METHANE ON MARS: THERMODYNAMIC EQUILIBRIUM AND PHOTOCHEMICAL CALCULATIONS. **J. S. Levine[1], M. E. Summers[2] and M. Ewell[2], [1]NASA Langley Research Center, Hampton, VA 23681 (joel.s.levine@nasa.gov), [2]Geroge Mason University, Fairfax, VA 22030 (msummers@gmu.edu) .**

Introduction: The detection of methane (CH_4) in the atmosphere of Mars by Mars Express [1] and Earth-based spectroscopy [2,3] is very surprising, very puzzling, and very intriguing. On Earth, about 90% of atmospheric ozone is produced by living systems [4]. A major question concerning methane on Mars is its origin—biological or geological.

Thermodynamic equilibrium caculations indicated that methane cannot be produced by atmospheric chemical/photochemical reactions [5]. Thermodynamic equilibrium calculations for three gases, methane, ammonia (NH_3) and nitrous oxide (N_2O) in the Earth's atmosphere are summarized in Table 1. The calculations indicate that these three gses should not exist in the Earth's atmosphere. Yet they do, with methane, ammonia and nitrous oxide enhanced 139, 50 and 12 orders of magnitude above their calculated thermodynamic equilibrium concentration due to the impact of life! Thermodynamic equilibrium calculations have been performed for the same three gases in the atmosphere of Mars based on the assumed composition of the Mars atmosphere shown in Table 2. The calculated thermodynamc equilibrium concentrations of the same three gases in the amosphere of Mars is shown in Table 3. Clearly, based on thermodynamic equilibrium calculations, methane should not be present in the atmosphere of Mars, but it is in concentrations approaching 30 ppbv from three distinct regions on Mars [3].

Table 1. Calculated Trace Gases in the Atmosphere of Earth Based on Thermodynamic Equilibrium Calculations [5]

Gas	Thermo-dynamic Equilibrium Concentration (Mole Fraction)	Measured Concentration (Mole Fraction)	Atmospheric Enhancement
Methane (CH_4)	10^{-145}	1.7×10^{-6}	10^{139}
Ammonia (NH_3)	2×10^{-60}	10^{-10}	10^{50}
Nitrous oxide (N_2O)	2×10^{-19}	3×10^{-7}	10^{12}

Table 2. Assumed Composition of the Atmosphere of Mars [5]

- Carbon dioxide (CO_2): 95.32%
- Nitrogen (N_2): 2.7%
- Argon (Ar): 1.6%
- Oxygen (O_2): 0.13%
- Carbon monoxide (CO): 0.07%
- Water vapor (H_2O): 10 ppmv at surface
- Mean atmospheric surface pressure: 6.4 mb
- Surface temperature range from
- 148K (polar winter) to 290K (southern summer)

Table 3. Calculated Trace Gases in the Atmosphere of Mars Based on Thermodynamic Equilibrium Calculations [5]

Gas	T = 100K	T = 200K	T = 300K
Methane (CH_4)	$<10^{-100}$	$<10^{-100}$	$<10^{-100}$
Ammonia (NH_3)	$<10^{-100}$	2×10^{-89}	4×10^{-62}
Nitrous oxide (N_2O)	6×10^{-54}	4×10^{-30}	5×10^{-23}

In the atmospheres of Earth and Mars, methane is destroyed by photolysis by solar ultraviolet radiation and by reaction with the hydtoxyl radical (OH)., according to the following reactions [6,7]:

$CH_4 + h\nu \rightarrow CH_2 + H_2$, and,

$CH_4 + OH \rightarrow CH_3 + H_2O$

The hydroxyl raical forms from the following two reactions involving water vapor (H_2O);

$H_2O + h\nu \rightarrow OH + H$

$H_2O + O(^1D) \rightarrow 2\ OH$,

where $O(^1D)$ is excited atomic oxygen.

The methane measurements are very intriguing since it appears that methane emanates and forms large seasonal plumes from three distinct areas of Mars—Terra Sabae, Nili Fossae and Syrtis Major [3]. In addition, the measurements suggest that methane has an atmospheric lifetime considerably less than the approximately 300 years lifetime calculated using methane loss from solar photolysis and reaction with the hydroxyl radical. This suggests that a major methane sink other than solar photolysis and reaction with the hydroxyl radical may exist. Other potential methane sinks, including surface sinks will be assessed.

Photochemical calculations to determine concentration, the vertical distribution and atmospheric lifetime of methane on Mars for a wide range of atmospheric conditions were performed using a one-dimensional photochemical model of the atmosphere of Mars [8]. The vertical distribution of species in the atmosphere of Mars using this model is shown in Figure 1. To assess the sensitivity of the methane concentration, its vertical distribution and atmospheric lifetime to a whole range of atmospheric parameters, sensitivity studies have been conducted for a wide range of atmospheic parameters, including assumed lower boundary flux conditions, assumed water vapor profiles, assumed eddy diffusion profiles, etc. The sensitivity of methane to these parameters will be discussed.

References: [1] Formisano et al. (2004) Science 306, 1758-1761. [2] Krasnopolsky et al. (2004) Icarus 172, 537-547. [3] Mumma et al. (2009) Science 323, 1041-1045. [4] Reeburgh (2004) Treatise on Geochemistry, Vol. 4, The Atmosphere, Elsevier Pergamon, 65-89. [5] Levine et al. (1989) The Case for Mars III: Strategies for Exploration-Technical, American Astronautical Society277-282. [6] Levine (1985) The Photochemistry of Atmospheres, Academic Press, Inc., 518 pages. [7] Levine et al. (1985) Nature, 318, 254-257. [8] Summers et al. (2002) Geophysical Research Letters,10.1029/2002GL015377.

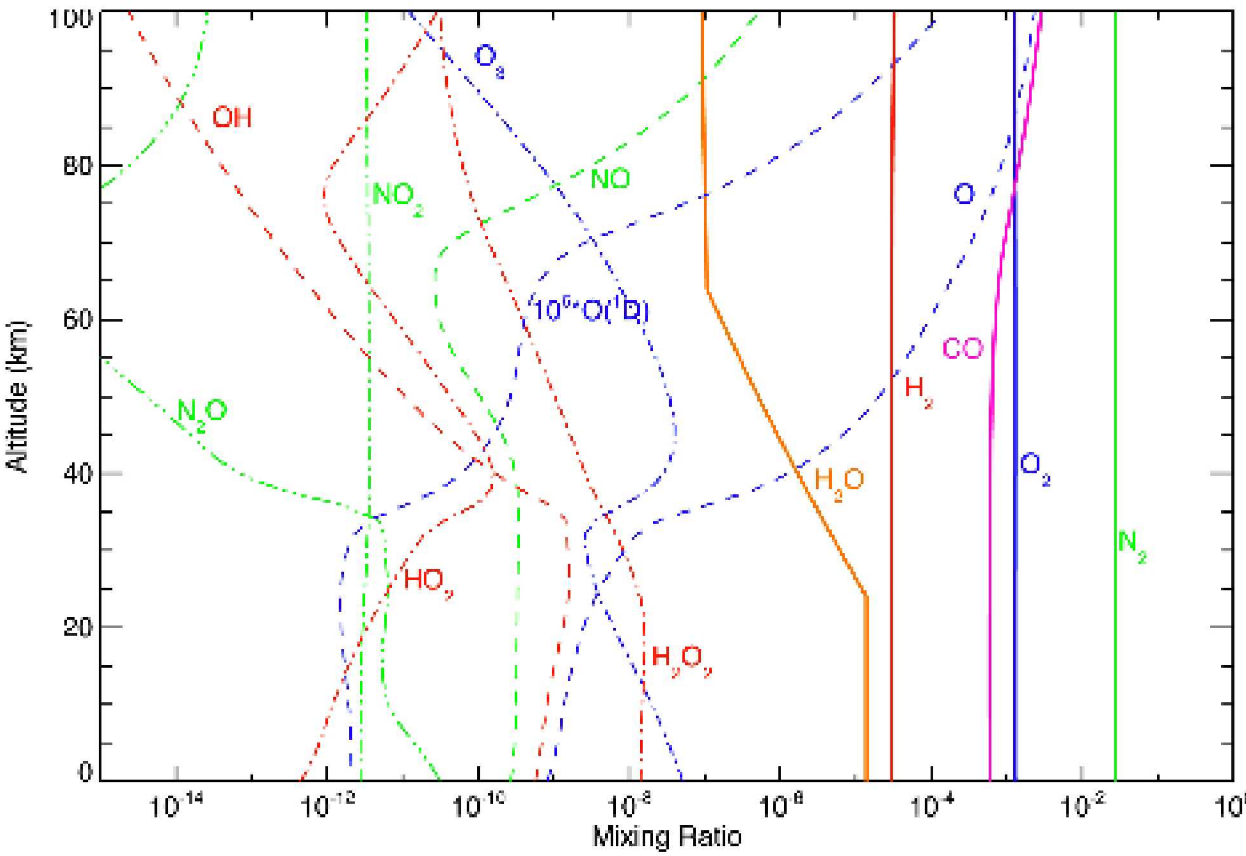

Figure 1. Standard Model of the Atmosphere of Mars (CO_2 = 6 mbar) [8].