ASL735 (Atmospheric Chemistry and Air Pollution)
Semester-I AY 2017-18
Minor-2 Exam (Oct 5, 2017)
Time 1 hour

Total Marks = 20

Answer either Q1 or Q2 + Q3:

Q1. In the atmosphere, the largest sinks for CO and CH_4 are via reactions with the hydroxyl radical OH. HCHO is a significant sink for OH.

The reaction rate constants at 298 K are given below

(1) CO + OH → CO2 + H ($k_1 = 1.5*10^{-13}$ $cm^3 \cdot molecule^{-1} \cdot s^{-1}$)

(2) CH4 + OH → CH3 + H2O ($k_2 = 6.3 \cdot 10^{-15}$ $cm^3 \cdot molecule^{-1} \cdot s^{-1}$)

(3) HCHO + OH → CHO + H2O (followed by CHO + O2 → CO + HO)
($k_3 = 9.4 \cdot 10^{-12}$ $cm^3 \cdot molecule^{-1} \cdot s^{-1}$)

In a polluted air mass in west Delhi, the following concentrations were measured on a sunny late morning during a field experiment:

[CO] = $1.0 \cdot 10^{13}$ $molecules \cdot cm^{-3}$ (380 ppb),

[CH4] = $5.3 \cdot 10^{13}$ $molecules \cdot cm^{-3}$ (2000 ppb),

[HCHO] = $1.4 \cdot 10^{10}$ $molecules \cdot cm^{-3}$ (0.5 ppb).

a) Calculate the lifetime of the OH radical in this air mass, considering reactions 1-3. Which is the dominant sink?
b) Can we assume a steady state for [OH]? Justify your answer.
c) The main source of OH radicals in this air mass is the reaction
   HO2 + NO → OH + NO2 (with reaction rate constant k_4)
   Give an expression for calculating [OH].
d) Calculate [OH] when $k_4 = 8.6 \cdot 10^{-12}$ $cm^3 \cdot molecule^{-1} \cdot s^{-1}$, and
   [HO2] = $8.2 \cdot 10^{7}$ $molecules \cdot cm^{-3}$ (0.003 ppb).
   [NO] = $1.0 \cdot 10^{10}$ $molecules \cdot cm^{-3}$ (0.38 ppb).

(Marks = 2 x 4 = 8)

Q2. The concentration of formaldehyde (HCHO) is 1.5×10^{11} $molecules \cdot cm^{-3}$ at the summer solstice, an altitude of 1 km and 40°N latitude. At this altitude, the incident light intensity is $I = 2.7 \times 10^{13}$ $photons \cdot cm^{-2} \cdot s^{-1}$ in the wavelength interval 295-305 nm. The HCHO photolysis cross section is $\sigma = 2.62 \times 10^{-20} cm^2 \cdot molecules^{-1}$ at these conditions. The quantum yield q describes how many molecules that are photolyzed for each photon that interacts with a HCHO molecule. The unit for q can therefore be written as $molecules \cdot photon^{-1}$, but since both "molecules" and "photon" denote numbers, the quantum yield is dimensionless. For HCHO the probability that the absorption of a photon leads to a photolysis reaction (the quantum yield) is 0.79. The photolysis reaction is:

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$$HCHO + h\nu \rightarrow CHO + H$$

Here, both CHO and H are radicals (the reaction is an initiation step). From the information given, calculate the photolysis rate constant, k. Also calculate the photolysis rate, that is how many HCHO molecules that are photolyzed (consumed) per unit time.

(Marks = 2 +2 = 4)

Q3. Stratospheric ozone can be consumed catalytically, where the compound that destroys ozone is regenerated and thus not consumed. This discovery was rewarded with the Nobel Prize in Chemistry in 1995 for Paul Crutzen, Mario Molina and Sherwood Rowland.

a) Name the reactions (one photolysis plus two additional) that together describe the catalytic ozone destruction by a catalyst X, and sum up these reactions to a net reaction.

b) Name four molecules or atoms that can work as catalysts X (all X are radicals)

(Marks = 2 +2 = 4)

Answer any four out of the next six questions given below:

Q4 ~~**Q2**~~. What are the primary sources of production of ozone in the troposphere?

(Marks = 3)

Q5 ~~**Q3**~~. What is the primary oxidant in the troposphere? How is it produced?

(Marks = 1 + 2 = 3)

Q6 ~~**Q4**~~. What is PAN? Why is PAN considered to be a reservoir for long-range transport of NO_x?

(Marks = 1 + 2 = 3)

Q7 ~~**Q5**~~. Explain why HO_x and NO_x catalyze O_3 production in the troposphere, and O_3 destruction in the stratosphere.

(Marks = 3)

Q8 ~~**Q6**~~. How does termination occur in radical chain reactions? What kind of impact do you expect to have on air pollution under low radical concentrations and slow termination and why?

(Marks = 3)

Q9 ~~**Q7**~~. What do you understand by 1^{st} and 2^{nd} indirect effect of aerosols?

(Marks = 3)

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