Please return your answers before March 13

Exercise 1

1. What is the energy, in kilojoules per mole, associated with photons having the following wavelengths? What is the significance of each of these wave- lengths?
(a) 280 nm (b) 400 nm (c) 750 nm (d) 4000 nm

2. The ΔH^0 for the decomposition of ozone into O_2 and atomic oxygen is +105 kJ/mol. What is the longest wavelength of light that could dissociate ozone in this manner? What is the region of sunlight (UV, visible, or infrared) in which this wavelength falls.

3. Using the enthalpy of formation information given below, calculate the maximum wavelength that can dissociate NO_2 to NO and atomic oxygen. Recalculate the wavelength if the reaction is to result in the complete dissociation into free atoms (i.e., N + 2O). Is light of these wavelengths available in sunlight?

ΔH_f^0 values (kJ/mol): NO_2 : +33.2; NO: +90.2; N: +472.7; O: +249.2

Of course, in order for a sufficiently energetic photon to supply the energy to drive a reaction, it first must be absorbed by the molecule. As you can infer from the examples of the absorption spectra of 02 and 03 (see lecture 1), there are many wavelength regions in which molecules simply do not absorb significant amounts of light. Thus, for example, because ozone molecules do not absorb visible light near 400 nm, shining light of this wavelength on them does not cause them to decompose, even though 400-nm photons carry sufficient energy to dissociate them to atomic and molecular oxygen. Furthermore, as discussed above, just because molecules of a substance absorb photons of a certain wavelength and such photons are sufficiently energetic to drive a reaction does not mean that the reaction necessarily will occur; the photon energy can be diverted by a molecule into other processes undergone by the excited state. *Thus the availability of light with sufficient photon energy is a necessary but not a sufficient condition for reaction to occur with any given molecule.*

4. Calculate the rate of the reaction between NO and O_3 at -30°C using the rate constant value with $A=1.8X10^{-12}$ E=10.4 kJ/mol and assuming NO and O3 concentrations of $5.0X10^9$ and $5.0X10^{12}$ molecules/cm^3, respectivly. Using the same concentrations, recalculate the rate of the reaction at -60^{o}C.

5.Consider the following 3-step mechanism for the production and destruction of excited oxygen atoms, O*, in the atmosphere:

O_2 + hv ---> O + O*
O* + M ----> O + M
O* + H_2O ---> 2 OH
Develop an expression for the steady-state concentration of O* in terms of the concentrations of the other chemicals involved.

6. Perform a steady-state analysis for the following mechanism
Cl_2 + hv ---> 2 Cl
Cl + O_3 ----> ClO + O_2
2 ClO ----> 2 Cl + O_2
ClO + NO_2 ----> $ClONO_2$

Obtain expression for the steady-state concentrations of Cl and ClO, and hence for the rate of ozone destruction.

7. Use the data about the rate constants for the reactions of atomic chlorine and of hydroxyl radical with ozone from NIST database: http://kinetics.nist.gov/kinetics/Search.jsp. Calculate the ratio of the rates of ozone destruction by these catalysts at 20 km, given that at this altitude the average concentration of OH is about 100 times that of Cl and that the temperature is about -50°C. Calculate the rate constant for ozone destruction by chlorine under conditions in the Antarctic ozone hole, when the temperature is about -80°C and the concentration of atomic chlorine increases by a factor of one hundred to about 4×10^5 molecules/cm^3•