Unit 15 ATM401, ATM601 and CHEM601

Application, analysis, and evaluation

- 1. All students: In the United States, the total sulfur dioxide and nitrogen oxide emissions amount to $19.9 \cdot 10^6 t$ and $21.3 \cdot 10^6 t$, respectively. Transport accounts for 3.3% of the sulfur dioxide total and 44.5% of the nitrogen oxide total. Determine the ratio of the total amount of nitrogen oxide generated by transport to the total amount of sulfur dioxide produced by transport.
- 2. Undergraduate students: Ammonia (NH_3) makes up a partial fractions of 10^{-8} % of the atmosphere, which has a mass of about $5 \cdot 10^{18} kg$. About $5 \cdot 10^{10} kg/y$ of NH_3 escape to space. Determine the residence time of NH_3 .
- 3. Undergraduate students: Water and CO_2 can be photolysed. The combined photolytic reaction chain of water and CO_2 reads

$$H_2O + hv \longrightarrow^{j_1} OH + H$$

 $CO_2 + hv \longrightarrow^{j_2} CO + O$
 $CO + OH \longrightarrow^{k_1} CO_2 + H$
 $OH + OH \longrightarrow^{k_2} O + H_2O$
 $O + O + M \longrightarrow^{k_3} O_2 + M$

Determine the net balanced reaction, the change in CO_2 and comment on whether the inclusion of CO_2 alters the net reaction of the photolysis series of H_2O alone. How many water molecules are required to form one O_2 molecule?

4. Graduate students: In an urban atmosphere, the following reactions may occur:

$$OH + CH_4 \longrightarrow^{k_1} H_2O + CH_3$$

$$OH + CO \longrightarrow^{k_2} H + CO_2$$

$$OH + CH_3CHO \longrightarrow^{k_3} H_2O + CH_3CO$$

$$CH_3 + O_2 \longrightarrow^{k_4} CH_3O_2$$

$$CH_3O_2 + NO \longrightarrow^{k_5} CH_3O + NO_2$$

$$CH_3O + O_2 \longrightarrow^{k_6} HCHO + HO_2$$

$$HO_2 + NO \longrightarrow^{k_7} NO_2 + OH$$

Determine the net balanced reaction. How many NO_2 molecules result from two CH_4 molecules? What would happen if CH_4 oxidized NO and NO_2 without consuming O_3 ?

5. Graduate students: In the stratosphere, the following reactions significantly affect chemistry of ozone:

$$O_3 + hv \longrightarrow_{j_1}^{j_1} O_2 + O^*$$
 with $j_1 = 10^{-4}s^{-1}$,
 $O^* + M \longrightarrow_{l_1}^{k_1} O + M$ with $k_1 = 10^{-17}m^3s^{-1}$,
 $O^* + H_2O \longrightarrow_{l_2}^{k_2} HO + HO$ with $k_2 = 2 \cdot 10^{-12}m^3s^{-1}$,
 $O + O_2 + M \longrightarrow_{l_3}^{k_3} O_3 + M$ with $k_3 = 6 \cdot 10^{-46}m^6s^{-1}$,

$$\begin{array}{l} HO+O_3 \longrightarrow^{k_4} HO_2+O_2 \text{ with } k_4=2\cdot 10^{-20}m^3s^{-1},\\ HO_2+O_3 \longrightarrow^{k_5} HO+O_2+O_2 \text{ with } k_5=3\cdot 10^{22}m^3s^{-1},\\ HO+HO_2 \longrightarrow^{k_6} H_2O+O_2 \text{ with } k_6=3\cdot 10^{-17}m^3s^{-1}.\\ \text{Here again } O^* \text{ is an electronically excited metastable state of atomic oxygen.} \end{array}$$

At that height assume that the molecular density, the molecular fraction of water vapor, ozone, and oxygen are equal to $5 \cdot 10^{23} m^{-3}$, $2 \cdot 10^{-6}$, $2 \cdot 10^{-6}$, and 0.2, respectively. Determine the steady state molecular fraction of O^* , HO, and HO_2 .