Unit 14 ATM401, ATM601 and CHEM601

Application, analysis, and evaluation

1. Undergraduate students: At summer solstice, the concentration of formaldehyde (HCHO) is $1.2 \cdot 10^{11}\, molecules\, cm^{-3}$ at an altitude of 1 km and 40N latitude. At this height, the incident light intensity is $2.7 \cdot 10^{13} photons\, cm^{-2}\, s^{-1}$ between 295 and 305 nm. The cross section for HCHO photolysis is $2.62 \cdot 10^{-20} cm^2\, molecules^{-1}$. The unit for the quantum yield can therefore be written as $molecules\, photon^{-1}$. Since both molecules and photon are numbers, the quantum yield is dimensionless. The probability that the absorption of a photon leads to a photolysis reaction and forms a CHO and H is 79%. Write down the photolysis reaction equation. What are CHO and H? What is this reaction with respect to atmospheric chemistry?

2. Undergraduate students: Assume an atmosphere at 20^oC with concentrations of NO and NO_2 of $0.9 ppb$ and $9 ppb$, respectively. Determine the photolysis rate constant, and photolysis rate. Assume that no other reactions than those of the triade $NO - NO_2 - O_3$ exist and calculate the concentration of ozone for a reaction rate coefficient of $3.1 \cdot 10^3 exp(-\frac{1.45}{T}) ppm^{-1} min^{-1}$ (T in K) and a photolysis rate of $5.5 \cdot 10^{-2} s^{-1}$.

3. Graduate students: Calculate the photo-stationary-state mixing ratio of O_3 at midday when $p = 1013 hPa$, $T = 298K$, $j = 0.01 s^{-1}$ for NO and NO_2 mixing ratios of $4.5 ppt$ and $9 ppt$, respectively. Assume a reaction rate of $k = 1.8 \cdot 10^{-14} cm^3 molecule^{-1} s^{-1}$. Convert the ozone mixing ratio to number concentration. Where in the troposphere are these values typical?

4. All students: In the troposphere, nitric oxides, NO, reacts with hydroperoxyl, HO_2, to form NO_2 and the hydroxyl radical, OH. In addition, the paths of the triad $NO - NO_2 - O_3$ occur. Assume that no other relevant paths exist and give the balanced equation for this chemical mechanism. Formulate the temporal change of concentrations for each of the involved trace gases, and express the ozone concentration for steady-state conditions under the assumption that hydroxyl-hydroperoxyl chemistry can be neglected. Discuss how hydroxyl-hydroperoxyl chemistry would change the chemical equilibrium, and what happens at night.

5. Graduate students: In problem 1, you have calculated the photolysis rate within a specific wavelength intervall. This programming task examines how the photolysis rate reactions depend on wavelength. Assume NO_2 undergoes photolysis and forms NO and O where $O = O(^3P)$, which in the troposphere is the only way of ozone production by the reaction of O_2 with O. The oxygen atom is a bi-radical and has 2 unpaired electrons. Calculate values for the photolysis rate constant j for the photolysis of NO_2 at 320, 380, 420 and 430 nm (i.e. just the values at these four wavelengths, not for broad wavelength interval). Plot your results as a function of wavelength. The photolysis rate constants for NO_2 photolysis depend on wavelength. Just think about the following, you don't need to

do it. How would you proceed if you were to calculate also the total photolysis rate constant for photolysis of NO_2? What would be the unit of this photolysis rate constant?