Exam 2
Atmospheric Composition and Chemical Processes (ACCP) 2012

Total number of points: 43 points
Problem 1 (general understanding questions): 15 points
Problem 2 (stratospheric chemistry): 15 Points
Problem 3 (isotopes): 13 Points

Please write your name and student number on each sheet!!!!!

Read all the questions carefully.

For the general understanding questions, please use the space on the sheets if possible. Try to answer as short and precise as you can, there will be no extra points for lengthy descriptions.

NO OPEN BOOK EXAM!
You need a calculator.

Name: ______________________________

Student number: ______________________________

1) **(15 Pt) General understanding questions**

a) **(2 Pt.)** We know that the stratospheric ozone hole chemistry is caused by CFCs, but the standard catalytic cycles of the CFCs alone are not sufficient to create an ozone hole. What are the critical ingredients that are necessary to create a strong ozone hole. Name at least 4 **(0.5 Pt. each)**

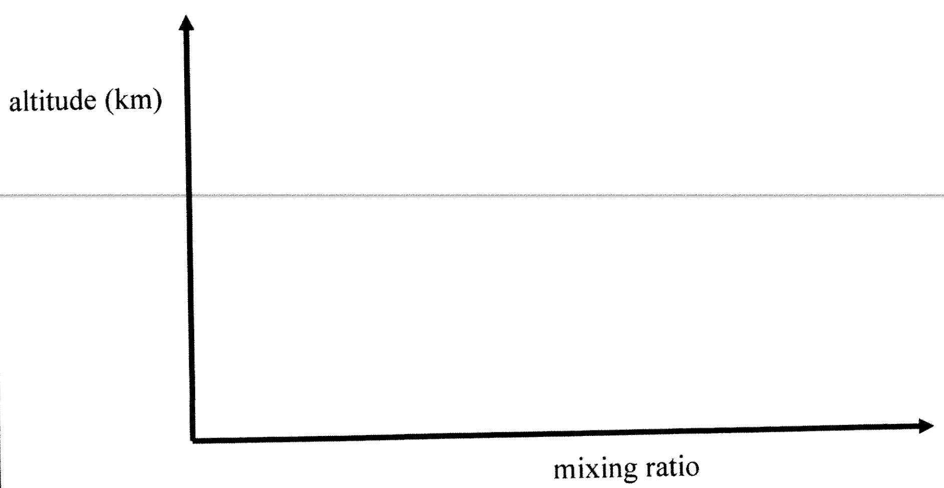
b) **(3 Pt.)** Name at least one example and sketch the altitude profile of

i) a typical Cl course gas in the stratosphere,

ii) a chemically active compound or short-lived reservoir

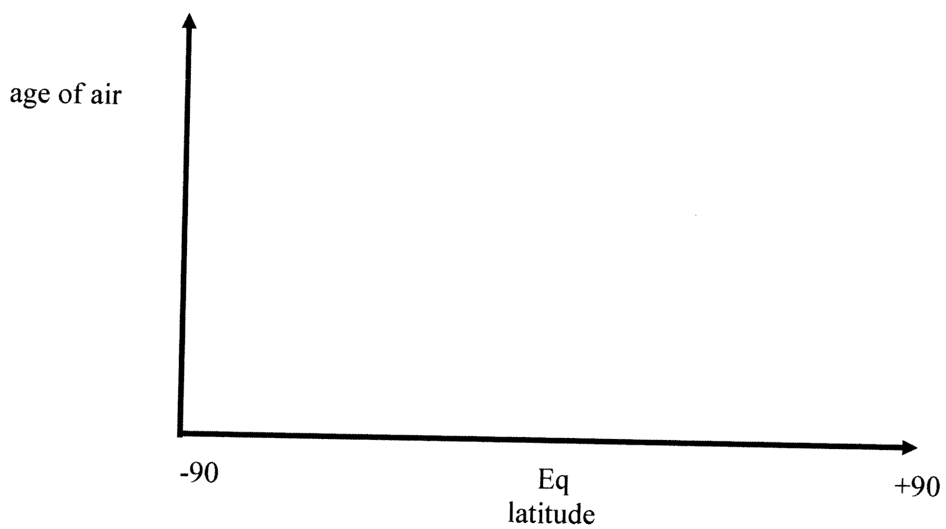
iii) the final sink of Cl

(0.5 Pt per name and per sketch of altitude profile)



c) **(1 Pt.)** Why do polar stratospheric clouds form only in the LOWEST part of the polar stratosphere?

d) **(1 Pt.)** How does a typical latitudinal distribution of the age of air at a certain altitude (e.g. 20 km) in the stratosphere look? Make a drawing in the diagram below.



e) **(1 Pt.)** How can global warming affect the recovery of the polar ozone holes

f) **(3 Pt)** What are the names of the three important aerosol modes **(0.5 Pt each)**? Sketch a typical distribution of aerosol i) number, ii) surface, iii) volume as a function of particle diameter **(0.5 Pt. each)**

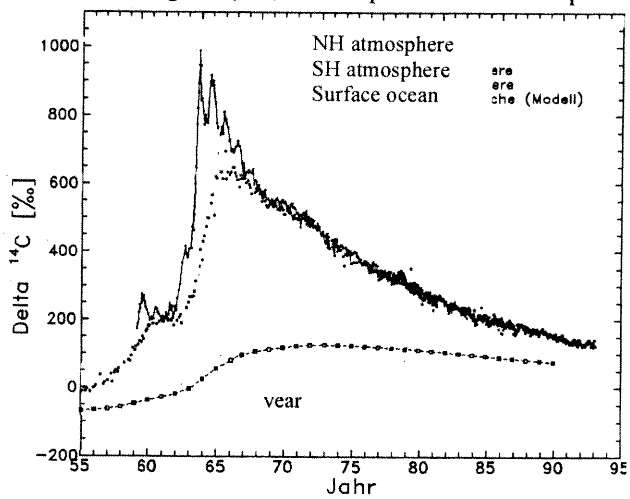
g) **(3 Pt)** Can you describe BRIEFLY how the elements S, N and C can be transferred from gas phase molecules into aerosols in the atmosphere **(1 Pt each)**?

h) (1Pt.)

The figure below shows the evolution of the atmospheric ^{14}C content

$$\left(\text{units of } \Delta^{14}C = \left(\frac{^{14}R_{atmosphere}}{^{14}R_{standard}} - 1\right) * 1000\ ‰\right)$$

before and after the "bomb peak" in the 1960s. The radioactive half-life of ^{14}C is 5730 years. Interpret the figure (i.e., which processes can explain the decay after the bomb peak?).



2) (15 Pt.) The stratospheric O_3 layer and catalytic destruction cycles

a) **(2 Pt.)** Write down the Chapman equations. Which reactions are fast/slow respectively **(0.5 Pt. each)**

b) **(1 Pt.)** From these equations, derive an equation for the steady-state O/O_3 ratio in the stratosphere.

c) **(1 Pt.)** Write down the generalized equation for a standard catalytic O_3 destruction cycle

d) **(3 Pt.)** HO_x (= H, OH, HO_2) radicals can catalytically destroy O_3 in the stratosphere in several ways. From the 8 reactions below, which are important in different regions of the stratosphere, identify 5 catalytic destruction cycles, starting with a reaction of OH **(3*0.5 Pt. and 2*0.75 Pt)**.

$OH + O \rightarrow O_2 + H$ (1)
$OH + HO_2 \rightarrow H_2O + O_2$ (2)
$OH + O_3 \rightarrow HO_2 + O_2$ (3)
$H + O_2 + M \rightarrow HO_2 + M$ (4)
$H + O_3 \rightarrow O_2 + OH$ (5)
$HO_2 + O \rightarrow OH + O_2$ (6)
$HO_2 + O_3 \rightarrow OH + 2O_2$ (7)
$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$ (8)

e) **(1 Pt.)** Which of the 8 reactions represent a sink of HO_x? **(0.5 Pt each)**

f) Consider an air parcel at 30 km altitude (30N, equinox), which contains:

$[O_3] = 3*10^{12}$ molec./cm^3
$[NO] = 7*10^{8}$ molec./cm^3
$[HO_2] = 8.5*10^{6}$ molec./cm^3
$[O] = 3*10^{7}$ atoms/cm^3
$[NO_2] = 2.2*10^{9}$ molec./cm^3
$[CH_4] = 2.8*10^{11}$ molec./cm^3

and the following reactions:

$Cl + O_3 \rightarrow ClO + O_2$	$k_1 = 9.5*10^{-12}$ cm^3 molec^{-1} s^{-1}
$Cl + CH_4 \rightarrow HCl + CH_3$	$k_2 = 2.6*10^{-14}$ cm^3 molec^{-1} s^{-1}
$ClO + O \rightarrow Cl + O_2$	$k_3 = 3.8*10^{-11}$ cm^3 molec^{-1} s^{-1}
$NO_2 + h\nu \rightarrow NO + O$	$k_4 = 5*10^{-3}$ cm^3 molec^{-1} s^{-1}
$ClO + NO \rightarrow Cl + NO_2$	$k_5 = 4.5*10^{-11}$ cm^3 molec^{-1} s^{-1}
$ClO + HO_2 \rightarrow HOCl + O_2$	$k_6 = 2.1*10^{-11}$ cm^3 molec^{-1} s^{-1}
$ClO + NO_2 + M \rightarrow ClNO_3 + M$	$k_7 = 1.3*10^{-13}$ cm^3 molec^{-1} s^{-1} (pseudo second order)
$OH + O_3 \rightarrow HO_2 + O_2$	$k_8 = 2.5*10^{-4}$ s^{-1}
$O + O_2 + M \rightarrow O_3 + M$	$k_9 = 2.8*10^{-14}$ cm^3 molec^{-1} s^{-1}

(3 Pt) Calculate the chemical lifetimes of Cl and ClO. Which reaction is the principle sink for each? **(1 Pt. per lifetime, 0.5 Pt. for each principle sink)**

g) **(1 Pt)** If ClO reacts with NO instead of O (reaction 5), do you still get a catalytic cycle for O_3 loss? Briefly explain.

h) **(3 Pt)** Calculate the lifetime of the chemical family ClO_x (=[Cl]+[ClO]). Compare to the lifetime of ClO. What do you conclude? (2 Pt for lifetime, 1 for explanation.)

(Hint: assume steady state for the Cl atoms and $[Cl]/[ClO] = \tau_{Cl}/\tau_{ClO} = 1.2 * 10^{-3}$ mol/mol)

3) (13 Pt.)

The global CO isotope budget

a) **(5 Pt.)** Oxidation of methane (CH_4) in the atmosphere is an important source of carbon monoxide (CO). We first consider a situation where CH_4 oxidation is the only source of CO and calculate the isotopic composition of CO under this assumption.
The $\delta^{13}C$ value of atmospheric CH_4 versus the international standard VPDB is

$$\delta^{13}C_{VPDB}CH_4 = (^{13}C/^{12}C)_{CH4} / (^{13}C/^{12}C)_{VPDB} - 1 = -47.2 ‰$$

The fractionation factor for CH_4 removal is $\alpha_{CH4} = k(^{13}CH_4) / k(^{12}CH_4) \sim 0.995$
The fractionation factor for CO removal is $\alpha_{CO} = k(^{13}CO) / k(^{12}CO) \sim 0.995$

i) (2 Pt.) Write down a rate equation for the change in the CO mixing ratio due to production from CH_4 (explicitly) and destruction of CO. Assume that each molecule of CH_4 removed produces one molecule of CO (i.e. neglect the intermediate steps) and assume chemical steady state.
Write down a similar equation for the rate of change of ^{13}CO **(1 Pt. each)**

ii) (3 Pt.) Combine the two equations by introducing the definitions for the δ values and fractionation constants to derive a value for the isotopic composition of atmospheric CO under these conditions.

b) **(1 Pt.)** What you have calculated is the CO isotopic composition in this source-sink equilibrium. What is the isotopic composition of the CH_4 oxidation source only (i.e. without the isotope effect in the CO removal reaction)? (hint set $\alpha_{CO} = 1$)

c) **(2 Pt.)** Now we go to the real atmosphere: The observed $\delta^{13}C$ value of CO in the atmosphere is -27‰. Taking into account the isotope effect in the CO sink again, what is the isotopic composition of the average source? (Hint: You may want to follow the calculations from a) again for a total source P_{CO} with averaged $\delta^{13}C$ value)

d) **(1 Pt.)** Assuming that CH_4 oxidation is responsible for 25% of the total source strength, calculate the isotopic composition of the remaining source.

e) **(1 Pt.)** Can you name two other important sources of CO to the atmosphere **(0.5 Pt. each)**?

f) **(3 Pt.)** In the stratosphere, a large fraction of CH_4 is removed by reaction with Cl. The fractionation factor for this reaction is $\alpha_{Cl+CH4} = k(Cl+^{13}CH_4) / k(Cl+^{12}CH_4) \sim 0.930$.

a) **(1 Pt.)** Qualitatively, what will be the effect on the isotopic composition of CO in the stratosphere when CH_4 is removed this way to produce CO?
b) **(1 Pt.)** Quantitatively, what is the isotopic composition of this source of CO?
c) **(2 Pt.)** If you add 1 ppb of CO from this source to 50 ppb of background CO with $\delta^{13}C_{VPDB}CO = -27‰$, how much will the CO isotopic composition change?

End of exam. Please check that all your sheets are complete and marked with your name and student number, and fill our the course evaluation sheet.