

NON-EQUILIBRIUM THERMODYNAMIC CHEMISTRY AND THE COMPOSITION OF THE ATMOSPHERE OF MARS

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A high priority objective of the Mars Exploration Program [1] is to “Determine if life exists today” (MEPAG Goal I, Objective A). The measurement of gases of biogenic origin may be an approach to detect the presence of microbial life on the surface or subsurface of Mars. Chemical thermodynamic calculations indicate that on both Earth and Mars, certain gases should exist in extremely low concentrations, if at all [2]. Microbial metabolic activity is an important non-equilibrium chemistry process on Earth, and if microbial life exists on Mars, may be an important non-equilibrium chemistry process on Mars. The non-equilibrium chemistry of the atmosphere of Mars is discussed in this paper.

Chemical thermodynamic equilibrium calculations indicate that certain trace gases in the Earth’s atmosphere, such as methane (CH₄), ammonia (NH₃), nitrous oxide (N₂O), and carbon disulfide (CS₂) should be at atmospheric concentrations many orders of magnitude below their actual atmospheric concentrations (Table 1). The role of microbial metabolic activity for establishing this chemical non-equilibrium is well known [3,4,5].

Chemical thermodynamic equilibrium calculations for certain trace gases in the atmosphere of Mars have been performed. As input parameters for these calculations, the following atmospheric composition was used: carbon dioxide (CO₂): 95.32%, nitrogen (N₂): 2.7%, argon (Ar): 1.6%, oxygen (O₂): 0.13%, carbon monoxide (CO): 0.07% [6]. The mean atmospheric surface pressure was assumed to be 6.4 mb and a surface temperature range from

148K (polar winter) to 290K (southern summer) was assumed [6]. The calculated equilibrium concentration of methane, ammonia, and nitrous oxide in the atmosphere of Mars is summarized in Table 2.

Table 1. Some Trace Gases in the Earth’s Atmosphere

<u>Gas</u>	<u>Thermo-Dynamic Equilibrium (Mole Fraction)</u>	<u>Measured Concentration</u>	<u>Atmospheric Enhancement</u>
Methane (CH ₄)	10 ⁻¹⁴⁵	1.7 x 10 ⁻⁶	10 ¹³⁹
Ammonia (NH ₃)	2 x 10 ⁻⁶⁰	10 ⁻¹⁰	10 ⁵⁰
Nitrous oxide (N ₂ O)	2 x 10 ⁻¹⁹	3 x 10 ⁻⁷	10 ¹²
Carbon disulfide (CS ₂)	0	10 ⁻¹¹	

Table 2. Calculated Trace Gases in the Atmosphere of Mars Based on Thermodynamic Equilibrium Calculations (Unit: Mixing Ratio)

<u>Gas</u>	<u>T = 100K</u>	<u>T = 200K</u>	<u>T = 300K</u>
Methane (CH ₄)	<10 ⁻¹⁰⁰	<10 ⁻¹⁰⁰	<10 ⁻¹⁰⁰
Ammonia (NH ₃)	<10 ⁻¹⁰⁰	2 x 10 ⁻⁸⁹	4 x 10 ⁻⁶²
Nitrous oxide (N ₂ O)	6 x 10 ⁻⁵⁴	4 x 10 ⁻³⁰	5 x 10 ⁻²³

Sulfur on the surface of Mars may prove to be an interesting raw material for microbial appetites. Viking lander measurements found that the surface sulfur concentrations at both landing sites ranged from 10 to 100 times higher

than in the terrestrial crust. The source of sulfur on Mars is believed to be volcanic emissions in the form of sulfur dioxide (SO₂). Microbial communities on Mars, if they exist, could utilize the widespread and readily available surface sulfur and produce atmospheric reduced sulfur species. Chemical thermodynamic equilibrium calculations indicate that reduced sulfur species should not exist in the atmosphere of Mars in detectable levels in the absence of microbial metabolic activity. Chemical thermodynamic equilibrium calculations of reduced sulfur species in the atmosphere of Mars are summarized in Table 3. These calculations assume an atmospheric sulfur dioxide partial pressure of 10⁻⁹ atm.

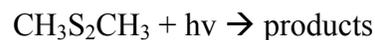
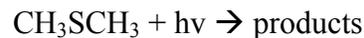
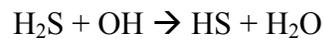
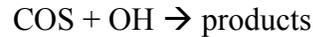
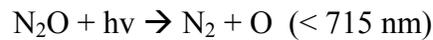
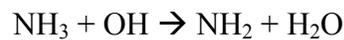
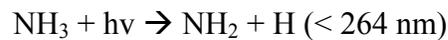
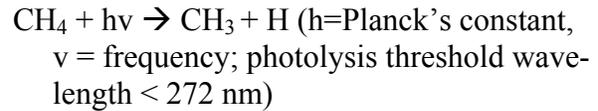
Table 3. Trace Sulfur Gases in the Atmosphere of Mars Based on Thermodynamic Equilibrium Calculations (In terms of partial pressure of sulfur species to partial pressure of sulfur dioxide, assumed to be 10⁻⁹ atm, for T = 200K)

<u>Gas</u>	<u>Partial Pressure of Gas/ Partial Pressure of SO₂</u>
Carbonyl sulfide (COS)	10 ⁻⁸³
Hydrogen sulfide (H ₂ S)	10 ⁻⁸⁴
Carbon disulfide (CS ₂)	10 ⁻¹⁸⁰
Methane thiol (CH ₃ SH)	10 ⁻¹⁹⁷
Dimethyl sulfide (CH ₃ SCH ₃)	10 ⁻³⁰⁷
Dimethyl disulfide (CH ₃ S ₂ CH ₃)	10 ⁻³⁶⁴

Based on thermodynamic equilibrium calculations, the carbon, nitrogen, and sulfur species in Tables 2 and 3 should be present in very small concentrations and they are expected to be destroyed efficiently and rapidly by photochemical and chemical processes. These species are destroyed by photolysis by both solar ultraviolet radiation and by chemical reaction with the hydroxyl radical (OH), which is formed by the photolysis of water vapor (H₂O) (except for nitrous oxide (N₂O), which is destroyed via reaction with excited atomic

oxygen (O(¹D))), rather than by OH). The photochemical processes that lead to the destruction of these gases are summarized in Table 3.

Table 4. Photochemical and Chemical Processes that Destroy the Gases in Tables 2 and 3 [7, 8,9].



The lifetime of these gases with respect to chemical destruction by the hydroxyl radical (OH) may be calculated using temperature-dependent reaction rates given in [8]. For these calculations, an atmospheric temperature of 200K and a surface OH number density of 1 x 10⁵ cm⁻³ [10] were assumed. The calcu-

lated lifetime against destruction by reaction with the hydroxyl radical for some of these species is very short, i.e., dimethyl disulfide: 14 days, dimethyl sulfide: 35 days, hydrogen sulfide: 3 months. Given a vertical eddy mixing timescale on the order of 3 months near the surface of Mars and a horizontal transport timescale on the order of several days [9], these gases will not diffuse far from their location of origin before they are destroyed via reaction with the hydroxyl radical. It is important to remember that these very short atmospheric lifetimes are only based on reaction with the hydroxyl radical and do not include the effect of photolysis by solar ultraviolet radiation on the lifetimes of these species.

Assuming the presence of gases of biogenic origin in the atmosphere of Mars, the very short atmospheric lifetime of these gases and their possible non-uniform source, most likely associated with surface and/or subsurface sites of liquid water, suggest their detection is a very difficult and challenging measurement problem. A mass spectrometer on a powered and controlled airplane flying 1 to 2 kilometers above the surface of Mars and capable of traversing regional scale distances over potential water sites, is an ideal platform to search for the presence of non-equilibrium gases resulting from microbial metabolic activity in the atmosphere of Mars.

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