FCH 511 Homework #04 - Catalytic Cycles Fall 2019

Exercises

A. Write a null cycle involving HO_x.

B. What is the primary source of HO_x in the stratosphere? NO_x? ClO_x?
Write two reactions that terminate HO_x cycles.

C. Based on Figure 5.29, at what altitude are NO_x cycles the largest fraction of O_3 destruction?
Based on Figure 5.28, at what altitude are NO_x cycles occurring with the highest rate?

D. Follow the link entitled ***CFC Degradation Pathways*** from the course web page and print the 1-page pdf file. Complete the missing reactants and products for $CFCl_3$ and CCl_4.

E. In *Burkholder*, upper limits to rate constants are listed with a "<" in the column for k(298).
What is the upper limit to the rate constant for $ClONO_2 + H_2O$ in the *gas* phase?
What is the upper limit to the rate constant for $ClONO_2 + HCl$ in the *gas* phase?

F. Approximately what fraction of collisions of $ClONO_2$ molecules with HCl molecules in the **gas phase** result in reaction? (Your answer will be an upper limit to the actual value.)

G. About what fraction of collisions of gas-phase $ClONO_2$ with liquid water lead to reaction? See section 5 of *Burkholder*.

H.1 What is the average speed of a $BrONO_2$ molecules at 220 K?

H.2 What is the total particle surface area if there are 5 particles/cm^3 of diameter 2 μm?

I. Under the conditions of Exercise H, and with $[BrONO_2] = 1 \times 10^6$ molecule cm^{-3} and what is the rate (molecule cm^{-3} sec^{-1}) at which $BrONO_2$ collides with surfaces?

J. Go to the page https://ozonewatch.gsfc.nasa.gov/monthly/monthly_2018-09_SH.html
... and scroll down to the "Calendar" of maps. You can find false color maps of column ozone for the Antarctic. To get maps for October and November, change the "09" to "10" and "11" in the URL. Click on one days image to get an enlarged view.
For the 1st and 15th of September, October, and November, and note how the lowest column ozone and area of the hole changes with time.

K. If the modelers start to use a rate constant for $OH + NO_2 \rightarrow HONO_2$ that is lower than currently used, would the predicted efficiency of ozone destruction by the standard X/XO cycle rise or fall for:

1) OH/HOO

2) NO/NO_2

3) Cl/ClO

Problems

1. The rate constant for $ClONO_2 + H_2O$ in the *gas* phase is quite low because its activation energy (E_a) is quite large. Basic knowledge of chemistry, as expanded upon in this course, should lead you to **expect** that E_a for $ClONO_2 + H_2O$ in the *gas* phase is large (or, at least, not small). Explain qualitatively why you would **expect** this E_a to be large (or, at least, not small).

2. Assume the reaction $OH + NO_2 \rightarrow HONO_2$ to be a more important pathway for loss of OH than NO_2. Based on this assumption and your answer to Exercise K, would you expect a lower rate constant for the reaction $OH + NO_2 \rightarrow HONO_2$ to lead to predictions of higher or lower $[O_3]$ at 30 km? 50km?

3. Given:

a) the species concentrations and photolysis rate constants provided in *DeMore*
b) the rate constants in Table 1 of *Burkholder*
c) $[Br] = 1.0 \times 10^4$ and $[HOBr] = [BrONO_2] = 2.0 \times 10^6$ molecule cm^{-3}
d) $J(BrONO_2 \rightarrow BrO) = 0.5 \times J(HOBr)$
e) $k(BrO + NO_2 \rightarrow BrONO_2) = 1.9 \times 10^{-12}$ cm^3 molecule^{-1} sec^{-1}

Question: Create a mechanism including ALL reactions creating or destroying BrO, and calculate the steady state [BrO] at 15 km in the normal stratosphere. Part of your grade will be the completeness of your mechanism.

Type of Answer: Calculation.

You should **NOT** include BrO + BrO in your calculation, or any reaction if it:

a) a species concentration is missing from *DeMore* (other than those given above)
b) a rate constant you want is not in Table **1** of *Burkholder* (don't use Table 2!)

You do not need to calculate the steady state concentration of any species besides [BrO]. Only take J values from *DeMore*; don't use a spreadsheet to calculate them.
Use rate constants **even if** *Burkholder* indicates that there is no data at this temperature.

To make it easier for me to grade, organize your answer into two tables structured as below: one for BrO production and one for BrO loss. Note that there are a total of **16** reactions to include!

BrO production rxn.	**[reactant 1]**	**[reactant 2]**	**k**	**Rate of production**
A + B	[A]	[B]		
A + C	[A]	[C]		

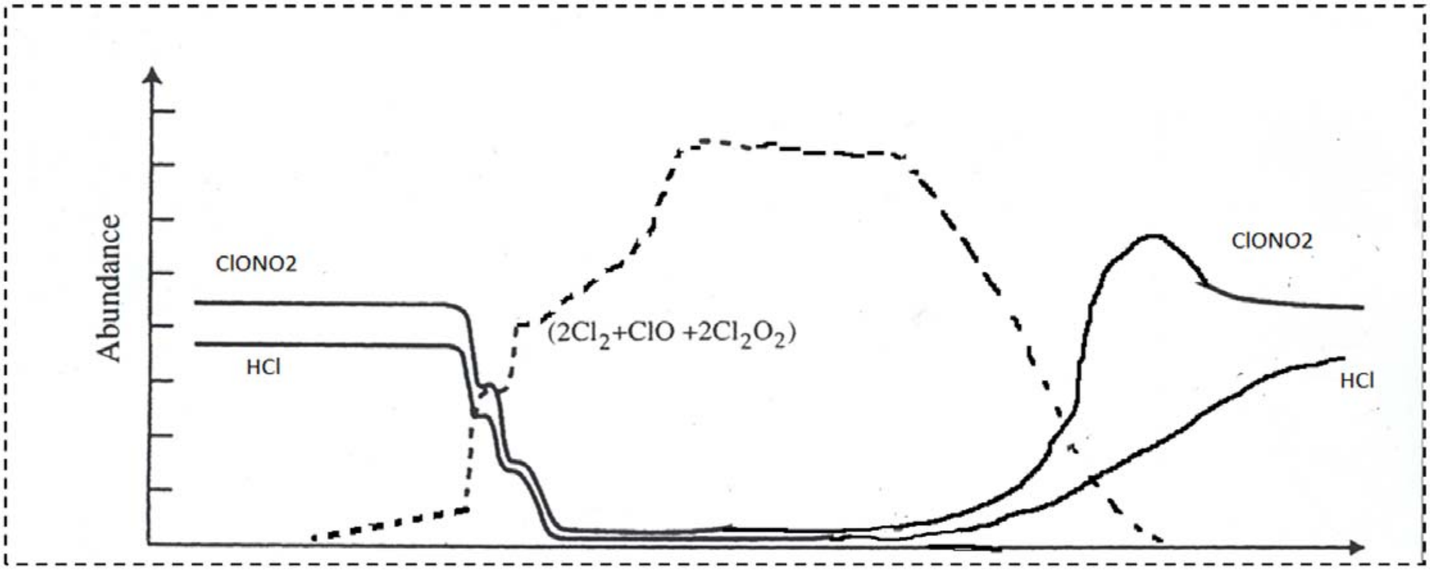
BrO loss reaction	**[reaction partner]**	**k**	**k'**
BrO + X	[X]		
BrO + Y	[Y]		

4. Consider the Figure here, which is adapted from Seinfeld and Pandis to represent the time history of the *Antarctic* ozone hole.

a) EXPLAIN the reasons for the time history of the concentration of HCl, $ClONO_2$, and (Cl_2 + ClO + ClOOCl) in this figure. Use <u>chemical reactions</u> to make your points and EXPLAIN how <u>physical processes</u> also influence concentrations.

A good answer to this will not be not short. My typewritten answer is a full page.

b) Consider your answer for Exercise J, and sketch the time history of ozone concentration on the same plot (don't worry about the y-axis scale)



Spring Equinox **mid- Spring**

Winter || Spring | Spring

5. Under the conditions of Exercise H and I, and using data from Section 5 of *Burkholder*, what is the lifetime for N_2O_5 <u>reaction</u> (not collision) at the surface of particles of Sulfuric Acid Tetrahydrate?