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In 2006/2007, the course NS-255b was given by R. Holzinger.

Klimaatfysica en chemie (NS-255b)
30 januari 2007

Question 1: CH_4 from CO oxidation *(10 points)*

Assume a clean atmosphere where CO is exclusively produced from the oxidation of CH_4 and removed by oxidation to CO_2.

a) Write down the chemical reaction equations for those two reactions (only the first step for CH_4 oxidation). *(2 points)*

b) Write down the differential equations for the removal of CH_4 and CO according to those two reactions. *(2 points)*

c) Assume that 0.8 molecules CO are produced for every molecule of CH_4 removed and calculate the *steady state* concentration of CO in this atmosphere as a function of $[CH_4]$. *(2 points)*

d) Does this value depend on OH levels? If so, why? If not, why not? *(2 points)*

e) Calculate $[CO]_{ss}$ for $T = 288$ K (summer) and $T = 27$ K (winter). Do you see the same change in the atmosphere? Why or why not? *(2 points)*

Note:
$k_{CH_4+OH} = 2.45 \cdot 10^{-12} \exp\{-1775/T\}$ cm^3 molec^{-1} s^{-1}
$k_{CO+OH} = 2.4 \cdot 10^{-13}$ cm^3 molec^{-1} s^{-1} at atmospheric pressure.

Question 2: Tropospheric O_3 formation *(10 points)*

a) Draw a conceptual diagram of the photochemical O_3 production mechanism. *(4 points)*

b) Which species play which role? *(2 points)*

c) Which reaction becomes important at very low NO_x levels? What is the effect on OH and on O_3? *(2 points)*

d) Which reaction becomes important at very high NO_x levels? What is the effect on OH and on O_3? *(2 points)*

Question 3: Stratospheric ozone *(10 points)*

a) The basis reactions of stratospheric ozone chemistry are included in the Chapman cycle in which oxygen atoms play a major role. What is the O_x family? Derive an equation for the photochemical steady state of $[O_x]$. *(3 points)*

b) The Chapman cycle misses important destruction reactions. Write down the general reaction cycle for a catalytic ozone destruction reaction. What is the net reaction? Which species are important catalysts? *(2.5 points)*

c) Name at least 3 important ingredients that lead to the stratospheric ozone hole. *(1.5 points)*

d) Why does the stratospheric ozone hole only occur in the polar regions? Why is it stronger in the Antarctic then in the Arctic? *(1 point)*

e) Typical mixing ratios in the ozone layer region are: $[CH_4]$~1 ppm and $[O_3]$~5 ppm. How many O_3 molecules can a Cl atom on average destroy at stratospheric temperatures (−60°C) before it is deactivated by reaction with CH_4? *(2 points)*

$k_{Cl+CH_4} = 1.1 \cdot 10^{-11} \cdot \exp\{-1400/T\}$ cm^3 molecule^{-1} s^{-1}
$k_{Cl+O_3} = 2.9 \cdot 10^{-11} \cdot \exp\{-260/T\}$ cm^3 molecule^{-1} s^{-1}

Question 4: Isotope fractionation of N_2O *(10+3 points)*

Scientists carry out laboratory experiments to determine the isotope effects in the photolysis of N_2O. They start with a concentration of 5 ppm N_2O and continue the reaction until 2 ppm of N_2O is left. They find an isotope enrichment of $\delta^{15}N = 35‰$ of the remaining N_2O relative to the initial gas.

a) Calculate the isotope fractionation constant ε (in ‰). *(4 points)*

Note: If you do not recall the Rayleigh fractionation equation, you can try to derive it from the first order removal reaction of two isotopic compounds X and X' with rate constants k and k'. Use $R = X'/X, \alpha = k/k'$, the definition of the δ formula $\delta = (R/R_0 - 1)$ and the remaining fraction $f = x/x_0$ *(3 extra points)*

b) What is the value for $\delta^{15}N$ when 4, 3 and 1 ppm of N_2O are left? *(3 points)*

c) The experiment takes 12 hours (until 2 ppm of N_2O is left). Calculate the photolysis rate constant for N_2O. What is the photolysis rate constant for ^{15}N-substuted N_2O? *(2 points)*

d) What is the requirement for the application of the Rayleigh fractionation equation? What is the problem of its application in the atmosphere to long-lived gases like N_2O? *(1 points)*