

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 $\lambda = 254$. nm.

- Find the energy of one photon of light with $\lambda = 254$. nm. Give your answer in units of J/photon and cm^{-1} .
- Find the energy of one mole of photons with $\lambda = 254$. nm. Give your answer in units of kJ/mol.

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

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

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

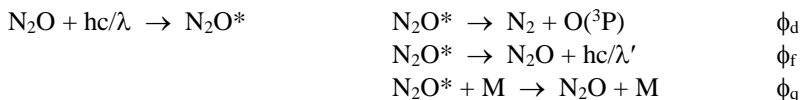
a) The absorption cross section for acetaldehyde (CH_3CHO) is $\sigma = 4.16 \times 10^{-20} \text{ cm}^2/\text{molecule}$ at $\lambda = 300$. nm. What is the concentration of acetaldehyde (in $\text{molecules}/\text{cm}^3$) in a system if $I_t/I_0 = 0.813$ for a pathlength $\ell = 552$. cm? Give your answer in units of $\text{molecules}/\text{cm}^3$. 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

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

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



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 $p(\text{air}) = 1.00 \text{ atm} \gg p(\text{N}_2\text{O})$) then the oxygen atom produced by the photodissociation process will quantitatively form ozone (O_3) by the reaction



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 experiments 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:

- 1600 hours, latitude = 30 °N, date = April 1st
- 1100 hours, latitude = 20 °S, date = December 5th
- 1200 hours, latitude = 25 °N, date = February 15th

5) Using the method discussed in class, find the photodissociation rate constant for HO₂NO₂ (peroxynitric acid, a reservoir species for NO₂ 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 HO₂NO₂ 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?

- H₂S → HS + S(³P)
- N₂O → N₂ + O(³P)
- N₂O → N₂ + O(¹D)
- CH₃COCH₃ → CH₃COCH₂ + H(²S)
- CH₃COCH₃ → CH₃CO + CH₃

species	ΔH°_f (kJ/mol)	species	ΔH°_f (kJ/mol)
H(² S)	218.0	H ₂ S	- 20.6
O(³ P)	249.2	N ₂	0.0
O(¹ D)	438.9	N ₂ O	82.1
S(³ P)	277.2	CH ₃ COCH ₂	- 23.9
HS	143.0	CH ₃ COCH ₃	- 217.2
CH ₃	146.4	CH ₃ CO	- 10.0

Solutions.

1) a) $E = \frac{hc}{\lambda} = \frac{(6.626 \times 10^{-34} \text{ J}\cdot\text{s})(2.998 \times 10^8 \text{ m/s})}{(254. \times 10^{-9} \text{ m})} = 7.82 \times 10^{-19} \text{ J/molecule}$

Since $E(\text{cm}^{-1}) = \frac{E(\text{J})}{hc}$, then $E(\text{cm}^{-1}) = \frac{7.82 \times 10^{-19} \text{ J/molecule}}{(6.626 \times 10^{-34} \text{ J}\cdot\text{s})(2.998 \times 10^{10} \text{ cm/s})} = 39370. \text{ cm}^{-1}$

b) For one mole of photons. $E = E_{\gamma} N_A$, where $N_A = \text{Avogadro's number}$

So $E = (7.82 \times 10^{-19} \text{ J/molecule})(6.022 \times 10^{23} \text{ molecule/mol})(1 \text{ kJ}/1000 \text{ J}) = 471. \text{ kJ/mol}$

2) a) $\ln(I_t/I_0) = -\sigma N \ell$

So $N = -\frac{\ln(I_t/I_0)}{\sigma \ell} = -\frac{\ln(0.813)}{(4.16 \times 10^{-20} \text{ cm}^2/\text{molecule})(552. \text{ cm})} = 9.02 \times 10^{15} \text{ molecule/cm}^3$

b) The conversion factor can be found as follows

$$\ln(I_t/I_0) = -\sigma N \ell$$

So $\ln(I_0/I_t) = +\sigma N \ell$

The conversion factor between \ln and \log_{10} is $\ln(10) = 2.303$, and so if we divide both sides of the above equation by $\ln(10)$, we get

$$\frac{\ln(I_0/I_t)}{\ln(10)} = \log_{10}(I_0/I_t) = \frac{\sigma N \ell}{\ln(10)}$$

But $\log_{10}(I_0/I_t) = a \ell$

Therefore $\frac{\sigma N \ell}{\ln(10)} = a \ell$

If we cancel the common factor of ℓ , and solve for the absorption coefficient a , we get

$$a = \frac{\sigma}{\ln(10)} \frac{N}{c}$$

To complete the work above, we only need the conversion factor between N (number density) and c (molar concentration).

$$\frac{1 \text{ mol}}{\text{L}} = 6.022 \times 10^{23} \frac{\text{molecule}}{\text{L}} = 6.022 \times 10^{20} \frac{\text{molecule}}{\text{cm}^3}$$

And so $c = \frac{N}{(6.022 \times 10^{20} \text{ molecule}\cdot\text{L}/\text{mol}\cdot\text{cm}^3)}$

Substituting above gives

$$a = \sigma \frac{1}{\ln(10)} (6.022 \times 10^{20} \text{ molecule}\cdot\text{L}/\text{mol}\cdot\text{cm}^3) = \sigma (2.615 \times 10^{20} \text{ molecule}\cdot\text{L}/\text{mol}\cdot\text{cm}^3)$$

The conversion factor is therefore the term in brackets above.

We can use this conversion factor to find the value for a for acetaldehyde at $\lambda = 300$ nm

$$a = (4.16 \times 10^{-20} \text{ cm}^2/\text{molecule}) (2.615 \times 10^{20} \text{ molecule} \cdot \text{L}/\text{mol} \cdot \text{cm}^3) = 10.88 \text{ L}/\text{mol} \cdot \text{cm}$$

3) a) The only process that removes N_2O from the system is photodissociation, and so

$$\Phi_{\text{N}_2\text{O}} = -\phi_d$$

This process produces a molecule of N_2 , and so

$$\Phi_{\text{N}_2} = +\phi_d$$

Photodissociation generates an $\text{O}(^3\text{P})$ atom, whose only fate is reaction with O_2 to form O_3 , and so

$$\Phi_{\text{O}_2} = -\phi_d \quad \Phi_{\text{O}_3} = +\phi_d$$

b) We would most easily be able to measure the overall quantum yield for O_3 because we begin with no ozone in the system, and ozone concentration can be found using absorption spectroscopy. The decrease in concentration for N_2O could be used to find the overall quantum yield for nitrous oxide, assuming that there was a significant decrease in concentration. This could be done using either absorption spectroscopy or fluorescence spectroscopy.

Since there is already a large amount of nitrogen and oxygen in the system, it is not possible to measure the small changes in these concentrations due to their production or removal.

c) We can find ϕ_d using either the overall quantum yield for production of O_3 or for removal of N_2O . Since

$$\phi_d + \phi_f + \phi_q = 1$$

Then

$$(\phi_f + \phi_q) = 1 - \phi_d$$

However, there is not sufficient information to determine individual values for ϕ_f and ϕ_q .

d) If we look at the three processes taking place from kinetic perspective, we can say

k_d = rate constant for dissociation

k_f = rate constant for fluorescence

$k_q' = k_q [\text{M}]$ = rate constant for quenching (a pseudo 1st order rate constant)

$$\phi_d = \frac{k_d}{k_d + k_f + k_q [\text{M}]}$$

If we invert both sides of this expression, we get

$$\frac{1}{\phi_d} = \frac{k_d + k_f + k_q [\text{M}]}{k_d} = 1 + (k_f/k_d) + (k_q/k_d) [\text{M}]$$

By studying the reaction at several pressures and plotting the data as suggested above, the values for k_f/k_d and k_q/k_d can be found, from which individual values for the primary quantum yields can be obtained.

4) Zenith angle and Earth-sun corrections can be found as follows

- a) 1600 hours = 0800 hours
30°N and April 1st are in the table

So $\theta = 62.1^\circ$ For April 1st the Earth-sun correction is 1.001

- b) 1100 hours is in the table
20°S December 5th = 20°N June 5th

For 20°N June 1st 1100 hours = 15.7°
July 1st 1100 hours = 15.1°

So $\theta = 15.7^\circ + (15.1^\circ - 15.7^\circ) (5 - 1)/(30 - 1) = 15.6^\circ$

For the Earth-sun correction December 1st = 1.027
December 15th = 1.031

So $\theta = 1.027 + (1.031 - 1.027) (5 - 1)/(15 - 1) = 1.028$

- c) 1200 hours is in the table. We may interpolate for February 15th and 25°N

	20°N	25°N	30°N
February 1 st	37.2	42.2	47.2
February 15 th	32.3	<u>37.2</u>	42.3
March 1 st	27.7	32.7	37.7

The interpolation factor for February 15th is $(15 - 1)/(28 - 1) = 14/27$

So $\theta = 37.2^\circ$

The Earth-sun correction factor for February 15th is 1.024

5) We will do this as in the example in the notes. The data are compiled on the next page. Note that $\theta = 37.2^\circ$. We have interpolated for both absorption cross-section and photon flux using the data in the Chapter 2 appendix and data provided in the problem.

The value obtained for the photodissociation rate constant is $k_d = 3.4 \times 10^{-6} \text{ s}^{-1}$. This corresponds to a half-life of

$$t_{1/2} = \frac{\ln(2)}{k_d} = \frac{\ln(2)}{(3.4 \times 10^{-6} \text{ s}^{-1})} = 57 \text{ hours (about 2 days)}$$

λ range (nm)	$\sigma(\lambda) \times 10^{20}$ ($\text{cm}^2/\text{molecule}, e$)	$F(\lambda) \times 10^{-14}$ ($\text{photon}/\text{cm}^2\text{-s}$)	$\Delta k_d \times 10^6$ (s^{-1})
290-292		0.00	0.00
292-294		0.00	0.00
294-296		0.00	0.00
296-298	2.0	0.00	0.000
298-300	1.6	0.01	0.016
300-302	1.3	0.03	0.039
302-304	1.1	0.09	0.099
304-306	0.9	0.18	0.162
306-308	0.74	0.31	0.2294
308-310	0.58	0.43	0.2494
310-312	0.46	0.68	0.3128
312-314	0.38	0.87	0.3306
314-316	0.30	1.01	0.3030
316-318	0.26	1.28	0.3328
318-320	0.22	1.33	0.2926
320-325	0.15	4.26	0.639
325-330	0.05	6.35	0.3175

$$k_d(\text{uncorrected}) = \sum_n \Delta k_{d,n} = 3.3231 \times 10^{-6} \text{ s}^{-1}$$

$$k_d(\text{corrected}) = f_s k_d(\text{uncorrected}) = (1.024) \times 3.3231 \times 10^{-6} \text{ s}^{-1} = 3.403 \times 10^{-6} \text{ s}^{-1} \cong 3.4 \times 10^{-6} \text{ s}^{-1}$$

6) We may use the data to find the values for $\Delta H^\circ_{\text{rxn}}$. The energy needed per molecule will then be

$$\Delta E = \Delta H^\circ_{\text{rxn}}/N_A, \text{ where } N_A \text{ is Avogadro's number, and}$$

$$\Delta H^\circ_{\text{rxn}} = [\sum \Delta H^\circ_{\text{rxn}}(\text{products})] - [\sum \Delta H^\circ_{\text{rxn}}(\text{reactants})]$$

If that energy comes from the absorption of a photon, then

$$\Delta E = hc/\lambda = \Delta H^\circ_{\text{rxn}}/N_A$$

or

$$\lambda = \frac{hcN_A}{\Delta H^\circ_{\text{rxn}}}$$

reaction	$\Delta H^\circ_{\text{rxn}}$ (kJ/mol)	λ (nm)
a	440.8	271.
b	167.1	716.
c	356.8	335.
d	411.3	291.
e	353.6	338.

Reactions b, c, and e are energetically possible in the troposphere, since the cutoff for the actinic UV region of the spectrum is $\lambda = 295$. nm. Reaction d is close, and so might also be energetically possible. Reaction a is only energetically possible in the stratosphere (as are all of the other reactions).

To actually occur, the reactant molecules would also have to absorb light, and have a primary yield for photodissociation $\phi_d > 0$ at at least some of the absorbing wavelengths in the actinic UV.