

1A NEW COUPLED 3D-MODEL OF THE DYNAMICS AND CHEMISTRY OF THE MARTIAN ATMOSPHERE AND SOME PROBLEMS OF THE CHEMICAL MODELING

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Introduction:

We introduce a new coupled global 3D-model of the dynamics and chemistry of the Martian atmosphere. The model is an adjustment of the model COMMA-IAP (Cologne Model of the Middle Atmosphere of the Institute of Atmospheric Physics in Kühlungsborn) to the conditions of the Martian atmosphere. It consists of a dynamical model calculating the dynamical fields wind components and temperature and a chemistry transport model (CTM) using these dynamical fields. The model is not self-consistent thus far meaning there is no online feedback from the CTM to the dynamical model. We present first model results and compare them with available observations. The outcomes will be discussed in terms of dynamics and chemistry. A particular problem consists in the stability of the Mars atmosphere. We discuss three additional catalytic cycles of the oxidation of CO returning to CO₂ and estimate their efficiency in different atmospheric regions and during different seasons and local times. The importance of the so-called photochemical Doppler-Sonnemann effect (DSE) (Sonnemann 2001) in the Martian atmosphere has been pointed out.

Much of our current knowledge of the global circulation of the Martian atmosphere stems from the spacecraft missions of Mariner 9 and Viking in the 1970th. Particularly, the long-term meteorological in situ measurements got by the two landers during the Viking mission and remote observations of the atmospheric thermal structure obtained by the IRIS instrument aboard of Mariner 9 (Zurek et al. 1992) yielded a lot of new results. Since this time, the understanding of the global circulation has increased and deepened thanks the adaptation of general circulation models, developed for weather forecast, climate simulation and modeling of dynamical and chemical processes in the Earth atmosphere, to the Martian atmosphere. In this way dynamical models were employed by Haberle et al. 1993, Hourdin et al. 1993, 1995, Collins et al. 1996, Wilson and Hamilton 1996 and Forget et al. 1999 and 2003. There is a large body of publications dealing with Martian chemistry both neutral gas and plasma components but using only reduced one or zero dimensional models. Only very recently, a coupled 3D-model of the dynamics and chemistry of the Martian atmosphere has been developed by Lefevre et al. 2004.

On Mars, the dynamics considerably influences the chemistry because the winds and the turbulent diffusion are much stronger than on Earth although the diameter is only 0.5273 times of that of the Earth. The pressure at the surface amounts, on average, to about 6 hPa (this corresponds to about 35 km height on Earth). Chemically active and fast constituents are, similar to those in the Earth mesosphere, the odd hydrogen (H, OH, and HO₂) and odd oxygen (O and O₃) constituents. Although CO₂ is the dominant source gas for the odd oxygen constituents, instead of O₂, the chemistry resembles of that of the Earth mesosphere. The strong impact of the dynamics on the chemistry requires the use of global models. Some special problems not known or not so pronounced on the Earth exist on the Mars:

1. A sizable fraction of atmospheric mass condensate and sublimate (mainly CO₂) on the poles.

2. The seasonal asymmetries in solar insolation owing to the large eccentricity of the Mars orbit and the seasonal phasing of its perihelion entails a strong annual variation of all dynamical and chemical parameters.

3. Particularly the very variable dust loading impacting significantly the diurnal, seasonal and inter-annual variation of all dynamical and consequently chemical parameters.

4. The temperature in Martian middle atmosphere can drop to values that a freeze-drying can take place. But what the clouds are made of? Water vapor or CO₂, too?

Other problems are already known from the Earth atmosphere:

5. The wave activity determines essentially the thermal structure and the wind system. Turbulence transports heat, momentum and minor constituents. What is known about gravity, tidal and planetary waves?

6. What is known about diabatic heat sources such as chemical heating, wave dissipation, or air glow (e.g. in the Meinel bands)?

7. A general problem is always connected with the boundary conditions used in the models.

We can, of course, neither give answers to all questions nor solve the problems mentioned. At best, we can try to take into consideration some individual points such as a freeze-drying in order to calculate the water vapor distribution or to consider the dust loading by dust parametrization.

Model description:

The dynamical model MAOAM (The Martian Atmosphere: Observation And Modeling) is described in detail in Hartogh et al. 2005. For further details see also related abstracts in this volume. MAOAM has been derived from COMMA-IAP, a coupled model describing the dynamics and chemistry of the middle atmosphere of the Earth. The model was described in more detail among other publications in Berger 1994, Sonnemann et al. 1998, Kremp et al. 1999, Berger and von Zahn 1999, Sonnemann and Körner 2003, or Hartogh et al. 2004, Sonnemann and Grygalashvily 2005, Sonnemann et al. 2005. Recently, the COMMA-IAP chemistry transport model (CTM) has been adopted to MAOAM.

The chemical transport model consists of a chemical, radiation and transport code. The chemical code is based on a family concept (Shimazaki 1985) for the odd oxygen and odd hydrogen families. The partition into the member of the fast constituents takes place then according to their current equilibrium concentrations. Only the family is subjected to transport. The dissociation rates depending on altitude and solar zenith angle are calculated before and adapted to the corresponding latitude, local time, and season for each grid point at each time step. The transport code considers both advective and turbulent and molecular diffusive transport. Particularly the numerical diffusion can become large. We employ a code developed by Walcek and Aleksic 1998 and Walcek 2000 marked by nearly zero numerical diffusion. The eddy diffusion is an external parameter in the CTM. An ice formation scheme has been included into the model.

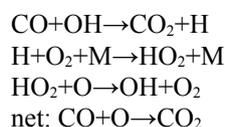
We present calculations of the distribution of the most important minor constituents. We compare the results with available observations and discuss them in terms of chemistry and dynamics.

1 The catalytic cycles of CO oxidation:

The main atmospheric constituent on Mars is CO₂. The permanent photolysis of CO₂ in the process CO₂+hν→CO+O (1) would destroy this constituent completely unless chemical reactions would continuously return CO to CO₂. The only effective process is given by the reaction CO+OH→CO₂+H (2). This is also the key reaction of smog formation in the Earth atmosphere. The direct recombination of CO to CO₂ is spin forbidden meaning the reaction CO+O+M→CO₂+M is negligible. As CO₂ is essentially more abundant (95.32%) as CO (about 0.1%, 0.083 to 0.125% according to Krasnopolsky 2003) in the Mars atmosphere this reaction has to be faster than the photolysis of CO₂. In other words the ratio of CO₂ to CO amounts approximately to 10³. The net source of the hydrogen radicals is the photolysis of H₂O and its oxidation and that of H₂ by O(¹D) result-

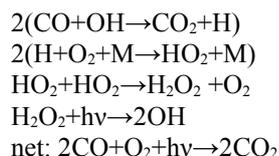
ing from the dissociation of ozone and CO₂. The loss of hydrogen radicals takes place, like in the Earth atmosphere, by reactions of the radicals among one another. In reaction (2) no radical loss takes place but only a radical conversion. As the net production of OH is small the question arose which processes return H and likewise HO₂ to OH? Two catalytic reaction schemes returning CO to CO₂ have been introduced in the past (McElroy and Donahue 1972, Parkinson and Hunten 1972). We will extend this list and introduce three additional reactions schemes and calculate their efficiency on the basis of our 3D-model. Calculation made by means of zero-dimensional models using diurnally averaged dissociation rates for middle latitudes and mean further conditions, for instance during equinox, etc. cannot reflect real relations. The chemistry is rather different between day and night, winter and summer, or upper and lower atmosphere. We compare the efficiency of the different catalytic cycles and calculate the regions and times where and when they are particularly effective. The lifetime of CO amounts approximately to τ_{CO}=(1000*J_{CO₂})⁻¹ in the lower Martian atmosphere (J_{CO₂} in the order of 10⁻¹² s⁻¹). This is a large time compared with the characteristic time of mixing. Thus, we have to integrate the effect of the different catalytic cycles over the whole globe and year in order to get an average value.

McElroy and Donahue 1972 (MD) introduced the following catalytic cycle:



M stands for a neutral collision partner mainly CO₂. Atomic oxygen results from the photolysis of CO₂ itself or that of O₂ or O₃, respectively, meaning the process is efficient during daytime. Other sources of O are unimportant. As catalysts act the hydrogen radicals OH, H and HO₂ which do not get lost within the cycle.

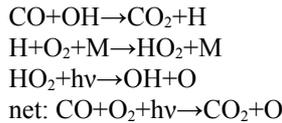
Parkinson and Hunten 1972 (PH) involved hydrogen peroxide H₂O₂ belonging to the even hydrogen constituents but it is actually a radical store as it can be easily photolysed into 2OH:



Also this process is only effective during daytime. The bottleneck is the third reaction owing to its relatively small reaction rate of I(HO₂-HO₂)=2.3*10⁻¹³ exp(600/T) cm³ s⁻¹. The photolysis rate amounts to

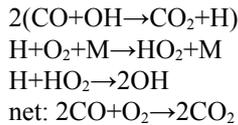
$J_{\text{H}_2\text{O}_2}=5*10^{-5} \text{ s}^{-1}$ at the top of the atmosphere but an order smaller at 10 km. The rate of the reaction of HO_2 with O is two orders in magnitude larger and thus it is a very fast reaction. $I(\text{HO}_2\text{-O})=2.9*10^{-11} \exp(200/T) \text{ cm}^3 \text{ s}^{-1}$. During the night, the hydrogen radicals will be converted into HO_2 and finally into H_2O_2 . However, because of missing radiation, a catalytic cycle cannot run then.

We discuss now some additional catalytic processes. A variant of the MD process is given by:



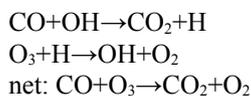
The dissociation rate of HO_2 at the top of the atmosphere is relatively large with $J_{\text{HO}_2}=2.5*10^{-4} \text{ s}^{-1}$ but it decreases strongly with decreasing height and has only an order of 10^{-6} s^{-1} at 10 km.

The next catalytic cycle considered also starts with the first two reactions but includes then the reaction with atomic hydrogen:



This is a scheme also running during the night. However, as the main net odd hydrogen source - the photolysis of water vapor - is zero during this time and the odd hydrogen family concentration decreases in this time the efficiency of this process also declines during the night. The reaction rate of the third reaction is large: $I(\text{H-HO}_2)=7.2*10^{-11}$ or $4.2*10^{-10} \exp(-950/T)$ (Krasnopolsky 1986) $\text{cm}^3 \text{ s}^{-1}$ but two branches of the reaction of H with HO_2 result in the formation of H_2O and H_2 exhausting the odd hydrogen reservoir. The same is valid for the reaction HO_2 with OH forming H_2O .

The last cycle discussed includes ozone:



Also this reaction scheme acts during the night, but its efficiency also reduces with the exhaust of the odd hydrogen reservoir during the night. The reaction of H with ozone is a very fast process: $I(\text{H-O}_3)=1.3*10^{-10} \exp(-500/T) \text{ cm}^3 \text{ s}^{-1}$. The additionally introduced catalytic cycles are differently effective in different altitudes, latitudes and times of day and season. They make a contribution to understand why the ratio of CO_2 to CO amounts to about 1000.

1The photochemical Doppler-Sonnemann effect (DSE) on Mars:

fect (DSE) on Mars:

The photochemical Doppler effect, abbreviated with DSE, was introduced by Sonnemann in 2001 in order to estimate the influence of the zonal wind on the chemistry of the Earth middle atmosphere. It describes the change of the period or frequency of an air parcel moving in zonal direction being subjected to solar insolation. According to the direction of the moving atmospheric parcel, with or against the rotation of the planet, the period of insolation shortens or increases. Using real zonal wind velocities of the Earth middle atmosphere the period changes by more than 8 hours within the strong mesospheric wind jet. The effect can be calculated by a modified Doppler formula:

$$\tau_D = \tau_{\text{Mars}} / (1 - u_{\text{zonal}} / u_{0\text{Mars}} * \cos\varphi) \quad (3)$$

u_{zonal} stands for the zonal wind velocity, $u_{0\text{Mars}}$ is the velocity of Mars at the equator, φ represents the latitude, and τ indicates the period. $u_{0\text{Mars}}$ amounts to 238.24 m s^{-1} . For $u_{\text{zonal}}=-100 \text{ m s}^{-1}$ (sign corresponds to eastward wind) and $\varphi=65.18^\circ$ the period amounts to half a day only. For a positive sign of the same absolute amount the period becomes even infinity meaning an air parcel would be subjected to permanent insolation or it has continuously nighttime conditions. In the Earth atmosphere the DSE entails a considerable change of the diurnal variations of the chemical active constituents (Sonnemann and Grygalashvily 2003). The odd oxygen-odd hydrogen system represents an enforced nonlinear chemical oscillator driven by the diurnally periodic solar insolation. This effect strongly influences the chemistry particularly of a system marked by a characteristic chemical time in the order of τ . Due to the smaller Mars radius compared with that of the Earth and the larger zonal wind velocities the effect is essentially more pronounced on Mars. According to model outputs a super-rotation of an atmospheric parcel can occur on certain locations. In this case the period becomes negative meaning, although the sun rises at a fixed longitude, the moving atmospheric parcel comes from the daylight side and moves into the night.

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