

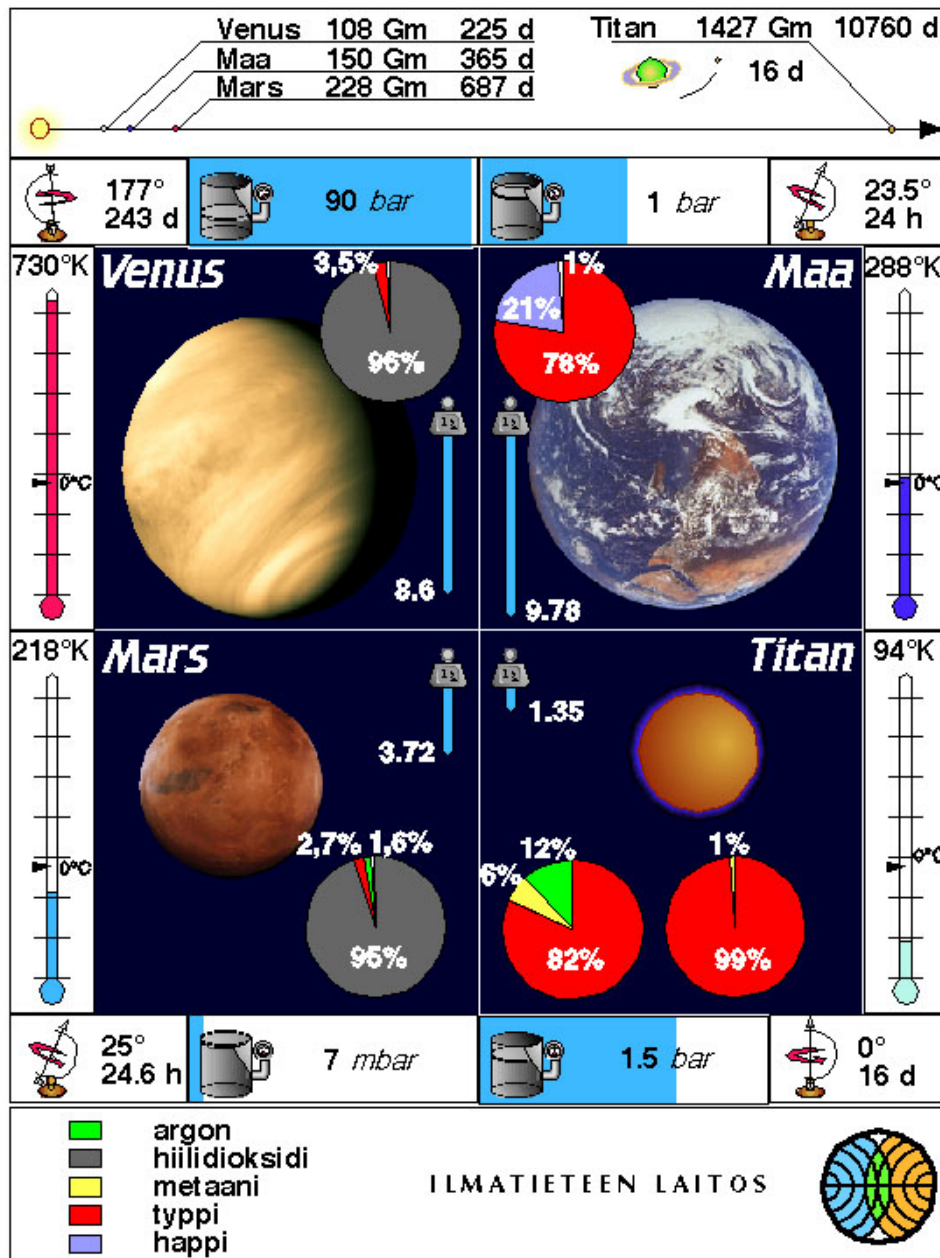
# The Martian Upper Atmosphere

- By Paul Withers, newly graduated from LPL's PhD program
- Dissertation on "Tides in the Martian Atmosphere"
- Lecture given to Roger Yelle's PTYS 544 class
- 2003.04.08

# Plan

- Summary of Atmospheric Properties
- Elemental and Isotopic Composition
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- Atmospheric Escape
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# Summary of Atmospheric Properties



Teemu Mäkinen 1997

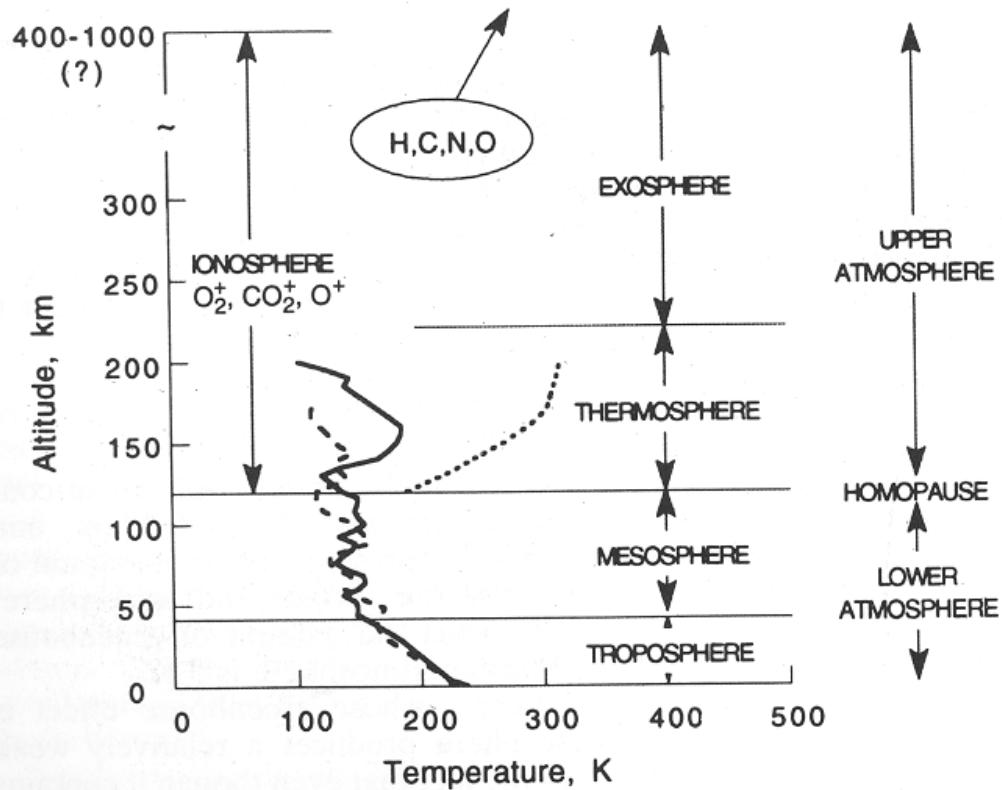
Teemu Mäkinen,  
Finland

- The Mars atmosphere consists of a troposphere, an isothermal mesosphere, and a thermosphere where the daytime temperature at the top of the thermosphere may vary depending on the time in the solar cycle. Photochemistry occurs throughout the entire Mars atmosphere, from the top of the thermosphere to the bottom of the troposphere. The photodissociation of the major constituent carbon dioxide produces carbon monoxide and atomic oxygen. The recombination of CO and O takes place in the troposphere through catalytic reactions involving the odd-hydrogen species, H, OH and HO<sub>2</sub>. Observational tests that confirm the general validity of the odd-hydrogen model are: (1) the observed abundances of molecular oxygen and carbon monoxide; (2) the observed seasonal variation of ozone over the polar caps of Mars; and (3) the observed density of atomic hydrogen in the thermosphere. Odd nitrogen is produced in the upper atmosphere from the reaction of N(2D) and CO<sub>2</sub>. Viking mass spectrometers have measured neutral nitric oxide molecules in the Mars atmosphere. Photochemical processes control the behavior of the ionosphere of Mars. The principal ion is O<sub>2</sub><sup>+</sup> with smaller amounts of CO<sub>2</sub><sup>+</sup> and O<sup>+</sup> at the ionospheric peak near 135 km. The density of the O<sup>+</sup> ion becomes comparable to the density of the O<sub>2</sub><sup>+</sup> ion near the top of the atmosphere. The most intense emissions in the ultraviolet airglow of Mars are the carbon monoxide Cameron bands. Strong ultraviolet emissions from CO<sub>2</sub><sup>+</sup> are the result of photoionization of carbon dioxide. The atomic oxygen airglow at 1304 Å is used to determine the density of atomic oxygen and the 1216 Å Lyman α line is used to calculate the density of atomic hydrogen and, when coupled with the temperature measurement, the escape flux of atomic hydrogen. The most intense airglow is the infrared atmospheric band of O<sub>2</sub> at 1.27 μm that results from the photodissociation of ozone. The escape mechanism for atomic hydrogen is thermal, or Jeans, escape while atomic oxygen escape is caused by a nonthermal process, namely, the dissociative recombination of O<sub>2</sub><sup>+</sup>. The ratio of deuterium to hydrogen is enriched by a factor of 6. This observation may be used to study the past history of water on Mars. Three-dimensional models of the Mars thermospheric circulation show that planetary rotation has a significant influence on the wind, composition and temperature structure. There is upward flow on the day side, downward flow on the night side. Observations of the thermospheric temperatures near solar minimum from Viking showed a mean dayside temperature of 195 K and near solar maximum from Mariners 6 and 7, a value of 310 K. The challenge for the future is to make observations to study the diurnal, seasonal and solar cycle changes that occur in the Mars atmosphere. (**Abstract of reference 1, Barth chapter in Mars book**)

- Table 7.1 Astronomical and atmospheric data for Mars
- Radius (equatorial) 3394.5 km
- Mass 6.4185E23 kg
- Mean density 3.9335 g cm<sup>-3</sup>
- Gravity (surface. equator) 3.711 m s<sup>-2</sup>
- Semimajor axis 1.52366 AU
- Obliquity (relative to orbital plane) 25.19 degrees
- Eccentricity of orbit 0.0934
- Period of revolution (Earth days) 686.98
- Orbital velocity 24.13 km s<sup>-1</sup>
- Period of rotation 24h 37m 22.663s
- Atmospheric pressure at surface 5.6 mbar
- Mass of atmospheric column 1.50E-2 kg cm<sup>-2</sup>
- Total atmospheric mass 2.17E16 kg
- Equilibrium temperature 216 K
- Surface temperature 220 K
- Annual variation in solar insolation (a) 1.45
- Atmospheric scale height (T = 210 K) 10.8 km
- Adiabatic lapse rate (dry) 4.5 K km<sup>-1</sup>
- Atmospheric lapse rate (b) 2.5 K km<sup>-1</sup>
- Escape velocity 5.027 km s<sup>-1</sup>

- Taken from Kieffer. H. H. et al. (1992).
- (a) Based on the ratio of aphelion to perihelion distance squared.
- (b) Mean observed value. variable.

- **Table 7.1 from reference 2, Yung and DeMore**



**Figure M25** Vertical structure of the Martian atmosphere. Solid and dashed curves represent the temperature profiles measured by the Viking Lander 1 and 2 respectively, as they descended to the surface. Dotted curve above 120 km represents a theoretical profile consistent with Mariner 9 airglow measurements.

From reference 7, Haberle  
chapter in Encyclopedia

Observations from Viking lander p, T sensors,  
mass spectrometer; orbiting IR spectrometers and  
entry accelerometers for T(z)

# Elemental and Isotopic Composition

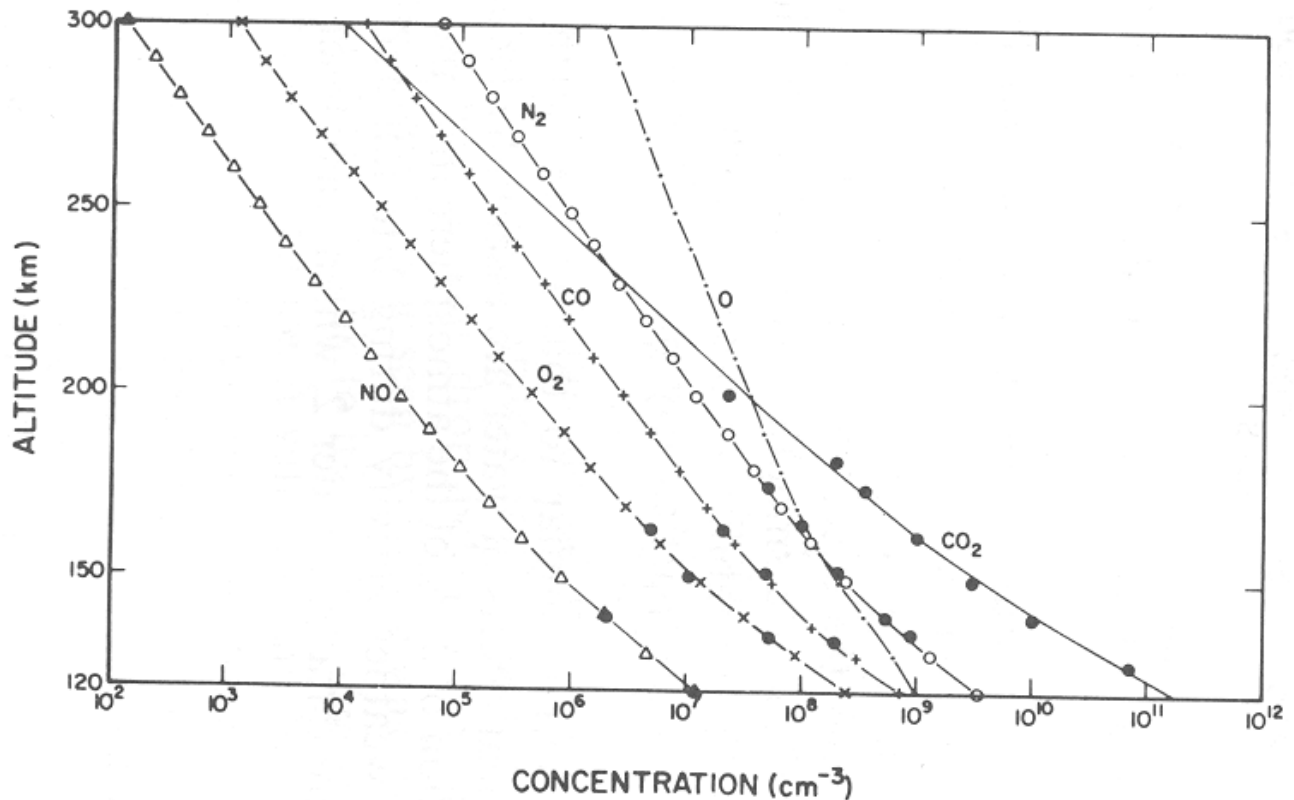


Fig 1.24 from Chamberlain and Hunten

Homopause at ~125 km  
Observations from mass spectrometers during Viking entry and after landing

**Table 7.2** Chemical composition of the atmosphere of Mars

Gas	Abundance	Reference and remarks
CO <sub>2</sub>	0.9532	(1)
N <sub>2</sub>	0.027	(1)
<sup>40</sup> Ar	0.016	(1)
O <sub>2</sub>	$1.3 \times 10^{-3}$	(1)
CO	$7.0 \times 10^{-4}$	(1)
H <sub>2</sub> O	$3.0 \times 10^{-4}$	(2); variable
<sup>36</sup> Ar+ <sup>38</sup> Ar	$5.3 \times 10^{-6}$	(1)
Ne	$2.5 \times 10^{-6}$	(1)
Kr	$3.0 \times 10^{-7}$	(1)
Xe	$8.0 \times 10^{-8}$	(1)
O <sub>3</sub>	$3.0 \times 10^{-8}$	(3); variable

(1) Owen et al. (1977); (2) Farmer and Doms (1979); (3) Barth (1974).

**Table 7.3** Isotopic composition of the atmosphere of Mars

Species	Ratio	Reference
D/H	$9 \pm 4 \times 10^{-4}$	(1)
	$7.8 \pm 0.3 \times 10^{-4}$	(2)
<sup>12</sup> C/ <sup>13</sup> C	$90 \pm 5$	(3)
<sup>14</sup> N/ <sup>15</sup> N	$170 \pm 15$	(3)
<sup>16</sup> O/ <sup>17</sup> O	$2655 \pm 25$	(2)
<sup>16</sup> O/ <sup>18</sup> O	$490 \pm 25$	(3)
	$545 \pm 20$	(2)
<sup>36</sup> Ar/ <sup>38</sup> Ar	$5.5 \pm 1.5$	(4)
<sup>40</sup> Ar/ <sup>36</sup> Ar	$3000 \pm 500$	(5)
<sup>129</sup> Xe/ <sup>132</sup> Xe	$2.5 \pm \frac{2}{1}$	(5)

(1) Owen et al. (1988); (2) Bjoraker et al. (1989); (3) Nier and McElroy (1977); (4) Biemann et al. (1976).

From reference 2



# Energetics and Thermal Structure (1)

- Short (<200nm) wavelength EUV is readily absorbed by most atmospheric species to either ionize or excite the electronic state. Other wavelengths (VIS, IR) in which significant energy is radiated from the Sun are less readily absorbed.
- So upper atmosphere is dominated by absorption of UV and charged particles from the solar wind. These fluxes are very variable (factors of few to ten) over 11 year solar cycle and short-term solar flares/CMEs.
- Observations from Viking entry accelerometers, orbiting IR spectrometers, radio occultations

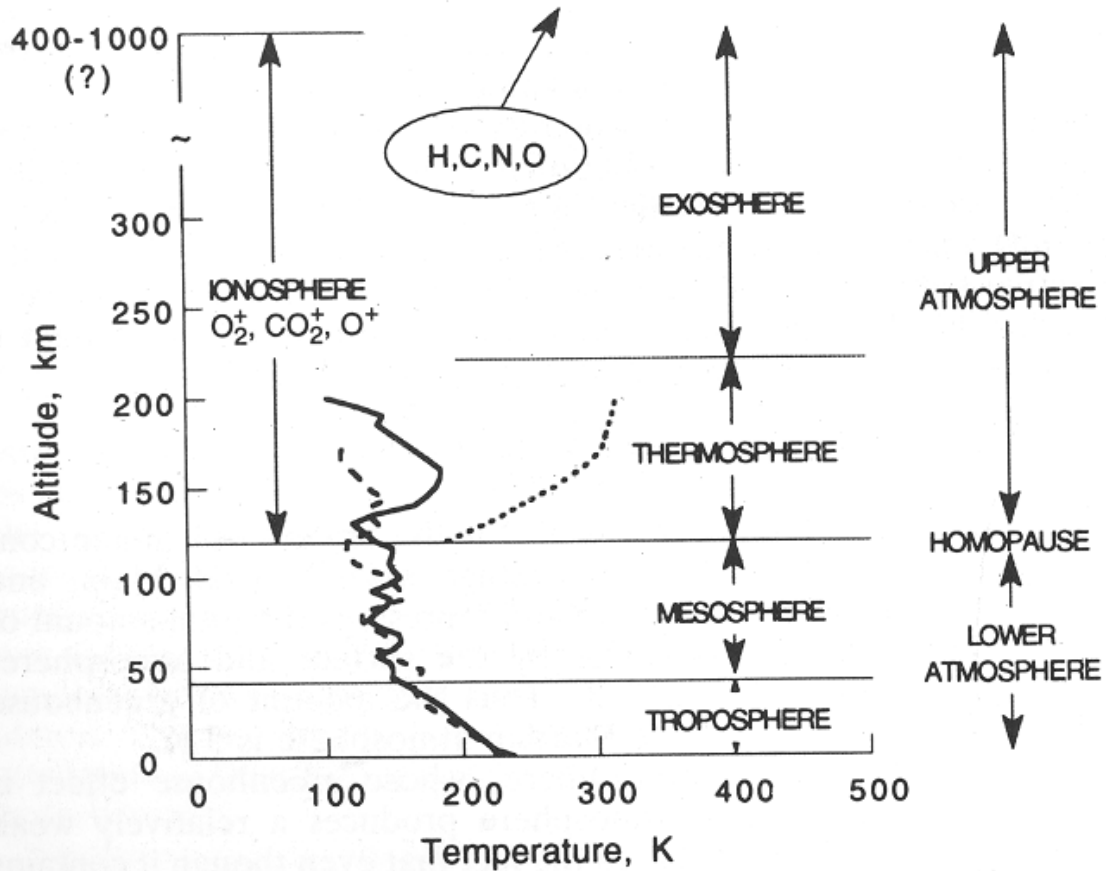
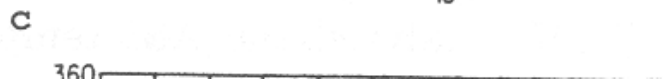
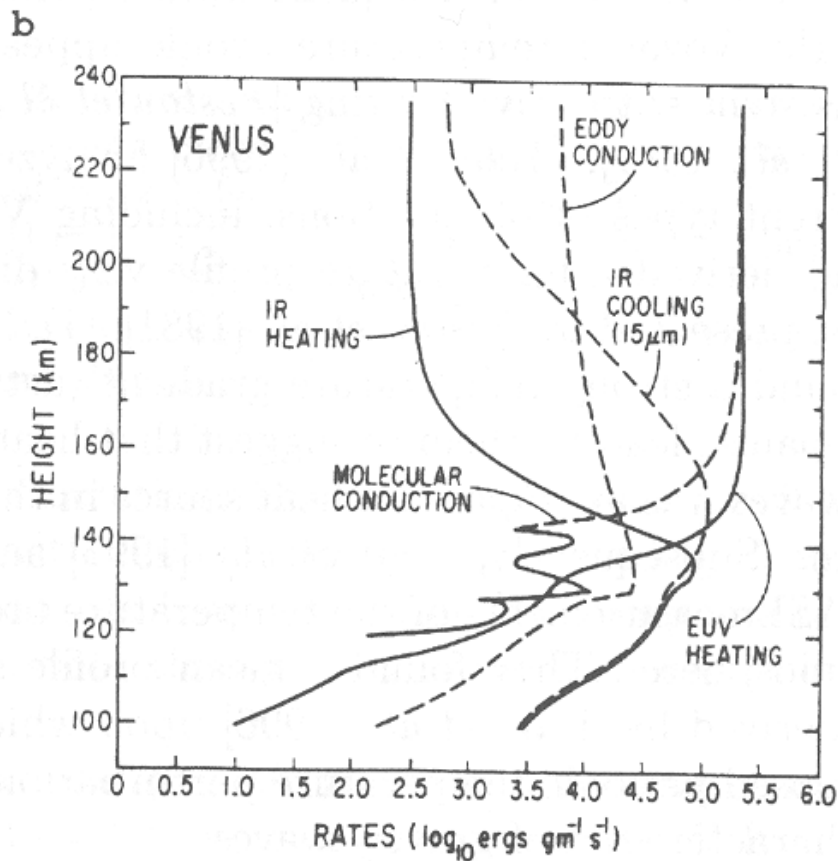
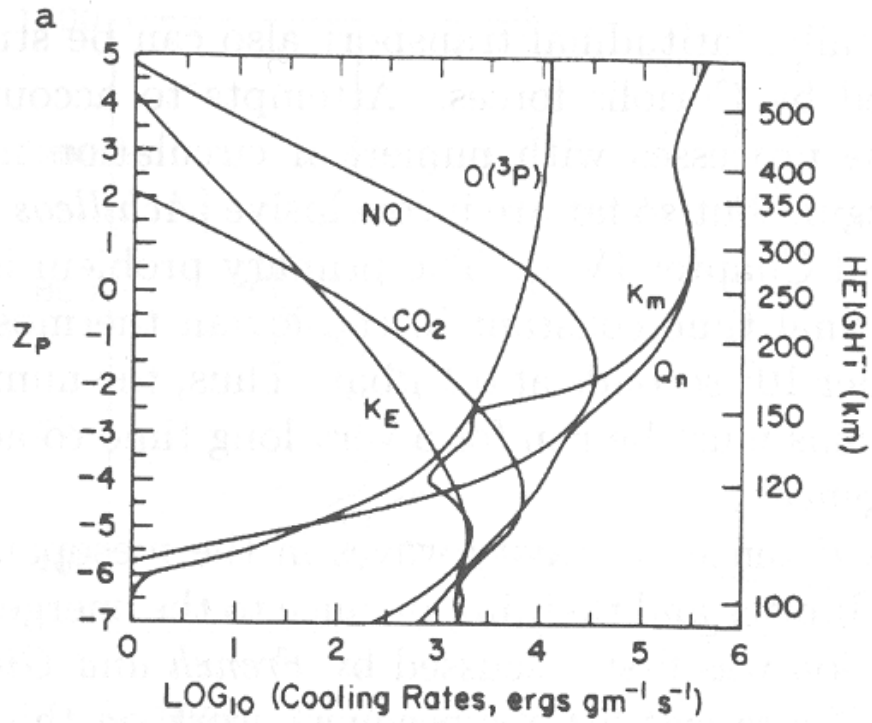


Figure M25 Vertical structure of the Martian atmosphere. Solid and dashed curves represent the temperature profiles measured by the Viking Lander 1 and 2 respectively, as they descended to the surface. Dotted curve above 120 km represents a theoretical profile consistent with Mariner 9 airglow measurements.

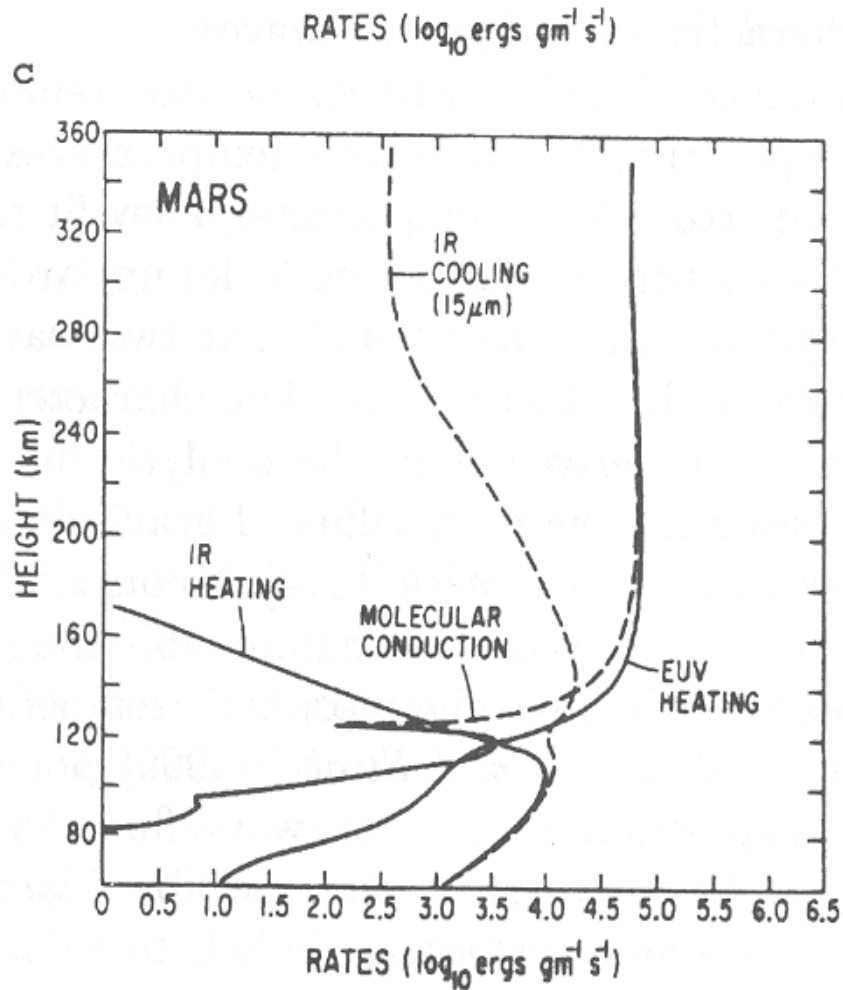
From reference 7, Haberle  
chapter in Encyclopedia

Energy also transported to upper atmosphere  
by upwardly-propagating tides

From reference 3...



...From reference 3



**Figure 2.** a) Heating and cooling rates for the Earth's upper atmosphere [Bougher and Roble, 1991, Fig. 3b]. b) Cooling rates in the atmosphere of Venus [Bougher and Roble, 1991, Fig. 3a].  $K_m$  represents cooling by molecular conduction and  $K_E$  cooling by eddy conduction. The curves labeled by molecular formulas represent radiative cooling by the indicated species.  $Q_n$  represents the net heating rate. c) Heating and cooling rates in the upper atmosphere of Mars [Bougher and Roble, 1991, Fig. 3c].

# Energetics and Thermal Structure (2)

- Exospheric T asymptotes to constant value since neither upwelling nor downwelling radiation fluxes change significantly when propagating through such low-density regions. Usually a relatively high value.
- Dominant mode of heat transfer at highest altitudes (exosphere and thermosphere) is molecular conduction since radiation can't carry enough of the energy. Have to conduct heat downwards, so T must decrease as z decreases. Eventually densities have increased enough to make radiative cooling viable – mesopause. Composition is important here as CO<sub>2</sub> has transition at 15μm that is at right wavelength for cooling. O/CO<sub>2</sub> collisions make 15μm cooling more efficient.

# Dynamics

- Essentially unobserved – that hasn't stopped anyone from speculating
- No strong global magnetic field to confuse matters, just a weak patchy magnetic field whose effects are not really included in models yet
- Need to worry about 3D, unlike much chemistry and  $T(z)$  work
- Winds caused by variations in solar heating (daily, seasonal, annual, solar cycle)  $\sim 100 \text{ ms}^{-1}$  plausible
- Hot dayside has  $p(z_0)$  greater than cold nightside, pressure differences drive global thermospheric circulation that transports heat from dayside to nightside, rotation timescale causes a phase lag.
- Lower atmosphere influences this. Dust storms heat and inflate lower atm, change day/night gradients and winds. Also large tides propagating upwards from lower atmosphere can cause pressure gradients and winds.
- Low mass  $\Rightarrow$  very responsive to changes in external forcings
- MGS accelerometer might provide some observations

# Chemistry

- Both lower and upper atmosphere
- Odd hydrogen species (H, OH, HO<sub>2</sub>) derived from photolysis of H<sub>2</sub>O catalyse the recombination of CO and O<sub>2</sub> into CO<sub>2</sub>.
- H<sub>2</sub>O and O<sub>3</sub> are anti-correlated. If H<sub>2</sub>O is present, it is photolysed into odd hydrogen species and then catalyses the conversion of O<sub>3</sub> into O<sub>2</sub> and O<sub>2</sub> back into CO<sub>2</sub>. If H<sub>2</sub>O is not present, then the O<sub>2</sub> can be converted into O<sub>3</sub>.
- There's some nitrogen as well
- 5 – 110 nm solar EUV changes by factors of a few over 11 yr solar cycle, might this alter the chemistry?
- Viking entry and landed mass spectrometers, VO MAWD, M9 UV Spec

## 7.2 Photochemistry

## From reference 2

### 7.2.1 Pure CO<sub>2</sub> atmosphere

The major constituent of the Martian atmosphere, CO<sub>2</sub>, is readily photolyzed by solar ultraviolet radiation under 2050 Å:



where near the threshold the O atom is in the ground state, O(<sup>3</sup>P), but at shorter wavelengths the atom could be in excited states O(<sup>1</sup>D) and O(<sup>1</sup>S). However, the primary fate of the excited atoms is quenching to the ground state by CO<sub>2</sub> (a small fraction of the excited atoms reacts with H<sub>2</sub>O). Once CO<sub>2</sub> is converted into CO and O(<sup>3</sup>P), it is difficult to restore it. The reverse of reaction (7.1),



is spin-forbidden. The three body rate coefficient at 200 K is  $3 \times 10^{-37} \text{ cm}^3 \text{ s}^{-1}$ , a value that is many orders of magnitude smaller than the corresponding rate coefficient for a typical three-body reaction such as



with rate coefficient equal to  $2.8 \times 10^{-32} \text{ cm}^3 \text{ s}^{-1}$  at 200 K. Hence, the net results of CO<sub>2</sub> photodissociation are



Thus, a pure CO<sub>2</sub> atmosphere exposed to solar ultraviolet radiation would have large amounts of CO and O<sub>2</sub> at a ratio of 2 : 1. Of course, O<sub>2</sub> cannot build up indefinitely, and eventually it would dissociate:



We can construct a self-consistent model with reactions (7.1)–(7.5), assuming that the only path for reversing the result of photodissociation (7.4) is the slow reaction (7.2), with the oxygen atoms being supplied by (7.5). Such a model predicts that the mixing ratios of CO and O<sub>2</sub> are  $7.72 \times 10^{-2}$  and  $3.87 \times 10^{-2}$ , respectively. However, the predictions of CO and O<sub>2</sub> are greater than the observed abundances summarized in table 7.2 by factors of 110 and 30, respectively. In addition, the model CO/O<sub>2</sub> ratio of 2 is significantly larger than the observed ratio of 0.5. It is of interest to point out that in this hypothetical model of Mars, the predicted O<sub>3</sub> mixing ratio at the surface is  $10^{-5}$  and the column-integrated O<sub>3</sub> is  $3.4 \times 10^{18} \text{ cm}^{-2}$  or 126 DU (1 Dobson unit =  $2.69 \times 10^{16} \text{ cm}^{-2}$ ). This amount of O<sub>3</sub> is sufficient for shielding the surface of Mars from harmful ultraviolet radiation.



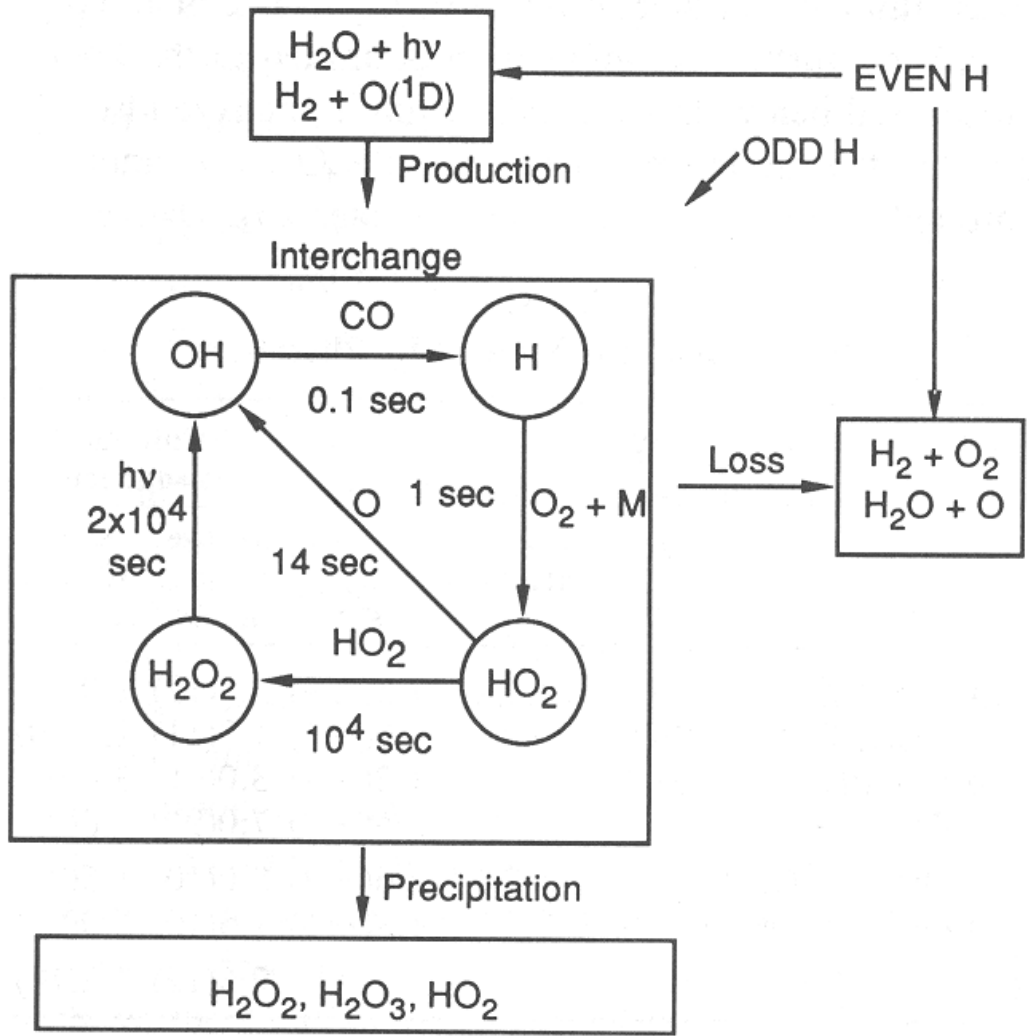


Fig.3. Odd hydrogen: flow diagram for odd hydrogen near the surface of Mars. Beside each arrow is the reaction time in seconds (figure from Chamberlain and Hunten 1987 adapted from Hunten 1979b).

From reference 3

## From reference 2

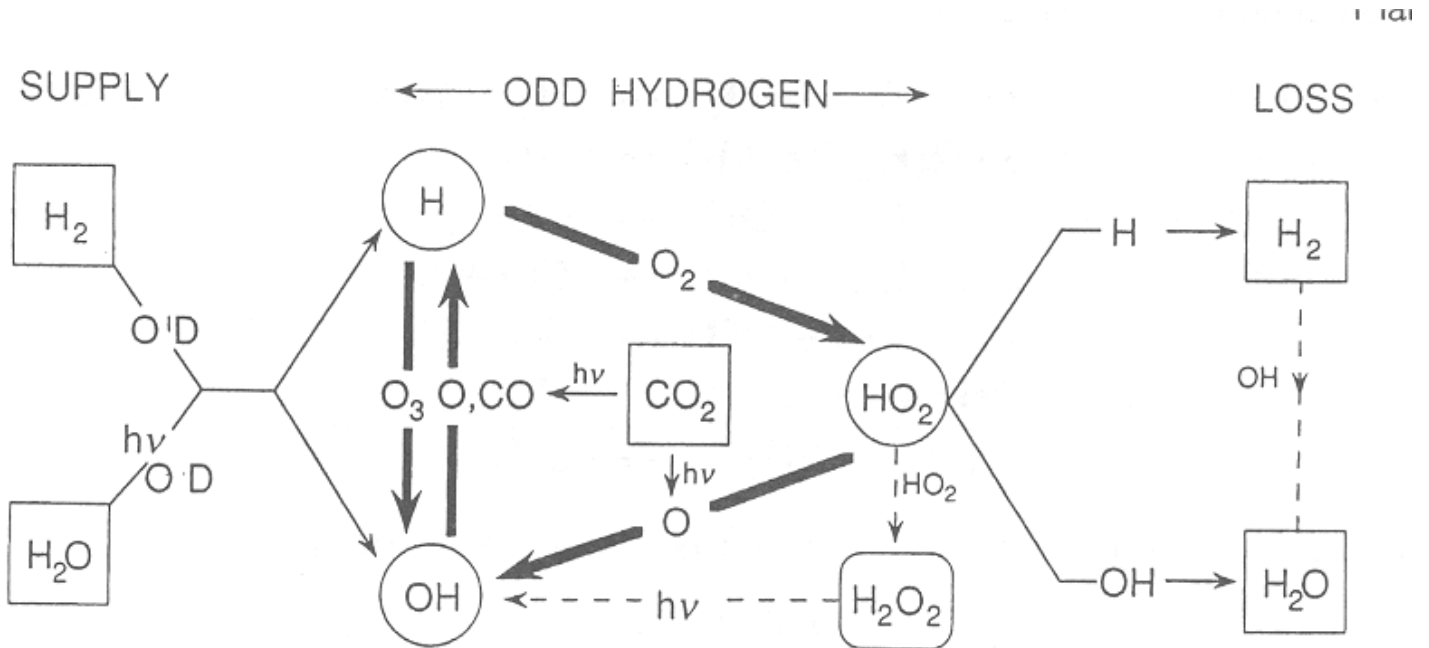


Figure 7.4 Schematic diagram showing the principal pathways for reactions involving hydrogen species. From Nair, H., Allen, M., Anbar, A. D., Yung, Y. L., and Clancy, R. T., 1994, "A Photochemical Model of the Martian Atmosphere." *Icarus* **111**, 124.

## From reference 3

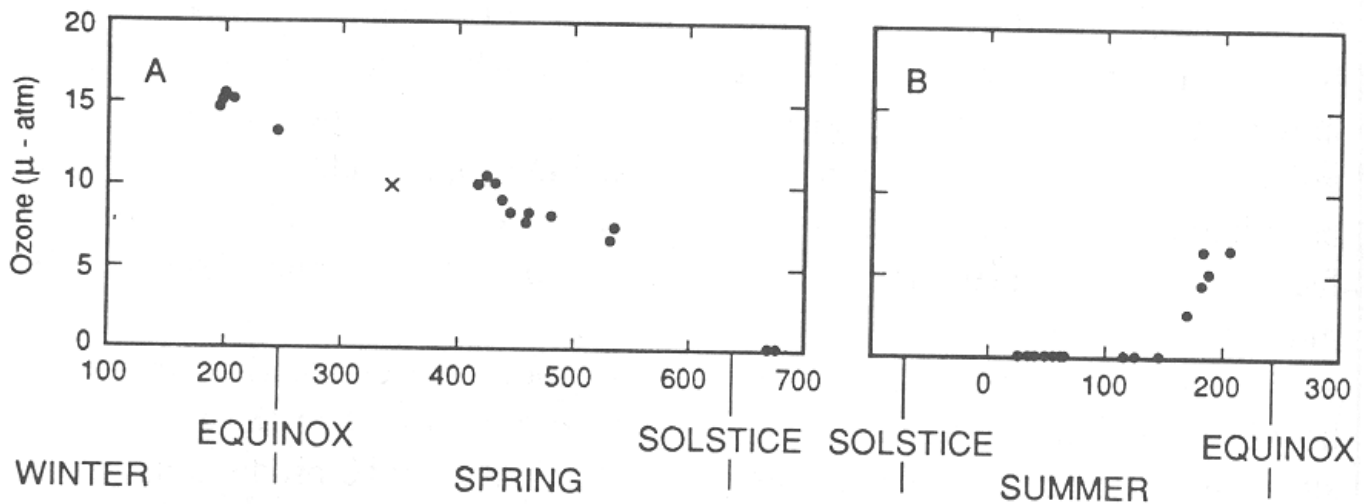
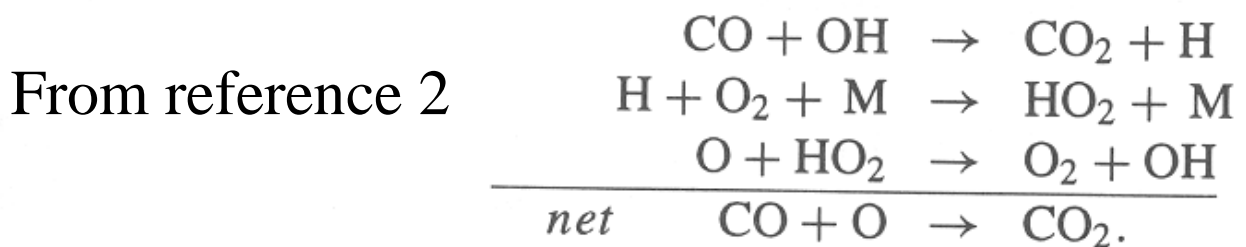


Fig.7. Mariner 9 ozone observations. (A) Amount of ozone observed over the north polar cap during the winter, spring and beginning of summer. The cross refers to the Mariner 7 measurement which was made over the south polar cap in 1969. (B) Amount of ozone observed over the south polar cap during the summer. (figure from Barth et al. 1973).

The sequence of reactions may be summarized as



The net result of chemical scheme (1c) is the conversion of CO to CO<sub>2</sub>.

# Ionosphere

- Odd nitrogen is important here
- Photoionization of CO<sub>2</sub> by solar EUV
- Peak plasma density  $\sim 1\text{E}5\text{ cm}^{-3}$  and height of peak is  $\sim 135\text{ km}$ , also a secondary peak around  $115\text{ km}$ . Primary peak is controlled by photochemistry, not dynamics.
- Patchy magnetic field has significant effects.
- Ionopause, or sharp drop in ion densities at top of ionosphere due to solar wind, at about  $400\text{ km}$ . Need to look at a Mitchell or Acuna paper for some details here.
- Nightside very poorly constrained
- Many radio occultations of electron density, Viking entry in situ RPA identified species

ionosphere. The predominance of  $O_2^+$  is the result of the ion molecule reactions (1) and (2) below, which transform very rapidly the originally produced  $CO_2^+$  and  $O^+$  ions to  $O_2^+$ :



From reference 3

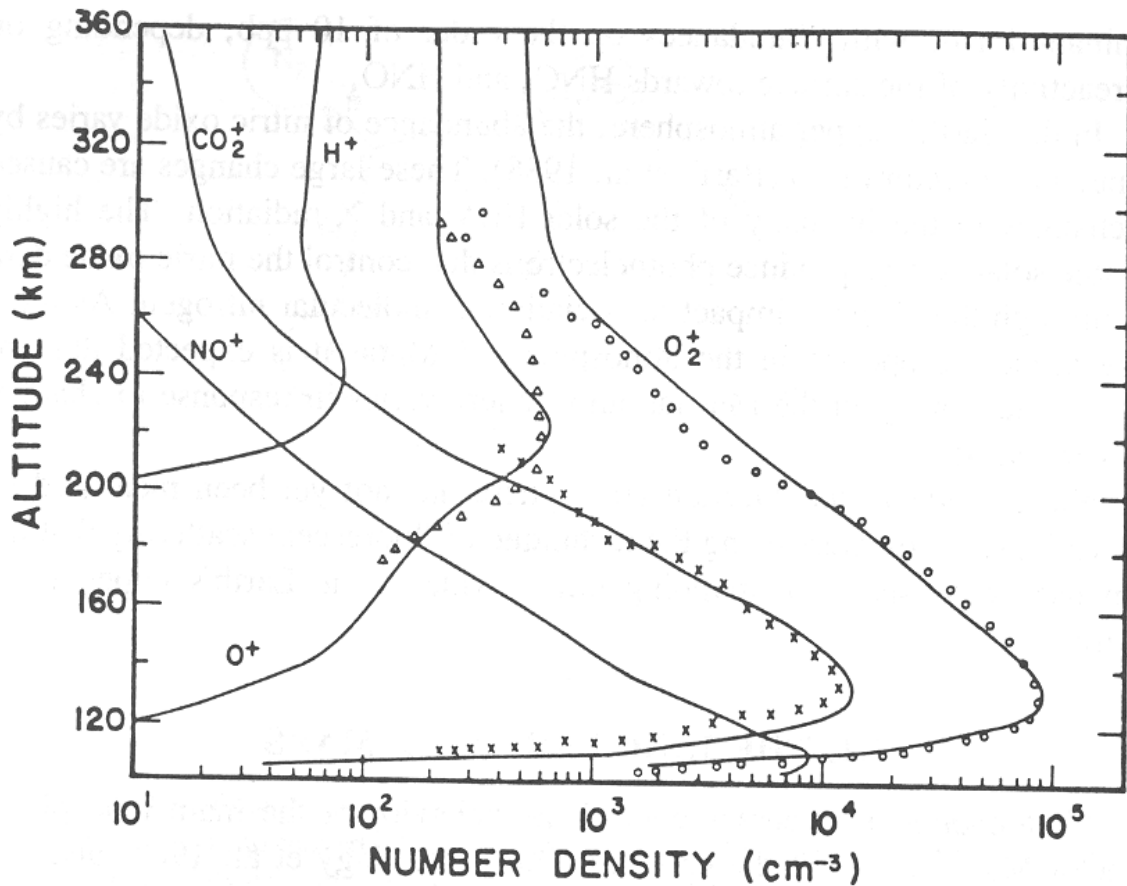


Fig.9. Ion density profiles: ion density profiles in which the solid lines are calculated profiles. The circles are  $O_2^+$  data, the triangles are  $O^+$  data and the crosses are  $CO_2^+$  data; the values were by Chen et al. (1978) from the Viking 1 RPA experiment (Hanson et al. 1977) (figure from Chen et al. 1978).

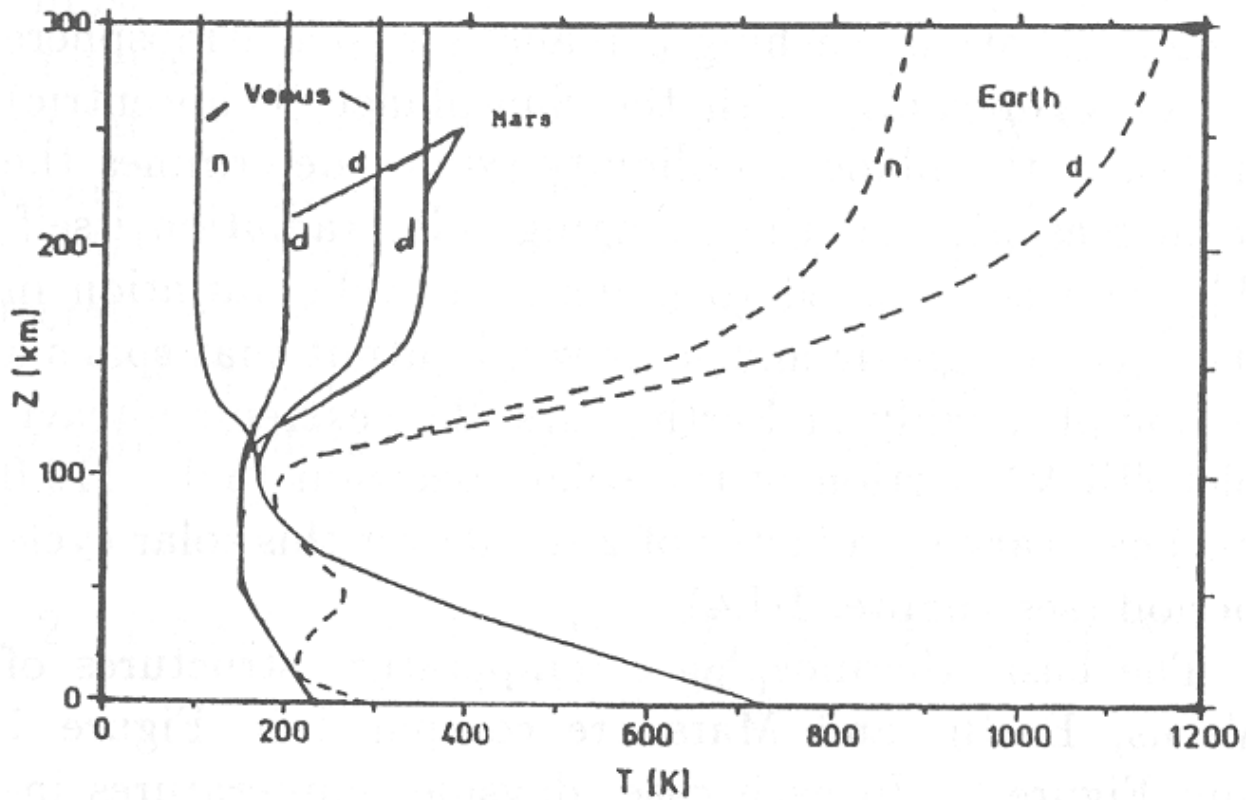
# Atmospheric Escape

- Affects elemental and isotopic composition over the lifetime of the solar system. Extremely uncertain.
- Light species escape easier than heavy ones, so get fractionation
- Exobase height  $\sim 160$  km at solar max. Corona of H observed by Ly  $\alpha$  emissions by UV spectrometers, thermal Jeans escape. Only H, He can use this mechanism.  $1E26$  H atoms  $s^{-1}$ .
- Low  $g$  means that escape is relatively easy. Dissociative recombination of  $N_2^+$  and  $O_2^+$  with an electron to form suprathermal  $2N$  or  $2O$  is a major current pathway.
- Current escape rates of H twice that of O, net loss of  $H_2O$ . Possibly regulated by lower atmosphere photochemistry.
- Bury  $CO_2$  and  $H_2O$  on/below surface
- Impact erosion strips atmosphere without mass selection
- History of magnetic field is important here
- Warm, wet early Mars?
- M9 UVS, ion profiles, isotopic ratios

# Modelling Efforts

- 1D coupled chemistry and radiative transfer models. Specify composition and solar flux, model chemical reactions and transfer of energy by radiation and other processes
- 3D General Circulation Models (GCMs). Couple dynamics, chemistry, and energy. Martian upper atmosphere not constrained enough by observations for these to be verified yet.
- Past and future extrapolations of escape rates – how does orbit change, magnetic field, subsurface volatile reservoirs? Current escape processes not measured or modelled with real accuracy.

# Venus, Earth, and Mars Compared



**Figure 2.** Temperatures of the neutral atmospheres of Earth, Venus, and Mars. Nightside temperatures of the Mars thermosphere (above 130 km) are not measured. Adapted from Fox and Bougher, [1991]

From reference 6



**Table Ia. Terrestrial Planet Parameters**

Parameter	Earth	Venus	Mars
Gravity, $\text{cm s}^{-2}$	982	888	373
Heliocentric distance AU	1.0	0.72	1.38-1.67
Radius, km	6371	6050	3396
Omega $\text{rad s}^{-1}$	7.3(-5)	3.0(-7)	7.1(-5)
Magnetic dipole moment (wrt Earth)	1.0	$\sim 4.0(-5)$	$\sim 2.5(-5)$
Obliquity, deg	23.5	1-3	25.0

**Table Ib. Implications of Parameters**

Effect	Earth	Venus	Mars
Scale heights, km	10-50	4-12	8-22
Major EUV heating, km	$\sim 200-300$	$\sim 140-160$	120-160
	broad	narrow	intermediate
O Abundance (ion peak)	$\sim 40\%$	$\sim 7-20\%$	$\sim 1-4\%$
CO <sub>2</sub> 15 $\mu\text{m}$ cooling	$\leq 130$ km	$\leq 160$ km	$\leq 125-130$ km
Dayside thermostat	conduction	CO <sub>2</sub> cooling	winds/conduction
Dayside solar cycle T	900-1500 K	230-310 K	220-325 K
Rotational forces	important	negligible	important
Cryosphere	no	yes	no
Auroral/Joule heating	yes	no	no
Seasons	yes	no	yes

From reference 6

# Recent and Upcoming Observations

- MGS RS, ACC, ER, MAG
- Mars Odyssey ACC
- Mars Express ASPERA will measure energetic neutrals, ions, electrons
- Mars Express PFS will measure atmospheric composition via a Fourier spectrometer
- Mars Express SPICAM will measure H<sub>2</sub>O and O<sub>3</sub>
- Nozomi is doomed
- Mars Reconnaissance Orbiter ACC

# Mars Aeronomy Orbiter Discussion

From Belton report

## **Mars Upper-Atmosphere Orbiter**

We include in our priority scheme an orbiter dedicated to studies of Mars' upper atmosphere and plasma environment. Interactions with the solar wind are thought to have played a significant role in the long-term evolution of the martian atmosphere, yet no measurements have been made to confirm or reject these ideas. A variety of atmospheric escape processes have been inferred from indirect measurements and/or predicted from theoretical models. This mission would provide quantitative information on the various potential escape fluxes and, thus, quantify current escape rates. Back extrapolation of such measurements might result in new understanding of the evolution of the martian atmosphere and maybe also provide important clues to atmospheric evolution on Venus and Earth. In carrying out these measurements, numerous other important questions of high scientific value associated with the middle and upper atmosphere, exosphere, ionosphere, solar wind interaction processes will also be addressed.

There are no existing plans in the current U.S. Mars Exploration Program to address any of the scientific questions identified by previous panels in this area. The Nozomi and Mars Express missions will address them to some extent, but much more data will be needed to meaningfully elucidate these issues. The measurements required for this mission could be accommodated as a science package on an international orbiter mission or as a stand-alone mission in the Scout program.

# Sources

- 1) Barth et al. (1992) "Aeronomy of the current martian atmosphere." In Kieffer et al. (Eds.) "Mars," pp. 1054-1089
- 2) Yung and DeMore (1999) "Photochemistry of Planetary Atmospheres," particularly pp. 244-281
- 3) Gladstone et al. (2002) "Solar System Upper Atmospheres: Photochemistry, Energetics, and Dynamics." In Mendillo et al. (Eds.) "Atmospheres in the Solar System Comparative Aeronomy," pp. 23-38
- 4) Nagy and Cravens (2002) "Solar System Ionospheres." In Mendillo et al. (Eds.) "Atmospheres in the Solar System Comparative Aeronomy," pp. 39-54
- 5) Hunten (2002) "Exospheres and Planetary Escape." In Mendillo et al. (Eds.) "Atmospheres in the Solar System Comparative Aeronomy," pp. 191-202
- 6) Bougher et al. (2002) "Simulations of the Upper Atmospheres of Terrestrial Planets." In Mendillo et al. (Eds.) "Atmospheres in the Solar System Comparative Aeronomy," pp. 261-288
- 7) Haberle (2000) "Mars: Atmosphere." In Shirley and Fairbridge (Eds.) "Encyclopedia of Planetary Sciences," pp. 432-440
- 8) Bougher (2000) "Thermosphere." In Shirley and Fairbridge (Eds.) "Encyclopedia of Planetary Sciences," pp. 819-825
- 9) Hunten (1993) "Atmospheric evolution of the terrestrial planets," *Science*, v259, pp. 915-920