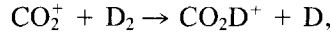
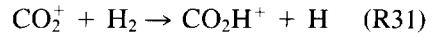
$$K_2 = \frac{k_{59}}{k_{60}} = 0.54e^{890/T}$$

(Friedl 1987, private communication).

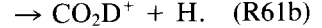
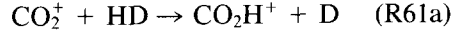
According to Yung *et al.* (1988), kinetic exchange can result in large isotopic fractionation in the solar nebula, where the abundance of H is high. In the Martian atmosphere the fractionation due to exchange is expected to be much less due to the lower abundance of H atoms.

(b) Below the homopause (~ 100 km), gravity does not distinguish the H and D species. However, above the homopause, the molecules assume their own scale heights determined by their molecular weights. This would lead to an enrichment of the light isotope between the homopause and the exobase of the order of 10%. The significance of this effect was first pointed out for the escape of oxygen from Mars by McElroy and Yung (1976). For H and D species, the enrichment is comparable (Hunten 1982).

(c) The ionic reaction for destroying H_2 has a slight preference for H_2 . The rate coefficients for the reactions,



have been measured by Karpas *et al.* (1979). The former reaction is about 40% faster than the latter. There is no measurement for the reaction



Based on the reactions with H_2 and D_2 , we adopt the following estimate: $k_{61a} = k_{61b} = \frac{2}{5}k_{31}$.

(d) The escape rate of species i at the exobase is given by

$$\phi_i = n_i \langle v_i \rangle,$$

where n_i and $\langle v_i \rangle$ are the number density and effusion velocity, respectively, for species i (see standard textbook, Chamberlain and Hunten 1987). Figure 1 shows values of $\langle v_i \rangle$ as a function of exospheric temperature for H, D, H_2 , and HD. For a standard exospheric temperature of 365°K, we have $\langle v \rangle = 6.8 \times 10^3$ cm sec⁻¹ for H, $\langle v \rangle = 1.7 \times 10^2$ cm sec⁻¹ for D and H_2 , and $\langle v \rangle = 4.0$ cm sec⁻¹ for HD. Clearly, the escape velocities are much less for the deuterated species.

We notice that each of the four steps would result in a preferential loss of H species from Mars. The precise fractionation factor must be computed from a de-

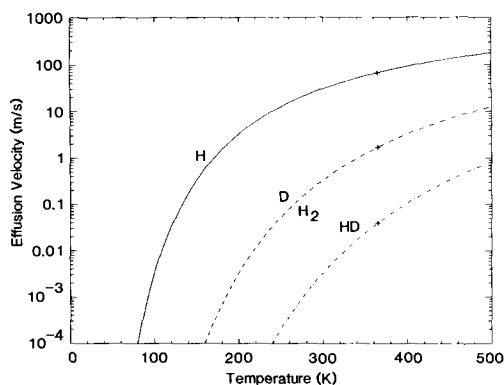
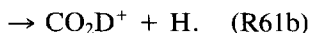
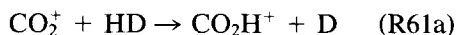
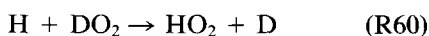
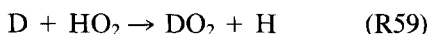
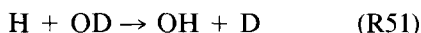
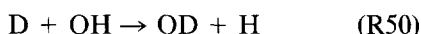


FIG. 1. Effusion velocities for H, D, H₂, and HD as a function of exospheric temperature for Mars. The values adopted in this work are marked by crosses.

tailed photochemical model of Mars, and this is pursued in the following section.

PHOTOCHEMICAL MODEL

The one-dimensional photochemical model is based on standard models published in the literature (McElroy and Donahue 1972, Liu and Donahue 1976, Kong and McElroy 1977), with appropriate updating of chemical kinetics, eddy diffusivity profile, and the inclusion of deuterated species. Table Ia summarizes the important reactions in our model, along with preferred rate coefficients. Reactions involving the deuterated species are given in Table Ib. Most of the reactions involving the deuterated species have been considered by Kasting and Pollack (1983) in their study of the evolution of water on Venus. However, Kasting and Pollack (1983) did not include reactions such as



It is difficult to evaluate the degree of completeness of our list of reactions, but

we have included more reactions than any previous study.

The eddy diffusivity profile $K(z)$ we adopt is similar to that used by Kong and McElroy (1977) with minor modifications due to Lindner (1985). From the surface to 20 km the value for K is $1 \times 10^6 \text{ cm}^2 \text{ sec}^{-1}$. Above this altitude $K(z)$ is constant, $1 \times 10^8 \text{ cm}^2 \text{ sec}^{-1}$. The abundance of water vapor below 10 km is kept fixed according to the profile given by Liu and Donahue (1976), multiplied by a factor of 0.65 to maintain the oxidation state of the atmosphere (discussed later). This is certainly within the uncertainties of our knowledge of Martian water vapor. Above this altitude, the H₂O concentration is determined by solving the continuity equation. The ion concentrations in the ionosphere are not solved in the model, but are taken from McElroy *et al.* (1976a) as inputs to the model.

The continuity equations are solved for all the important species in the model, except CO₂, which is fixed by the model atmosphere with exospheric temperature equal to 365°K. The lower boundary is at the surface; the upper boundary is at 240 km. The boundary conditions for the various species are summarized in Table II. The model is a diurnally averaged photochemical model for midlatitude solstice insolation. The numerical method of solution is described by Allen *et al.* (1981). In the actual computer runs, we first obtain a solution without considering the deuterated species. Then, the relevant species are fixed, and we run the model again for the deuterated species. This is justified in view of the fact that deuterium is many orders of magnitude less abundant than hydrogen and to the first order deuterated chemistry does not affect the hydrogen chemistry.

The reaction R21b is the major source of H₂ in the model. The exact value of this rate constant directly controls the escape flux of hydrogen, which needs to be in a fixed stoichiometric balance with that of oxygen so that the oxidation state of the atmosphere does not change and the evolution

TABLE II
BOUNDARY CONDITIONS FOR THE STANDARD
MODEL

Species	Lower boundary (0 km)	Upper boundary (240 km)
H ₂ O	See text	$\phi = 0$
O	$\phi = 0$	$\phi = 8.0 \times 10^7$
O(¹ D)	$\phi = 0$	$\phi = 0$
O ₂	$f = 1.3 \times 10^{-3}$	$\phi = 0$
O ₃	$\phi = 0$	$\phi = 0$
H	$\phi = 0$	$\langle v \rangle = 6.8 \times 10^3$
H ₂	$\phi = 0$	$\langle v \rangle = 1.7 \times 10^2$
OH	$\phi = 0$	$\phi = 0$
HO ₂	$\phi = 0$	$\phi = 0$
H ₂ O ₂	$\phi = 0$	$\phi = 0$
CO	$f = 7.0 \times 10^{-4}$	$\phi = 0$
D	$\phi = 0$	$\langle v \rangle = 1.7 \times 10^2$
HD	$\phi = 0$	$\langle v \rangle = 4.0$
OD	$\phi = 0$	$\phi = 0$
DO ₂	$\phi = 0$	$\phi = 0$
HDO ₂	$\phi = 0$	$\phi = 0$

Note. There are types of boundary conditions. We can specify the mixing ratio, f , the flux, ϕ (cm⁻² sec⁻¹), or the effusion velocity, $\langle v \rangle$ (cm sec⁻¹).

model is consistent (see discussion in previous section). We adopt a value for k_{21} of 7.2×10^{-11} cm³ sec⁻¹, which is within the uncertainties of the laboratory measurement at 300°K as reported by Keyser (1986) and in good agreement with the value of Sridharan *et al.* (1982). For the branching ratio k_{21b}/k_{21} we use a value of 0.04 which

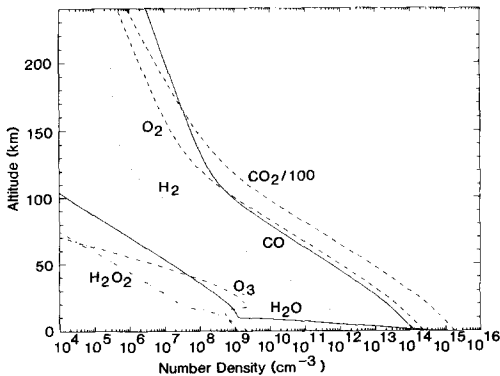


FIG. 2. Altitude profiles of the number densities of the more abundant species computed by our photochemical model using reactions in Table Ia.

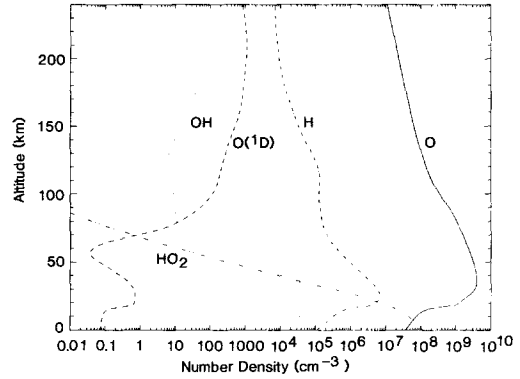


FIG. 3. Same as Fig. 2 for minor species in our model.

again is within the uncertainties of both the Sridharan *et al.* (1982) and Keyser (1986) laboratory measurements.

Results obtained from our model computation for the more abundant species CO₂, CO, O₂, O₃, H₂O, H₂O₂, and H₂ are shown in Fig. 2. The concentrations of the less abundant radical species O, O(¹D), H, OH, and HO₂ are given in Fig. 3. In general, the agreement between our results and those of Kong and McElroy (1977) is fairly good. The minor differences may be attributed to revisions in the rate coefficients. The concentrations of deuterated species, HDO, HD, HDO₂, D, OD, and DO₂, are shown in Fig. 4. These results are new.

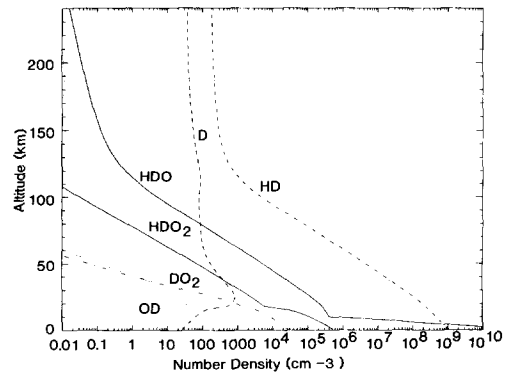


FIG. 4. Altitude profiles of the number densities of the deuterated species computed by our model using reactions in Table Ib.

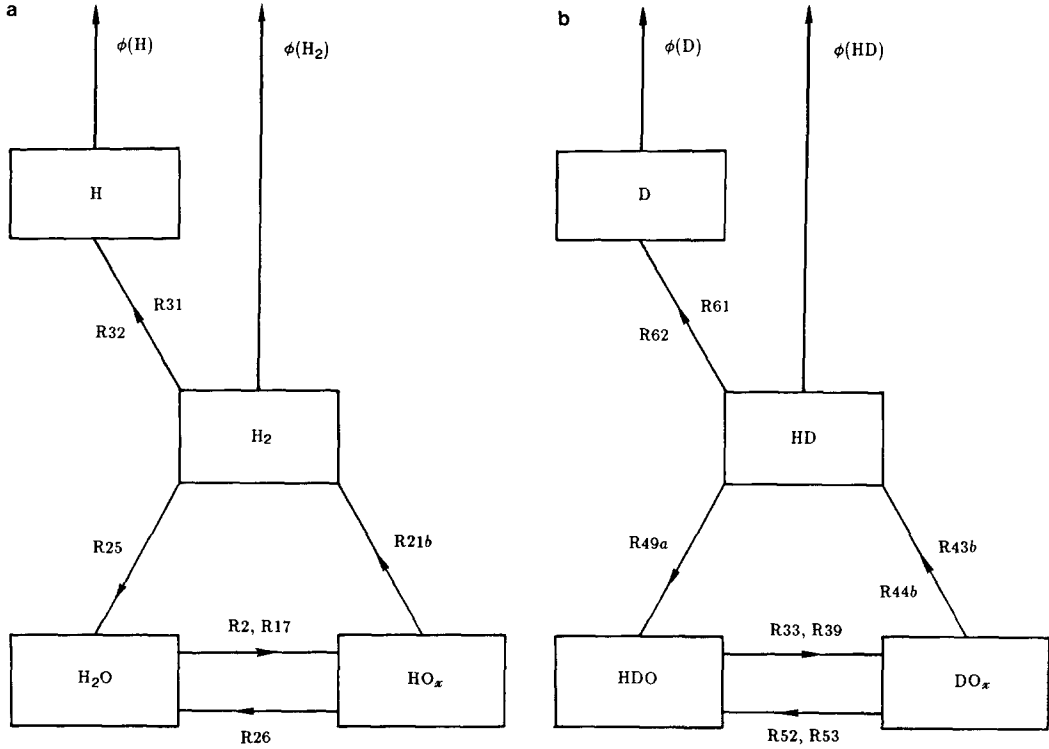


FIG. 5. (a) Flow chart for hydrogen species in the photochemical model $HO_x = H, OH, HO_2,$ and H_2O_2 . Only the principal reactions responsible for the interconversion of species are shown. The total integrated rate of H_2O destruction is 1.1×10^9 molecules $cm^{-2} sec^{-1}$. The escape fluxes of H and H_2 are $\phi(H) = 5.4 \times 10^7$ and $\phi(H_2) = 5.3 \times 10^7$ molecules $cm^{-2} sec^{-1}$. (b) Same as (a), for deuterium species. $DO_x = D, OD, DO_2,$ and HDO_2 . The total integrated rate of HDO destruction is 3.5×10^5 molecules $cm^{-2} sec^{-1}$. The escape fluxes of D and HD are $\phi(D) = 7.4 \times 10^3$ and $\phi(HD) = 8.6 \times 10^2$ molecules $cm^{-2} sec^{-1}$.

The most important result computed in this model is the rate of escape of hydrogen versus that of deuterium. Let

$$\phi_1 = \phi(H) + 2\phi(H_2) + \phi(HD),$$

$$\phi_2 = \phi(D) + \phi(HD),$$

and

$$R = \frac{\phi_2/\phi_1}{[HDO]_0/2[H_2O]_0},$$

where $[H_2O]_0$ and $[HDO]_0$ are the concentrations of H_2O and HDO, respectively, at the ground (the D/H ratio for water in the bulk atmosphere is assumed to be equal to that in the terrestrial oceans). The numerical values are

$$\phi_1 = 1.6 \times 10^8 \text{ atoms } cm^2 \text{ sec}^{-1},$$

$$\phi_2 = 8.3 \times 10^3 \text{ atoms } cm^2 \text{ sec}^{-1},$$

$$R = 0.32.$$

Since R is a measure of the efficiency of escape of D relative to H, this result implies that the atmosphere of Mars would become greatly enriched in D as a result of planetary evolution.

Figure 5a shows a flow chart for the hydrogen species in the model. Destruction of H_2O , mainly by R2 and R17, results in the production of HO_x ($= H, OH, HO_2,$ and H_2O_2). The HO_x species recombine mostly through R26 to regenerate H_2O . However, a small fraction ($\sim 10\%$) is converted into H_2 via R25. H_2 flows to the upper atmosphere where it is partially dissociated into H by R31 and R32. Both H and H_2 can

TABLE III

SENSITIVITY STUDY OF THE DEPENDENCE OF THE EFFICIENCY FACTOR R TO THE VARIOUS CHEMICAL AND PHYSICAL PROCESSES IN THE MODEL

Case	Parameters changed	R	Remarks
1	—	0.32	Standard model
2	a	0.32	Test exchange reactions
3	b	0.33	Test branching ratios
4	c	0.09	Test ion reactions
5	d	0.42	Test diffusive separation
6	e	0.85	Test effusion velocities
7	$d + e$	0.97	Test isotope mass effect
8	$d + e + b$	1.0	Verify dominance of d , e , and b

^a Turn off exchange reactions: $k_{50} = k_{51} = k_{59} = k_{60} = 0$.

^b Set deuterium reactions and their branching ratios to be those for hydrogen: $k_{38a,b} = \frac{1}{2}k_{15}$; $k_{42} = k_{20}$; $k_{43a,b,c} = k_{21a,b,c}$; $k_{48a,b} = \frac{1}{2}k_{25}$; $k_{49a,b} = \frac{1}{2}k_{25}$; $k_{55a,b} = \frac{1}{2}k_{28}$; $k_{61a,b} = \frac{1}{2}k_{31}$.

^c Turn off the ion reactions: $k_{61a} = k_{61b} = k_{62} = 0$.

^d Set the mass of deuterium $m_D = 1$, so that the diffusion coefficients and scale heights for deuterium species are the same as those for the corresponding hydrogen species. The effusion velocities are not changed.

^e Set the effusion velocities of the deuterated species equal to those of the corresponding hydrogen species: $\langle v \rangle_D = \langle v \rangle_H$, $\langle v \rangle_{HD} = \langle v \rangle_{H_2}$.

escape from Mars. The fluxes are 5.4×10^7 and $5.3 \times 10^7 \text{ cm}^{-2} \text{ sec}^{-1}$, respectively. Figure 5b shows a similar flow chart for the deuterium species in the model. The detailed pathways are obvious from an inspection of Fig. 5b and will not be described. The fluxes for D and HD are 7.4×10^3 and $8.6 \times 10^2 \text{ cm}^{-2} \text{ sec}^{-1}$, respectively. We notice that the main loss of deuterium is via D and not via HD, whereas in the escape of hydrogen the losses via H_2 and H are about the same. This is the result of the very low effusion velocity for HD (see Fig. 1).

The question arises as to which processes and assumptions in the model are primarily responsible for the computed value of R . A large number of runs were carried out to determine the contributions of the various chemical and physical processes to this efficiency factor. The results are summarized in Table III. Case 1 is our standard case, with $R = 0.32$. In case 2, we turn off the exchange reactions R50, R51, R59, and R60. There is no effect mainly because the D atoms are a minor com-

ponent of DO_x in the photochemical region (see Fig. 4). In case 3, we show that the value of R is not affected by the choice of branching ratios for the reactions involving the deuterated species. Case 4 shows that the ion reactions R61 and R62 are important. The reason is that these reactions convert HD to D, and the latter escapes much more efficiently than the former. By suppressing this conversion mechanism, the escape of deuterium becomes more difficult and R is accordingly smaller.

The next three cases are intended to test the sensitivity of R to the mass difference between D and H. Case 5 tests the importance of diffusive separation between deuterium and hydrogen species. Case 6 tests the sensitivity of the model to effusion velocities. The result of case 7, which combines case 5 and case 6, suggests that the physical difference in mass between deuterium and hydrogen is the dominant factor. Case 8 suppressing all the important physical and chemical differences between D and H yields a value of $R = 1$, indicating no differentiation between D and H species. This provides a check for our model.

In summary, the most important factors responsible for determining the efficiency factor, R , are the physical processes (molecular diffusion and effusion velocities), and the ion reactions R61 and R62. The kinetic fraction due to neutral reactions is less important.

IMPLICATIONS FOR THE ABUNDANCE OF CRUSTAL WATER

Having computed the efficiency factor R for the escape of deuterium relative to that of hydrogen, we can now apply the formalism developed by McElroy and Yung (1976) to place constraints on the subsurface reservoirs of water on Mars. Let ϕ_1 denote the rate at which hydrogen atoms escape to space ($\text{cm}^{-2} \text{ sec}^{-1}$). Let a_0 denote the total number of hydrogen atoms (cm^{-2}) present in the atmosphere as H_2O , 5×10^{19} . We assume the initial D/H ratio of water on Mars is f_0 , equal to the terrestrial value. As

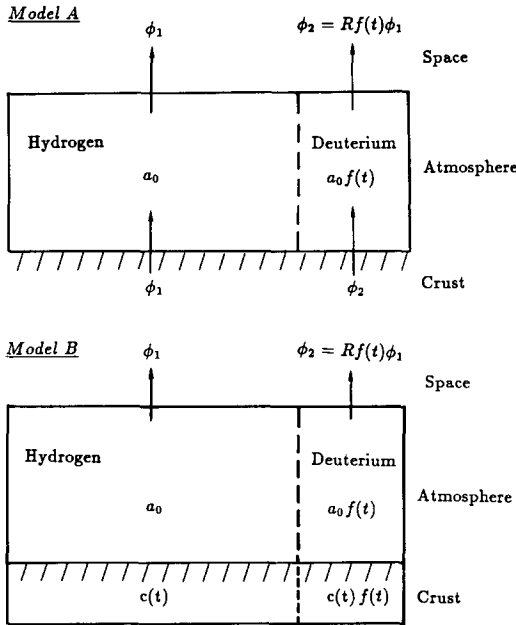


FIG. 6. A schematic diagram of the evolution of hydrogen and deuterium on Mars. In model A the crust is a source of water but does not equilibrate isotopically with atmospheric water. In model B the crustal and atmospheric water are equilibrated isotopically.

a consequence of atmospheric evolution, the D/H ratio of atmospheric water would evolve, as determined by the function

$$f(t) = \frac{[\text{HDO}](t)}{2[\text{H}_2\text{O}](t)},$$

where $[x](t)$ denotes the column abundance of species x as a function of time. Note that $f(0) = f_0$. The rate of escape of deuterium is $\phi_2 = Rf(t)\phi_1$, where we have assumed that R is approximately a constant.

We consider two very simple models. In model A we assume that the atmospheric water does not exchange with the bulk reservoir of subsurface water. However, H_2O is supplied at the rate just sufficient to replenish the rate of loss of hydrogen escape. The isotopic ratio of subsurface water is assumed to be equal to f_0 . The mechanics of this model are illustrated in Fig. 6. It is easy to solve the equation that

governs the evolution of $f(t)$. The details are given in McElroy and Yung (1976). The isotopic ratio of atmospheric water is given by

$$f(t) = f_0 \left[\frac{1}{R} + \frac{1-R}{R} \exp\left(-\frac{R\phi_1 t}{a_0}\right) \right].$$

It is clear that the atmosphere would become enriched in deuterium,

$$\lim_{t \rightarrow \infty} f(t) = \frac{f_0}{R} \approx 3f_0,$$

on a time scale t given by

$$t = \frac{a_0}{R\phi_1} \approx 10^5 \text{ years.}$$

Since this enrichment is lower than that reported by Owen *et al.* (1987), we conclude that the assumption of no exchange between atmospheric and crustal water must be modified.

Consider now a slightly more complicated model, model B, as shown schematically in Fig. 6. We assume the presence of a crustal reservoir of hydrogen $c(t)$, which can actively exchange with the atmosphere. In this case, the isotopic ratio for atmospheric water vapor and crustal ice differs because of fractionation between the two phases. For mean surface conditions on Mars, we have

$$\frac{\left(\frac{\text{HDO}}{\text{H}_2\text{O}}\right)_{\text{vapor}}}{\left(\frac{\text{HDO}}{\text{H}_2\text{O}}\right)_{\text{ice}}} \approx 0.79$$

(Matsuo *et al.* 1964, Merlivat and Nief 1967, Jancso and van Hook 1974). Letting f_a be the isotopic ratio in the atmosphere and $f(t)$ the ratio in crustal water, then

$$\frac{f_a}{f_0} = \frac{f_a}{f(t)} \cdot \frac{f(t)}{f_0}$$

and for $\frac{f_a}{f(t)} = 0.79$ and $\frac{f_a}{f_0} = 6$ from the observations, we have $\frac{f(t)}{f_0} = 7.6$. The time

evolution of $f(t)$ in this case is given by

$$f(t) = f_0 \left\{ \frac{a_0 + c(o)}{a_0 + c(t)} \right\}^{(1-R)}$$

(see McElroy and Yung (1976) for details), where $c(o)$ is the initial endowment of crustal water, and

$$c(t) = c(o) - \phi_1 t$$

since $c(t) \gg a_0$, we have

$$c(t) \approx \frac{\phi_1 t}{\alpha - 1},$$

where

$$\alpha = \left(\frac{f(t)}{f_0} \right)^{1/(1-R)}$$

Taking $f(t)/f_0 \approx 7.6$, we have $\alpha = 19.7$, and $c(t) = 0.05\phi_1 t$. For $\phi_1 = 1.6 \times 10^8$ atoms $\text{cm}^{-2} \text{sec}^{-1}$ and $t = 4.5$ by, we obtain an estimate of $c(t)$, the present reservoir of H_2O , of 6.0×10^{23} molecules of $\text{H}_2\text{O} \text{ cm}^{-2}$ or 0.2 m of water. On the basis of the above analysis, a general relation between isotopic enrichment, $f(t)/f_0$, and the implied abundance of crustal water is derived and is given in Fig. 7. Note that the time constant for losing the H_2O currently present in the atmosphere is of the order of 10^5 years. But the factor of 6 enrichment must be accumulated over 4.5 by.

It is of interest to compare our estimate of the amount of H_2O reservoir on Mars with abundance estimates of previous workers. Numerous arguments have been advanced in the past for and against the existence of large amounts of H_2O on Mars. Table IV summarizes the various estimates.

McElroy *et al.* (1976b, 1977) derived the quantity of H_2O outgassed on Mars in examination of nitrogen isotope abundances. Presently 2.7% N_2 exists in the Martian atmosphere with a $^{15}\text{N}/^{14}\text{N}$ ratio 1.7 times that of the Earth. This enrichment was interpreted as remains from a greater nitrogen atmosphere in the past. If only atmospheric escape is considered, this enrich-

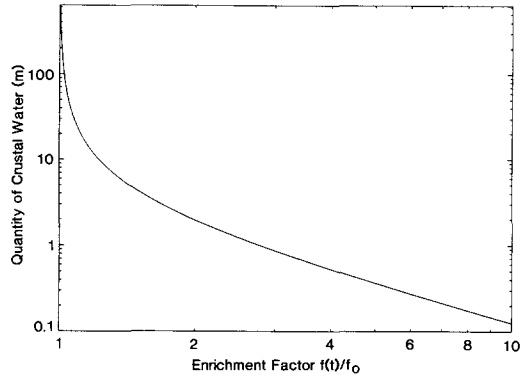


FIG. 7. Relation between deuterium enrichment factor, $f(t)/f_0$, for atmospheric water and implied abundance of crustal water.

ment points back to an initial nitrogen partial pressure of 1.3 mbar. If, however, loss to HNO_2 and HNO_3 is included, this enrichment points back to an initial 30 mbar. Assuming an $\text{N}/\text{H}_2\text{O}$ ratio similar to the Earth's, these partial pressures translate into 8–133 m of outgassed H_2O .

Accretionary models have also been used to estimate the amount of H_2O outgassed from Mars' interior. The most recent of these, by Dreibus and Wänke (1984, 1986), can be applied to any of the inner planets with accumulation of two components: one highly reduced and volatile-poor versus one fully oxidized and volatile-rich. To match the Martian mantle composition, they found 20% more of the volatile-rich com-

TABLE IV
ESTIMATES OF H_2O RESERVOIR ON MARS

(1) Analysis of HDO (this work) ^a	3.6 m
(2) Accretional model	1–50 m
(3) Scaling based on nitrogen	8–133 m
(4) Geological estimates ^b	494–544 m

Note. Abundance is expressed in equivalent thickness of H_2O in meters averaged over the surface of the planet.

^a About 3.4 m has escaped, and 0.2 m remains in the reservoir.

^b Summation of fretted terrain, outflow channel, megaregolith clay, polar layered terrain, and volcanic lava estimates.

ponent accumulated on Mars than on the Earth. However, this initial large volatile content was lost when the two components accreted together and iron reacted to produce FeO and H₂. The H₂ molecules then escaped. Unlike the Earth, which accreted inhomogeneously and retained its volatiles, Mars was left with only 1–50 m of H₂O to outgas.

Geological inventories (Carr 1986) contrast sharply with these above estimates with values almost two orders of magnitude larger. With 10–20% ice in debris aprons of fretted terrains in the cratered high latitudes, Carr finds 75–125 m of H₂O associated with the top 1 km of the Martian crust; 350 m should have been lost from the deeper megaregolith based on calculations of ground water needed to carve the outflow channels. Another 9 m may have been chemically bound into clays produced during the heavy bombardment period and folded into the megaregolith 3.8 billion years ago. The polar layered terrains, furthermore, may have stored 14 m of H₂O, given an average thickness of 2 km and a 1:1 ratio of dust to ice. Finally, Greeley (1987) estimated another 46 m of H₂O released over Martian history through volcanism, using mapped volcanic flows and an assumed 1% by weight H₂O content in the lava. These geological estimates amount to a cumulative abundance of 494–544 m of H₂O over time. It should be noted, however, that exchange may have occurred between these geological reservoirs.

In summary, our estimate of crustal H₂O on Mars is similar to other geochemical estimates, but much lower than the geological estimates. There may not be a serious conflict because we have estimated the exchangeable reservoir, whereas part of the crust water on Mars may not readily exchange with the atmosphere.

CONCLUSION

An accurate measurement of the D/H ratio of water in the Martian atmosphere, together with detailed modeling of the

chemistry and dynamics of hydrogen, may provide the only reliable way to estimate the magnitude of the exchangeable reservoir of crustal water on Mars. Based on the preliminary data of Owen *et al.* (1987), we conclude that Mars currently contains at least 0.2 m of subsurface water. This estimate is considerably smaller than the recent geological estimates. However, we must emphasize that only the *exchangeable* part of the crustal reservoir would have any impact on the isotopic evolution of hydrogen. Thus, we conclude that the bulk of the hypothesized 0.5–1 km water, if it exists, must have remained immobilized throughout geological time. On the other hand our result is based on two fundamental assumptions: that the D/H ratio in the primordial Martian H₂O is the same as the terrestrial value, and that the escape rate of hydrogen has remained constant throughout geological time. Hence our result must be taken with caution. There is a need to improve the chemical kinetics of deuterated species (as summarized in Table Ib) with appropriate laboratory studies, and obviously a precise determination of the D/H ratio in the Martian atmosphere would narrow the range of uncertainties of this analysis.

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