

## AOSC/CHEM 433 & AOSC 633 Atmospheric Chemistry and Climate

### Problem Set #3 (185 points for 433 / 235 points for 633)

**Due: Tues, 9 April 2019 (start of class)**

*Late penalty: 10 points* per day late, unless there is a legitimate medical or extra-curricular circumstance (i.e., band, athletics, GREs, etc) brought to our attention *prior to the due date!*

*Final deadline:* Monday, 15 April, 5 pm: **no credit** will be given after final deadline.

*Please show all work!*

**1. (55 points)** The Montreal Protocol regulates production of methyl bromide ( $\text{CH}_3\text{Br}$ ), which has been used as a fumigant, as well as halon-1211 ( $\text{CF}_2\text{BrCl}$ ) used to extinguish fires. Bromoform ( $\text{CHBr}_3$ ) and dibromomethane ( $\text{CH}_2\text{Br}_2$ ) are produced by algae in the biologically productive tropical oceans and are not regulated because they do not have significant industrial sources. Here, we will examine the loss processes for removal of these compounds.

**a) (15 points).** Assuming a temperature of 270 K and a value for global mean (24 hour average) tropospheric  $[\text{OH}]$  of  $1 \times 10^6$  molecules /  $\text{cm}^3$ , find the lifetime for removal of  $\text{CH}_3\text{Br}$ ,  $\text{CHBr}_3$ , and  $\text{CH}_2\text{Br}_2$  by reaction with OH in the troposphere and the “lower limit” for removal of  $\text{CF}_2\text{BrCl}$  by reaction with OH in the troposphere. Express the results in units of *days*.

Why do we express the result for  $\text{CF}_2\text{BrCl}$  as a lower limit?

To complete this question, you will need to use the table of bimolecular rates constants given at:

[https://www.atmos.umd.edu/~rjs/class/spr2019/problem\\_sets/JPL2015\\_Biomolecular\\_Rates\\_pset03.pdf](https://www.atmos.umd.edu/~rjs/class/spr2019/problem_sets/JPL2015_Biomolecular_Rates_pset03.pdf)

**b) (15 points).** Considerable scientific interest resides in the loss of these compounds in a region of the atmosphere known as the tropical tropopause layer, which exists at about 15 km altitude. Convection rapidly lofts air containing these compounds to about 15 km altitude in the tropical atmosphere.

**Find the lifetime due to loss by photolysis**, over a 24 hour period, for halon-1211, methyl bromide, bromoform, and dibromomethane at **15 km** altitude. Again, express the results in units of *days*.

To complete this question you must first find the J value (photolysis frequency) for each species at 15 km altitude, using the values of solar actinic flux that appear in Table A and the values for the absorption cross sections for these compounds given in Table B. ***Please pay close attention to units.*** Hard copies of these tables are given at the end of this problem set. Electronic copies of these tables, available either as text files (\*.txt) or Excel files (\*.xls), can be downloaded from:

[www.atmos.umd.edu/~rjs/class/spr2019/problem\\_sets/TableA\\_pset03.txt](http://www.atmos.umd.edu/~rjs/class/spr2019/problem_sets/TableA_pset03.txt)

[www.atmos.umd.edu/~rjs/class/spr2019/problem\\_sets/TableB\\_pset03.txt](http://www.atmos.umd.edu/~rjs/class/spr2019/problem_sets/TableB_pset03.txt)

or:

[www.atmos.umd.edu/~rjs/class/spr2019/problem\\_sets/TableA\\_pset03.xls](http://www.atmos.umd.edu/~rjs/class/spr2019/problem_sets/TableA_pset03.xls)

[www.atmos.umd.edu/~rjs/class/spr2019/problem\\_sets/TableB\\_pset03.xls](http://www.atmos.umd.edu/~rjs/class/spr2019/problem_sets/TableB_pset03.xls)

The solar actinic flux values are from Table 3.15 of *Chemistry of the Upper and Lower Atmosphere* by Finlayson-Pitts and Pitts, for solar zenith angle (SZA) of 30°, which represents daytime conditions. Assume all quantum yields are unity: i.e., if a photon is absorbed the process is fully dissociative. For those keeping careful track of units, the quantum yield = 1.0 molecule / photon.

Notes:

1) for one compound the J value is the result of a “trivial” calculation you could carry out in your head (really!). We are asking you to conduct this calculation to emphasize the fact that the J value is the product of the cross section × the solar actinic flux (at a particular altitude).

2) once you’ve computed the J value (photolysis frequency) for each compound, you should be able to estimate the lifetime for loss by photolysis.

However: the sun is only up for half of the time; it is dark at night and **we asked for the lifetime to represent conditions over a 24 hour period of time** (i.e., a “real calendar day”). Factor into your calculation a simple estimate for how the *photolysis lifetime* is affected by the fact *it gets dark at night*.

c) (15 points). Calculate the **overall tropospheric lifetime** for each of these four compounds, using lifetimes for loss by reaction with OH and loss for photolysis found in parts a) and b), and the following expression that relates overall lifetime (for loss) to individual lifetimes for loss by two separate processes, such as photolysis and reaction with OH:

$$\frac{1}{\tau_{\text{OVERALL}}} = \frac{1}{\tau_{\text{LOSS PROCESS \#1}}} + \frac{1}{\tau_{\text{LOSS PROCESS \#2}}}$$

where of course  $\tau$  represents lifetime.

d) (10 points). Based on your answers above, if scientists happen to observe bromine radicals in the tropical tropopause layer (TTL), during a field campaign that conducted measurements of these compounds such as this effort:

[https://www.eol.ucar.edu/field\\_projects/contrast](https://www.eol.ucar.edu/field_projects/contrast)

would these bromine radicals likely be supplied by the decomposition of:

- a) industrial chemicals or
- b) natural compounds

and why would this be the case?

**2. (130 points) Production of Tropospheric Ozone.** Here, we will evaluate the dependence of the production of tropospheric ozone on the abundance of NO, which is central to tropospheric chemistry.

Our calculation will be conducted at the surface, for a hot summer day with a temperature of 94 degrees Fahrenheit and an atmospheric density  $[M]$  of  $2.5 \times 10^{19}$  molecules  $\text{cm}^{-3}$ .

The production of tropospheric ozone is limited by the reaction of  $\text{HO}_2 + \text{NO}$ ; hence, we write:

$$\text{Prod Ozone} = k_{\text{HO}_2 + \text{NO}} [\text{HO}_2] [\text{NO}] \quad (1)$$

The loss of  $\text{HO}_x$  is equal to:

$$\text{Loss of HO}_x = 2 k_{\text{HO}_2 + \text{HO}_2} [\text{HO}_2]^2 + k_{\text{OH} + \text{NO}_2 + \text{M}} [M] [\text{OH}] [\text{NO}_2] \quad (2)$$

Assume that the production rate of  $\text{HO}_x$  due to the reaction  $\text{O}(^1\text{D}) + \text{H}_2\text{O}$  occurs at a rate of  $0.70 \text{ ppt s}^{-1}$  (parts per trillion per second) and also that production of  $\text{HO}_x$  is balanced by loss of  $\text{HO}_x$ , which is given by the above expression.

The ratio of  $[\text{OH}]$  to  $[\text{HO}_2]$  is controlled by two reactions:  $\text{OH} + \text{CO}$  which causes loss of OH and  $\text{HO}_2 + \text{NO}$  which reforms OH. Hence, a balance of production and loss for OH leads to:

$$k_{\text{CO} + \text{OH}} [\text{CO}] [\text{OH}] = k_{\text{HO}_2 + \text{NO}} [\text{HO}_2] [\text{NO}] \quad (3)$$

We will represent the entire mix of VOCs in the atmosphere as CO, which we will assume has a mixing ratio of 1000 ppb (this is a simplified treatment for a highly polluted atmosphere). Finally, assume the ratio  $[\text{NO}_2]/[\text{NO}] = 9$  at all times. This final assumption allows us to solve the problem using pencil and paper, rather than a computer code.

By substituting (3) into (2), we can show:

$$\text{Prod of HO}_x = 2 k_{\text{HO}_2 + \text{HO}_2} [\text{HO}_2]^2 + R [\text{HO}_2] [\text{NO}]^2 \quad (4)$$

**a) (20 points) What is the symbolic value of R in equation (4): i.e., what combination of rate constants and other parameters does R represent?**

**b) (20 points) What is the numerical value of R ?**

Note: rates for all reactions should be obtained from the table of bimolecular rates constants posted at:

[https://www.atmos.umd.edu/~rjs/class/spr2019/problem\\_sets/JPL2015\\_Biomolecular\\_Rates\\_pset03.pdf](https://www.atmos.umd.edu/~rjs/class/spr2019/problem_sets/JPL2015_Biomolecular_Rates_pset03.pdf)

except for:

a) the rate constant of the three body reaction  $\text{OH} + \text{NO}_2 + \text{M}$  that has a value of  $4.8 \times 10^{-31} \text{ cm}^6 \text{ sec}^{-1}$

b) the rate constant for  $\text{OH} + \text{CO}$  that has a value of  $2.4 \times 10^{-13} \text{ cm}^3 \text{ sec}^{-1}$  for our conditions.

We've provided numerical values for both of these rate constants because the expressions are more complicated to evaluate than those used for standard bimolecular reactions.

**c) (20 points) Use expression (4) to find  $[\text{HO}_2]$ , in units of molecules/ $\text{cm}^3$ , for the following values of  $[\text{NO}]$ :**

10, 350, 1000, 2000, and 3000 ppt (parts per trillion)

Note: you must first convert  $[\text{NO}]$  to molecules  $\text{cm}^{-3}$ .

**d) (30 points) Evaluate expression (1), the production rate of tropospheric ozone, for each value of  $[\text{NO}]$  given in part C. Express the answer in units of molecules  $\text{cm}^{-3} \text{ s}^{-1}$ .**

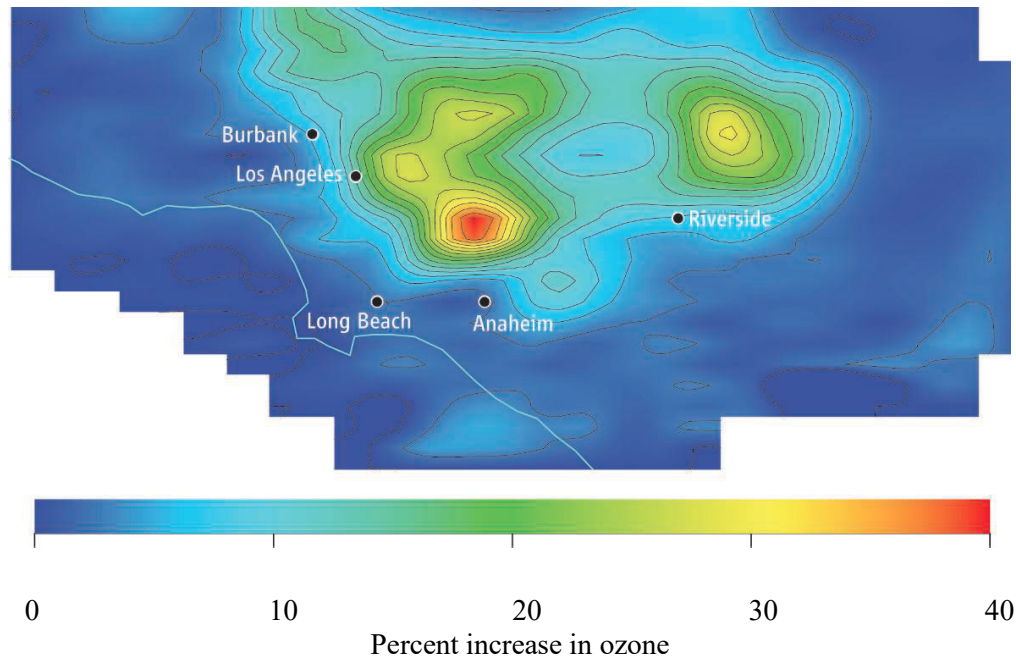
**e) (20 points) Sketch, or use a program to plot, the production rate of tropospheric ozone as a function of  $[\text{NO}]$ .**

**f) (20 points) Explain why the production rate of ozone varies in such a non-linear manner as a function of the value of  $[\text{NO}]$  and state why knowledge of where the troposphere lies, on the curve drawn in part f), is so important for air quality regulation.**

### 3. 633 Students Only (50 points)

This question is assigned only to students enrolled in AOSC 633.

- i) (10 points) Produce a plot of the production rate of ozone, using **units of ppb hour<sup>-1</sup>**, for the following values of the HO<sub>x</sub> production rate: 0.2 ppt s<sup>-1</sup>, 0.70 ppt s<sup>-1</sup> (value used above) and 1.5 ppt s<sup>-1</sup>. Note: results above were found, presumably, in units of molecules cm<sup>-3</sup> s<sup>-1</sup>, so you will need to convert to ppb hour<sup>-1</sup>.
- ii) (10 points) Determine the value of NO where each of these three curves reaches a maximum.
- iii) (10 points) Explain why the maximum value of the production curve varies with NO in the manner determined above.
- iv) (20 points) Scientists at the University of California, San Diego reported that the reaction of electronically excited NO<sub>2</sub> with H<sub>2</sub>O may provide an important source of HO<sub>x</sub> ([Li et al., Science, 319, 1657, 21 March 2008](#)) that until their study had been overlooked in models of atmospheric composition. In a commentary that accompanied this article ([Wennberg and Dabdub, Science, 319, 1624, 21 March 2008](#)), Drs. Wennberg and Dabdub showed that this new source of HO<sub>x</sub> leads to a considerable increase in the amount of tropospheric O<sub>3</sub> at the surface in Southern California, as illustrated below:



**More pollution?** The difference between photochemical simulations for 27 to 29 August 1987 in California obtained with and without including the OH source from the reaction of electronically excited NO<sub>2</sub> with H<sub>2</sub>O described by Li et al. (2008). The figure shows the percentage increases in O<sub>3</sub> due to this new chemical process.

**Explain why Drs. Wennberg and Dabdub found that this new source of HO<sub>x</sub> leads to a considerable increase in modeled surface ozone.**