UNIQUENESS OF A SOLUTION OF A STEADY-STATE PHOTOCHEMICAL PROBLEM:
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Based on conservation of chemical element in chemical reactions, a rule is proved that the number of boundary conditions given by densities and/or non-zero velocities should not be less than the number of chemical elements in the system, and the components given by densities and velocities should include all elements in the system. Applications of this rule to Mars are considered. It is proved that a problem of CO₂-H₂O chemistry in the lower and middle atmosphere of Mars, say, in the range of 0-80 km does not have an unique solution, if only CO₂ and H₂O densities are given at the lower boundary, while all other boundary conditions are fluxes. Two models of this type are discussed. These models fit the same boundary conditions, are balanced with a relative uncertainty of 10⁻⁴ for H₂ (and much better for other species), and predict the O₂, CO, and H₂ mixing ratios which differ by orders of magnitude. One more species density, e. g. that of O₂, should be specified at the boundary to obtain the unique solution. The situation is better if the upper boundary is extended to the exobase where thermal escape velocities of H and H₂ can be specified. However in this case either oxygen nonthermal escape rate (and hence the total hydrogen escape rate) or the O₂ (or other species) density at the surface should be given as the boundary condition. Two models of Mars' photochemistry, with and without nitrogen chemistry, are considered. The oxygen nonthermal escape rate of 1.2×10⁶ cm²s⁻¹ is given at 240 km and is balanced with the total hydrogen escape rate within uncertainty of 1% for both models. Both models fit the measured O₂ and CO mixing ratios, the O₃ line absorption at 9.6 μm and the O₂ 1.27 μm dayglow within the uncertainties of the measured values, though the model without nitrogen chemistry fits better. The importance of nitrogen chemistry in the lower and middle atmosphere of Mars depends on a fine balance between productions of NO and N in the upper atmosphere which is not known within the required accuracy.

Model of Mars’ photochemistry without nitrogen chemistry. The effective absorbing O₃ abundance is equal to 0.44 μm, and the O₂ 1.27 μm dayglow intensity is equal to 3.2 MR (the measured values are 0.54±0.15 μm and 3±1 MR, respectively).