# Chemistry Problems for ATMS 501

I. **OH Production in the Stratosphere and Troposphere**

The oxidizing capacity of the troposphere depends critically on the production of hydroxyl radicals (OH) by $O_3$ photolysis. Initially it was thought that OH production was only significant in the stratosphere, we evaluate that assumption here.

1. $O_3 + h\nu \rightarrow O^* + O_2$ $k_1$

2. $O^* + M \rightarrow O + M^*$ $k_2$
3. $O^* + H_2O \rightarrow 2OH$ $k_3$

| Rate Constant | Stratosphere | Troposphere |
|---|---|---|
| $k_1$ $s^{-1}$ | $2x10^{-4}$ | $2x10^{-5}$ |
| $k_2$ $cm^3$ $molec^{-1}$ $s^{-1}$ | $3.8x10^{-11}$ | $3.4x10^{-11}$ |
| $k_3$ $cm^3$ $molec^{-1}$ $s^{-1}$ | $2.2x10^{-10}$ | $2.2x10^{-10}$ |

a. Show that $O^*$ is in steady state in either the stratosphere or troposphere. Assume that $[M]_{strat} = 3x10^{18}$ molec $cm^{-3}$, $[M]_{trop} = 2x10^{19}$ molec $cm^{-3}$, $[H_2O]_{strat} = 2$ ppm, $[H_2O]_{trop} = 1\%$.

b. Assuming that O* is in steady state, derive an equation for the rate of OH production in terms of $[O_3]$, [M], $[H_2O]$, and the rate constants.

c. Calculate the OH production rate for both the stratosphere and the troposphere. Assume $[O_3]_{strat} = 3000$ ppb and $[O_3]_{trop} = 50$ ppb. Explain any similarities or differences between the two locations and comment on the oxidizing nature of the stratosphere relative to the troposphere.

II. **$NO_x$ Cycling**

Photochemical cycling of nitrogen oxides is responsible for the net production of tropospheric ozone. Early in atmospheric chemistry, it was assumed that NO – $NO_2$ – $O_3$ were in a photochemical equilibrium via the reactions:

1. $NO + O_3 \rightarrow NO_2 + O_2$ $k_1 = 1.6x10^{-14}$ $cm^3$ $molec^{-1}$ $s^{-1}$ at 288 K
2. $NO_2 + h\nu \rightarrow NO + O$ $k_2 \sim 0.01$ $s^{-1}$ cloud-free noon-time conditions
3. $O + O_2 + M \rightarrow O_3$

Since the abundance of $O_2$ is so large, we can assume that reaction 3 is instantaneous so that $NO_2$ photolysis is the rate at which both NO and $O_3$ are regenerated.

a) Under this assumption, and assuming that either NO or $NO_2$ are in steady state derive an equation for the ratio of $NO/NO_2$. Evaluate this ratio for typical daytime values of the rate coefficients given, and an ozone mixing ratio of 50 ppb in the boundary layer.

b) Nitric oxide (NO) reacts with other radical species, such as peroxy radicals, quite rapidly.

4. $NO + HO_2 \rightarrow OH + NO_2$ $k_4 = 8x10^{-12}$ $cm^3$ $molec^{-1}$ $s^{-1}$
5. $NO + RO_2 \rightarrow RO + NO_2$ $k_5 = k_4$

Suppose the mixing ratio of the sum of peroxy radicals ($HO_2 + RO_2$) is about 50 ppt. What fraction of the time does NO react with peroxy radicals instead of with $O_3$?

c) Assuming that these peroxy radicals are in steady state, calculate the instantaneous rate of ozone formation for the above conditions in units of ppb/hr. If losses are negligible during the day, how long would it take for the given conditions for $O_3$ to double (reach 100 ppb)?