Exercises

- **A.** Species X, emitted primarily in the Eastern U.S., has a lifetime of 6 months in the troposphere. Will it be uniformly distributed throughout the troposphere (consider vertical, latitude, and longitude)?
- **B.** Methane has an atmospheric lifetime of about a decade. Will it be uniformly distributed throughout the troposphere even though its sources are unevenly distributed?
- C. Of the 250 nm light entering the top of the stratosphere, what percentage is absorbed/scattered in passing from 50 to 0 km (to the nearest percent)? Answer the same question for 310 nm light and 350 nm (less precision is possible).
- **D.** At 50 km, what is the ratio of the light flux at 350 nm to the light flux at 250 nm?
- **E.** At 10 km, what is the lifetime (1/e decay time) for O₃ with respect to photolysis (ignoring other reactions of O₃)?
- **F.** What is the quantum yield for photodissociation of NO₂ at 400 nm? What is the overall quantum yield for photodissociation of O₃ at 300 nm?
- G. What is the energy (kcal/mole or kJ/mole) of a photon of 400 nm light? Of 300 nm light?
- **H.** Use the spreadsheet on the course web "SZA Calculation" to find the SZA at noon EDT (4 p.m. GMT) for the New York City and the City of Syracuse, NY, for September 10.
- I. The graphs on page 2 show the solar flux (10¹⁴ photons cm⁻² sec⁻¹ nm⁻¹) at two SZA and two altitudes versus wavelength (in nm). The second graph is a detail of the first.

Consider a compound which absorbs both at 400 nm and at 220 nm. The quantum yield for dissociation is 1.00 at both wavelengths, but the absorption cross-section is 10 times higher at 220 nm than at 400 nm.

i) At SZA=30 and h= 40 km, which of these two wavelengths (220 nm vs. 400 nm) contributes more to photolysis? Explain!

(In answering (ii) and (iii) include factors relevant to the particular wavelengths specified)

- ii) At a given h and 400 nm, what causes the change in flux between SZA 30 and SZA 70?
- iii) At 290 nm and SZA = 30, what causes the change in flux between h=40 and h=0 km?
- **J.** Using the spreadsheet "Calculating Photolysis Rates" that is linked from the course web page, compute J for NO₂:
- i) for SZA=40 degrees if $\phi = 1.0$ for $\lambda \le 440$ nm. Why does J increase so much (double) when in the original calculation photolysis was already occurring with $\phi = 1.0$ from 290-400 nm?
- ii) for for SZA=40 degrees and the correct ϕ if σ doubled for all wavelengths.
- iii) at SZA=78 degrees.





Problems

1. Using the spreadsheet for "Calculating Photolysis Rates" as a template, calculate the photolysis rate constants for HOCl and $CH_3CHO \rightarrow CH_3 + HCO$:

- a) Delete all the tabs except the one labeled "NO2" which has the calculation.
- b) Modify the spreadsheet to delete data at SZA other than 30 or 70 degrees.
- c) Within the same Excel file, make a copy of the tab for the calculations.
- d) Name one copy "HOCl" and the other "CH3CHO
- e) Find the cross-sections listed as "JPL-2010(2011)" in <u>http://satellite.mpic.de/spectral_atlas</u> for HOCl and CH₃CHO.
- f) In another worksheet of the same Excel file, interpolate and/or average the cross-sections listed to match the wavelength ranges in the Excel file.
- g) Copy the <u>values</u> (not any formulas) of those interpolated/averaged cross-sections into the tabs for HOCl and CH₃CHO.
- h) Modify the quantum yields as needed, using the values in *Burkholder*

Compare your results for HOCl in Problem 1 with the data in the corresponding Figure in *DeMore*. If your answer is off by powers of 10, then find the error in your calculations. If you can't find the error, then note that your answer is incorrect in responding to this question.

when you turn in nardcopy of	y of your answers to this problem, use the following table.		
Species	From Spreadsheet		L (DoMoro) of 10 km
	J(SZA=30)	J(SZA=70)	J (Demore) at 10 km
HOCI			
$CH3CHO \rightarrow CH3 + HCO$			

When you turn in hardcopy of your answers to this problem, use the following table.

E-mail me (tsdibble@esf.edu) your edited copies of the spreadsheet <u>prior</u> to class on the due date (Tuesday September 10).

2. List and evaluate **at least two** possible explanations for the difference between J(HOCl) you obtained (or would have obtained if you did the calculation correctly) and that in *DeMore*.

3. The altitude dependence of the photolysis rate constant (J) in *DeMore* is somewhat large for HONO₂ but rather small for NO₃.

Explain this observation in terms of solar flux vs. both wavelength and altitude (Figure 7 of *DeMore* or page 2 of this Homework) together with the absorption spectra of both compounds (from the Figures in FP+P or elsewhere). Consider the cartoon I gave you in which I asked you do determine whether molecule A or D had the higher value of J.

The two Prompts below are designed to help you with the logic of the question. You do **not** have to use them for this question nor provide me answers.

Prompt 1: Does NO₃ absorb mostly at wavelengths longer than 300 nm ($\lambda > 300$ nm)?

Prompt 2: Consider light with $\lambda > 300$ nm: is it one or more orders of magnitude more abundant at 50 km than at 0 km?

Questions #4 and 5 are not due until Thursday, 9/12.

You are STRONGLY ENCOURAGED to discuss your answers with other students.

4. My goal with this Homework was for you to learn how SZA, altitude, $\sigma(\lambda)$, and $\phi(\lambda)$ combine to control J.

1) Analyze how well you learned this at the time this Homework was due.

2) What could the instructor have done differently in the course (in class, reading, handouts, etc.) or the design of this Homework to help you learn this better?

3) What could **you** have done differently to help you learn this better?

5. Read a brief article about active vs. passive learning (for example, on Wikipedia)

Consider the "Course Goals and Objectives" on pages 3-4 of the Course Guide/Syllabus. What learning strategies will help you earn a good grade in this course (aka, understand the material well)?