Exercises

A. Given data in the text (Tables B4-6 in Appendix B) and $[OH]_{day} = 1.6 \times 10^6$ molecules cm^{-3}, $[NO_3]_{night} = 5 \times 10^8$ molecules cm^{-3}, $[O_3]_{day} = 100$ ppbv and $[O_3]_{night} = 30$ ppbv.

QUESTION: is cyclohexene removed more rapidly at night or during the day?

B. Re-calculate $[C_2H_5O_2]_{ss}$ and $[C_2H_5O\bullet]_{ss}$ from Exercise D on Homework **#5**, given:
the following reaction added to the mechanism:

$C_2H_5O_2 + HOO \rightarrow C_2H_5OOH + O_2$ $k_5 = 8 \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1}.

Assume [HOO] = 0.03 ppbv and change [NO] to 0.05 ppbv

C. Sketch out the fates of the organic species formed in the degradation of 2-pentene in polluted air during the day (initiated by OH) with rural NO_x concentrations.
Follow all *significant* branches until all *organic* species are converted to non-radicals.
Leave out $ROO\bullet + NO \rightarrow RONO_2$

D. Compute $[NO_2]_{ss}$ at t=190.6 on the graphs from Homework #5 given:

$ROO\bullet + NO \rightarrow RO\bullet + NO_2$ $k_{ROO+NO} = 8 \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1}.

$HOO\bullet + NO \rightarrow OH + NO_2$ $k_{HOO+NO} = 8 \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1}.

$OH + NO2 \rightarrow HONO2$ k_{OH+NO2} from Excel spreadsheet on termolecular reactions

$O_3 + NO \rightarrow O_2 + NO_2$ k_{O3+NO} from Burkholder Table 1 (section on NO_x)

E. If an OH radical reacts with a VOC molecule in a remote area, is it likely that the organic radical chemistry is going to lead to an NO-to-NO_2 conversion?

F. Given the mechanism and rate constants (in the "model" worksheet) and the concentration data in the file **CO_oxidation_model_results.xls** (available on the Homework page of the course website). The conditions are 1 atm air at 298 K. This particular simulation was run at constant volume, so concentration is proportional to moles.

a) Verify that at t=0 and t=3600 seconds there is a mass balance in carbon and reactive nitrogen (N-containing compounds other than N_2)
b) Considering the mechanism, would you expect the concentration of $[HO_x]$ to be constant over the course of the simulation?
c) Use numerical differentiation to determine the rate of the OH + CO reaction at t = 2400 sec.

G. Given global average $[CH_4]$ and Northern Hemisphere [CO], what is the lifetime of OH radical and what fraction of OH reacts with CH_4 (ignoring other fates of OH).
Use $k(OH + CO) = 2.4 \times 10^{-13}$ cm^3 $molecule^{-1}$ sec^{-1}
Re-calculate your answers if there is also 5 ppbv of isoprene present.

Problems

1. Compare $[C_2H_5O_2]_{ss}$ and $[C_2H_5O\bullet]_{ss}$ in Exercise B, above, to the values in Exercise D on Homework **#5.** Explain with quantitative arguments why $[C_2H_5O_2]_{ss}$ and $[C_2H_5O\bullet]_{ss}$:
- rise or fall
- why they rise or fall as much or as little as they do (in approximate terms)

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2. Using the mechanism and concentrations in Exercise B, calculate the rate at which O_3 is produced from the catalytic cycle involving ethane oxidation to $CH_3CH{=}O$. This is a variant on Question 1 of Homework #5, but here you need to think about the rate-limiting step.

3. Do any of the competing reaction pathways of alkoxy radicals in Exercise C lead to more NO-to-NO_2 conversions than others? Don't answer this from your notes, but work through the logic for this case!

4.A. Show that $[NO_2]_{ss}$ in Exercise D barely changes if you take out: $OH + NO_2 \rightarrow HONO_2$.
4.B. If the reaction $OH + NO_2 \rightarrow HONO_2$ barely changes the answer to Exercise D, how can we also claim (correctly) that it is an important reaction for the concentration of NO2 under the conditions of these measurements. Use quantitative arguments!

5. Write one question at each of levels 1, 2, and 3 of Boom's Taxonomy of Knowledge (defined below). That is a total of three (3) questions, only! The questions should be based on the material in section 16.A.1.a-d (pages 871 to the middle of 877) of the book by Finlayson-Pitts and Pitts (on reserve at Moon Library).

Questions should be designed so that they can be answered without using resources <u>other than</u>

- the specified section of the Finlayson-Pitts and Pitts
- general concepts taught in the course

Finally, specify whether the answer should be quantitative or quantitative arguments (no calculations requiring a calculator!) or some combination.

Table 2. Bloom's Taxonomy of Knowledge
(a famous way to think about levels of knowledge)

Level Of Learning	Examples
1. Information	What is the average $[CH_4]$ in atmosphere? *The answer is a data point which is in the book.*
2. Knowledge / Comprehension	Why is $[CH_4]$ greater than [CO] in the atmosphere despite the fact that CO emissions are much larger than $[CH_4]$ emissions? *You need to **recall** the reason from the answer in Homework #3. This would be a level 3 question if you forgot that you answered this already and thought through it again.*
3. Knowledge Skill / Application	Given a compound, X, emitted at 1% the rate of CH_4 but whose lifetime is 500 years, which compound will be at higher concentration in the atmosphere? *You need to apply steady state calculation or concepts, plus the* $[CH_4]$ *lifetime, to determine the answer.*
4. Problem Solving	Given a data set for emissions and concentration of an anthropogenic species versus location and time, determine its approximate tropospheric lifetime. *Consider this a major project, the procedure for which you need to determine.*
5. New Knowledge (Research)	Design and carry out a field campaign and analysis to determine the rate of transport of CO between the Northern and Southern hemispheres. *Research for a PhD or two!*

See https://www.cloud.edu/Assets/PDFs/assessment/revised-blooms-chart.pdf

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