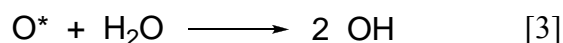
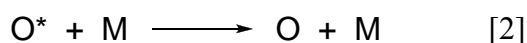
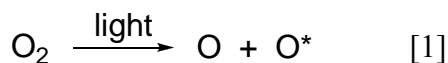


**Environmental Chemistry****Problem Set 1****Due Friday, September 25, 2009** (we do not have class on this day)

Report all final numerical results to the correct number of significant figures.

1. The most strongly absorbed wavelength that causes the  $\pi \rightarrow \pi^*$  transition in  $O_2$  is around 140 nm. Now consider the analogous transition in  $N_2$ . Give one reason why we would expect the most strongly wavelength driving the  $\pi \rightarrow \pi^*$  transition to be shorter than 140 nm. (There are at least two reasons, actually.)
2. Problem 1-3 on p. 39 of Baird and Cann. You need to show your work only for the  $NO_2 \rightarrow NO + O$  calculation. Also, answer the question of wavelength availability at the earth's surface.
3. (Inspired by Problem 1 of Box 1-1 in Baird and Cann) Consider the following three-step mechanism for the production and destruction of excited oxygen atoms,  $O^*$ , in the atmosphere:



- (a) Briefly explains what happens in Step 2 to the extra electronic energy possessed by  $O^*$ .
- (b) Use the steady-state approximation to derive an expression for  $[O^*]$  in terms of the concentrations of the other species in the above mechanism. (Assume that the rate constant for Step 1 is  $k_1$ , etc.)
- (c) Atmospheric chemists often use a big Teflon bag as an “environmental chamber” in which to simulate atmospheric reactions under precisely controlled conditions. Imagine simulating the above mechanism using extremely dry air. How would this let you simplify the expression you derived in part (b)?

(A more precise label for  $O^*$  is  $O(^1D)$ , where the superscript of “1” tells us that the atom has no unpaired electrons, and the “D” tells us that the atom has two units of orbital angular momentum.)

Problem Set 1 continues on the back.

4. (a) Calculate to one significant figure the concentration of ozone (in molecule  $\text{cm}^{-3}$ ) at 40 km in the stratosphere. Use the following data and expressions in your calculation:

|             |  |
|-------------|--|
| Temperature | 251 K  |
| Pressure    | 2.1 Torr   |
| $k_1$       | $2 \times 10^{-9} \text{ s}^{-1}$  |
| $k_2$       | $(6.0 \times 10^{-34} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}) \left(\frac{T}{300.}\right)^{-2.4}$ |
| $k_3$       | $1.9 \times 10^{-3} \text{ s}^{-1}$  |
| $k_4$       | $(8.0 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}) \exp\left(\frac{-2060}{T}\right)$   |

- (b) In order to derive the steady-state expression for  $[\text{O}_3]$  you used in part (a), we assumed that the rate of  $\text{O}_2$  photolysis was much slower than the rate of  $\text{O}_3$  photolysis. Using the given data and your results in part (a), verify this assumption.
5. Problem 1-7 on p. 51 of Baird and Cann.
6. (Inspired by Additional Problem 8 on p. 57 of Baird and Cann) Two species that can attack ozone are atomic chlorine and hydroxyl radical. The rate constant for the Cl reaction is  $(3 \times 10^{-11} \text{ molecule cm}^{-3} \text{ s}^{-1}) e^{(-250/T)}$ , and the rate constant for the OH reaction is  $(2 \times 10^{-12} \text{ molecule cm}^{-3} \text{ s}^{-1}) e^{(-940/T)}$ , where  $T$  is measured in K.
- (a) Calculate the ratio of the rates of ozone destruction by these catalysts at 20 km. At this altitude, the average concentration of OH is 100 times that of Cl, and the temperature is  $-50^\circ\text{C}$ .
- (b) In the Antarctic ozone "hole," typical conditions are  $T = -80^\circ\text{C}$ ,  $[\text{Cl}] = 4 \times 10^5 \text{ molecule cm}^{-3}$ , and  $[\text{O}_3] = 2 \times 10^{12} \text{ molecule cm}^{-3}$ . Calculate the rate of the chlorine-ozone reaction under these conditions.