CHM 5423 – Atmospheric Chemistry
Problem Set 2
Due date: Thursday, February 7^{th}.

Do the following problems. Show your work.

1) Before the development of lasers, atomic mercury lamps were a common source for UV radiation. The strongest light emission for a low pressure mercury lamp occurs at λ = 254. nm.

a) Find the energy of one photon of light with λ = 254. nm. Give your answer in units of J/photon and cm^{-1}.

b) Find the energy of one mole of photons with λ = 254. nm. Give your answer in units of kJ/mol.

2) Beer's law, as derived in class, can be written as

$$\ln(I_\ell/I_0) = - \sigma N \ell \quad (2.1)$$

where I_0 is the initial intensity of light (at a specific wavelength λ), I_ℓ is the intensity after the light has traveled a distance ℓ (in cm), σ is the absorption cross-section for the absorping molecule (in cm^2/molecule), and N is the number density of absorbing molecules (in molecule/cm^3). Beer's law is a common method for monitoring concentrations of absorbing molecules both in the laboratory and in in the atmosphere.

a) The absorption cross section for acetaldehyde (CH_3CHO) is σ = 4.16 x 10^{-20} cm^2/molecule at λ = 300. nm. What is the concentration of acetaldehyde (in molecules/cm^3) in a system if I_ℓ/I_0 = 0.813 for a pathlength ℓ = 552. cm? Give your answer in units of molecules/cm^3. You may assume that at this wavelength acetaldehyde is the only molecule in the system that absorbs light.

b) Chemists often use a different form of Beer's law

$$A = \log_{10}(I_0/I_\ell) = ac\ell \quad (2.2)$$

where c is the concentration of absorbing molecules (in mol/L), $\ell$is the pathlength (in cm), and a is the absorption coefficient of the molecule (in L/mol·cm). Find the numerical value for the conversion factor between σ and a, and use it to calculate the value for a for acetaldehyde at λ = 300. Nm.

3) Consider the UV photodissociation of nitrous oxide (N_2O). The following primary processes could occur following the absorption of a photon by the molecule

$N_2O + hc/\lambda \rightarrow N_2O^*$	$N_2O^* \rightarrow N_2 + O(^3P)$	ϕ_d
	$N_2O^* \rightarrow N_2O + hc/\lambda'$	ϕ_f
	$N_2O^* + M \rightarrow N_2O + M$	ϕ_q

In the above processes ϕ_d is the primary quantum yield for each of the two photodissociation processes, ϕ_f is the primary quantum yield for fluorescence, and ϕ_q is the primary quantum yield for collisional quenching.

a) If the above process is carried out in synthetic air (with p(air) = 1 00 atm >> p(N_2O)) then the oxygen atom produced by the photodissociation process will quantitatively form ozone (O_3) by the reaction

$$O(^3P) + O_2 + M \rightarrow O_3 + M$$

a) What will be the value for Φ, the overall quantum yield, for N_2O, N_2, O_2, and O_3? Give your answers in terms of the primary quantum yields for the three primary processes discussed above.

b) Which of the overall quantum yields could actually be measured in an experiment? Which could not? Justify your answer.

c) For which of the primary quantum yields (if any) is there sufficient information to find their value based on the overall quantum yields for a photodissociation experiment? Indicate how the overall quantum yield would be used to find the primary quantum yield when this can be done.

d) Suggest additional experiments that could be done to find values for the primary quantum yields for the processes where they could not be found by the above single experiment. How would these additional eperiments allow you to find the missing primary quantum yield values? Be specific.

4) Find the value for θ (zenith angle) and f_s (Earth-sun correction factor) for the following conditions:

a) 1600 hours, latitude = 30 °N, date = April 1st
b) 1100 hours, latitude = 10 °S, date = December 5th
c) 1200 hours, latitude = 25 °N, date = February 15th

5) Using the method discussed in class, find the photodissociation rate constant for HO_2NO_2 (peroxynitric acid, a reservoir species for NO_2 in the troposphere) for the following conditions: 1200 hours, latitude = 25 °N, date = February 15th (the conditions in part c of problem 4). The absorption cross-sections for this molecule as a function of wavelength are given below. You may assume the primary quantum yield for photodissociation of HO_2NO_2 is equal to 1 at all wavelengths.

λ (nm)	σ (cm^2/molecule)	λ (nm)	σ (cm^2/molecule)
290.	3.9×10^{-20}	310.	0.5×10^{-20}
295.	2.4×10^{-20}	315.	0.3×10^{-20}
300.	1.4×10^{-20}	320.	0.2×10^{-20}
305.	0.9×10^{-20}	325.	0.1×10^{-20}

6) Using the procedure discussed in class and the data below (given at T = 298. K), find the longest wavelength of light (in nm) capable of carrying out the following photodissociation reactions. Based on your calculations, which of the reactions (if any) be an important process in the troposphere? Which of the reactions (if any) could be an important process in the stratosphere?

a) $H_2S \rightarrow HS + S(^3P)$
b) $N_2O \rightarrow N_2 + O(^3P)$
c) $N_2O \rightarrow N_2 + O(^1D)$
d) $CH_3COCH_3 \rightarrow CH_3COCH_2 + H(^2S)$
e) $CH_3COCH_3 \rightarrow CH_3CO + CH_3$

species	ΔH°_f (kJ/mol)	species	ΔH°_f (kJ/mol)
$H(^2S)$	218.0	H_2S	- 20.6
$O(^3P)$	249.2	N_2	0.0
$O(^1D)$	438.9	N_2O	82.1
$S(^3P)$	277.2	CH_3COCH_2	- 23.9
HS	143.0	CH_3COCH_3	- 217.2
CH_3	146.4	CH_3CO	- 10.0