# Exam Atmospheric Chemistry and Physics

## June 4, 2015 at 8:00-13:00

You may use: Calculator, Table booklet (Tefyma or similar), Equation sheet of the course
Answer each question (1-5) on ***separate sheets.***

## 1. The Atmosphere

a) The atmospheric concentration of $CO_2$ is since a long time increasing. Which are the main reasons for the increase? (1 p)

b) Fig. 1 shows the change in $CO_2$ concentration from year 1960 to present at Mauna Loa, Hawaii. What is causing the annual variation (*årstidsvariation*)? (1 p)

c) The yearly average concentration at Mauna Loa is a good estimate of the global yearly average. Why can we use data from one place for a global estimate? (1 p)

d) Use the data in Fig. 1 to calculate the increase of carbon mass in the atmosphere during the industrial era (i.e. the increase from pre-industrial concentration to the concentration year 2014). The pre-industrial $CO_2$ concentration was 280 ppmv. (3 p)

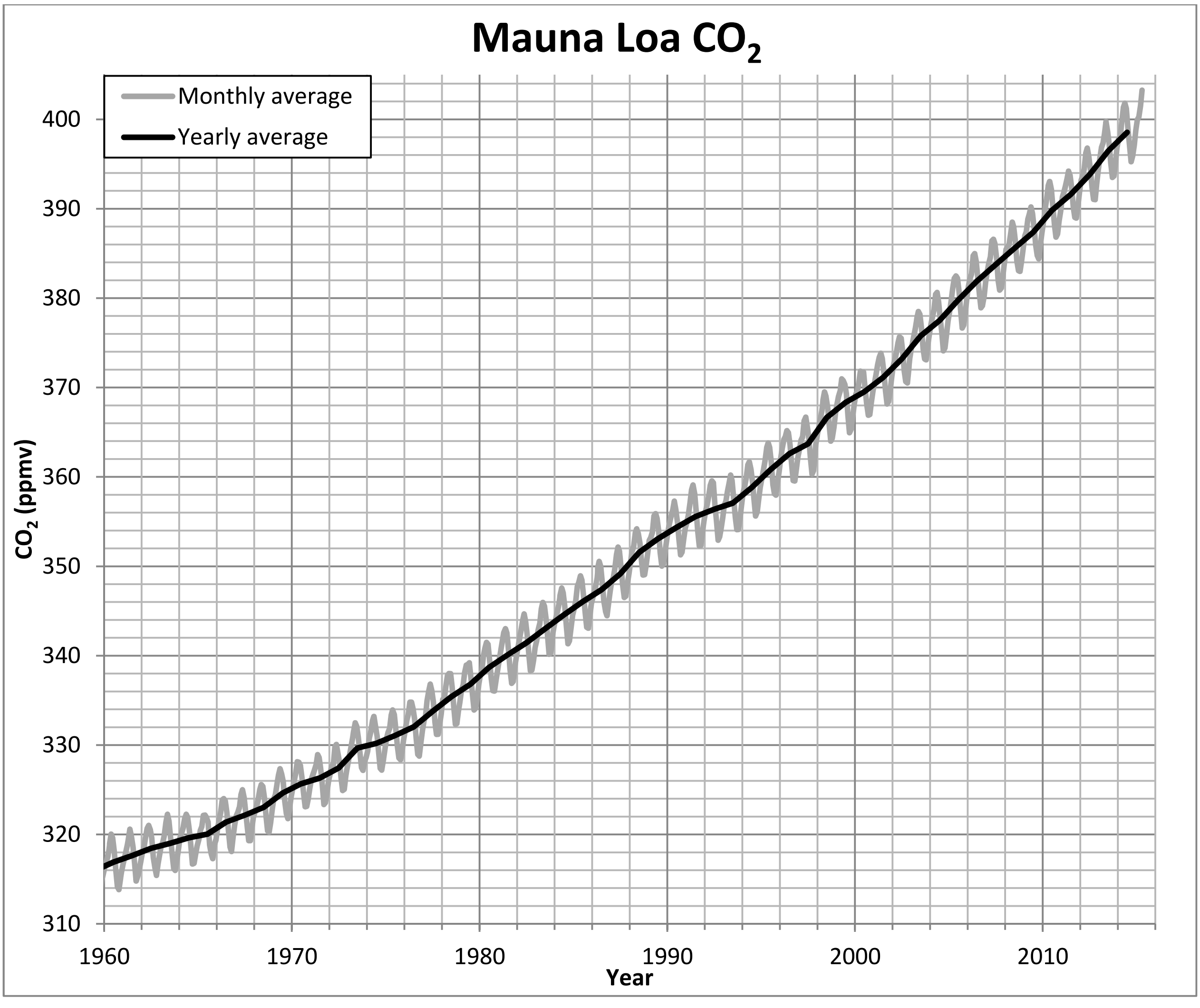


Figure 1. The $CO_2$ concentration in the air at Mauna Loa, Hawaii.

## 2. Climate

a) The Earth emits radiation approximately like a black body (Fig. 2 a). In Fig. 3 we see that the shape of the spectrum measured from a satellite deviates significantly from a spectrum of a black body. What is the reason for these deviations? (2 p)

b) In which wavelength region can we (approximately) identify the temperature of the Earth's surface in Fig. 3? Explain. (1 p)

c) Explain the greenhouse effect based on the radiation spectrum in Fig. 3. (2 p)

d) In the course we use a simple climate model where the atmosphere is approximated by a single isothermal layer. According to this model we obtain maximum greenhouse effect when the absorption of the atmosphere is 100% ($\varepsilon_\lambda = 1$). In reality the absorption can exceed 100%. How does that affect the greenhouse effect? Explain. (1 p)

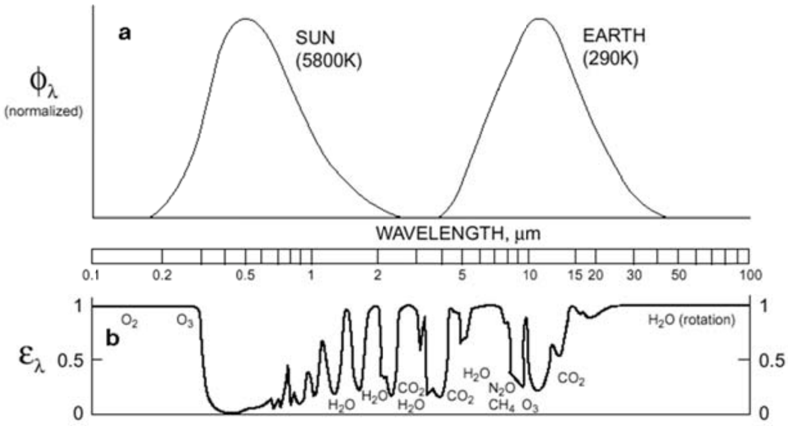


Fig. 2. a) Normalized radiation intensity from the sun and from the earth as a function of wavelength. b) The fraction absorbed by the atmosphere of radiation of a given wavelength ($\varepsilon_\lambda$).

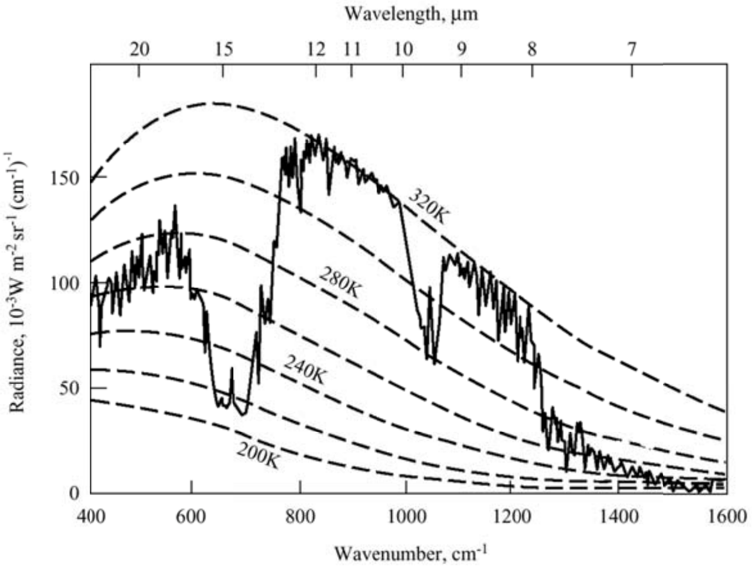


Fig. 3. Radiation spectrum (full line) from the Earth measured by satellite (wavelength at the upper axis). The spectrum was taken over North Africa. The broken lines show radiation spectra from blackbodies at several temperatures.

## 3. Aerosol-water interaction

a) An aerosol particle has taken up water, formed a droplet, and obtained its equilibrium size with respect to relative humidity (RH). What is the RH (in %) if the droplet diameter (D) is 400 nm? The particle consists of $1.12 \cdot 10^{-18}$ kg sodium chloride (100 nm dry diameter). Assume that the dissociation ($\nu$) of NaCl is complete and that the temperature is 298 K. Also assume that the molar mass, surface tension and density of the solution equals that of water. *[Water: $M_w = 18.02$ kg/kmol, $\sigma_{Dw} = 0.073$ N/m, $\rho = 998$ kg/m$^3$; Sodium chloride: $M_{NaCl} = 58.44$ kg/kmol]* (2p)

b) How will the droplet react if the RH increases slightly (by 1%)? Will the droplet still be in equilibrium state? (1p)

c) Make a sketch diagram that describes the relation between RH (> 95%) and droplet diameter. Mark the critical RH, and critical diameter. (1p)

d) How will the droplet react if the RH increases above the critical level of the droplet? Describe in general terms. Motivate. (2p)

## 4. Stratospheric ozone

In the stratosphere, both $O_2$ and $O_3$ are photolyzed by UV-radiation (reactions (1) and (2) below).
a) Why is photolysis of $O_2$ not enough to protect life on Earth from hazardous UV-radiation from the sun? (1p)
The reactions below are the most important for the production and destruction of stratospheric ozon. Here, O denotes $O(^3P)$.

(1) $O_2 + h\nu \rightarrow O + O$
(2) $O_3 + h\nu \rightarrow O_2 + O(^1D)$
$Cl + O_3 \rightarrow ClO + O_2$
$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$
$NO_2 + O_3 \rightarrow NO_3 + O_2$
$O_3 + O \rightarrow 2O_2$
$OH + O_3 \rightarrow HO_2 + O_2$
$NO_3 + NO_2 + M \rightarrow N_2O_5 + M$
$OH + HO_2 \rightarrow H_2O + O_2$
$O + O_2 + M \rightarrow O_3 + M$
$Cl + CH_4 \rightarrow HCl + CH_3$
$NO_2 + O \rightarrow NO + O_2$
$ClO + NO_2 + M \rightarrow ClNO_3 + M$
$O(^1D) + M \rightarrow O + M$
$NO_2 + OH + M \rightarrow HNO_3 + M$
$HO_2 + O_3 \rightarrow OH + 2O_2$
$ClO + O \rightarrow Cl + O_2$
$NO + O_3 \rightarrow NO_2 + O_2$

Use these reactions to write
b) the Chapman mechanism for ozone production in the stratosphere (1p)
c) the catalytic ozone loss via the $HO_x$, $NO_x$ and $ClO_x$ families. (2p)
d) How are $HO_x$, $NO_x$ and $ClO_x$ radicals formed in the stratosphere? (1p)
e) Which of the reactions above constitute termination steps for catalytic ozone loss propagated via the $HO_x$, $NO_x$ and $ClO_x$ radicals? (1p)

## 5. Acidification

The gas $SO_2$ dissolves in water according to the equilibrium

(1) $SO_2(g) \Leftrightarrow SO_2 \cdot H_2O$

$H_{SO2}$ is Henry's law constant for $SO_2$. At T=298 K, $H_{SO2}$ = 1.23 M·atm$^{-1}$, which would yield an aqueous phase concentration of $SO_2$ of $1.23 \cdot 10^{-9}$ M at a typical gas phase concentration [$SO_2$(g)] = 1 ppb at standard atmospheric pressure. Figure 4 below shows that the dissolution of S(IV) in water is actually strongly dependent on the pH of the solution. For all pH>1, the concentration of S(IV) in water is much greater than what is expected from the Henry's law constant $H_{SO2}$. For "neutral" pH in the atmosphere, pH=5.6, the concentration is about $10^4$ times larger. This example with $SO_2$ clearly shows that the Henry's law constant is in many cases totally inadequate in describing how a gas dissolves in water.

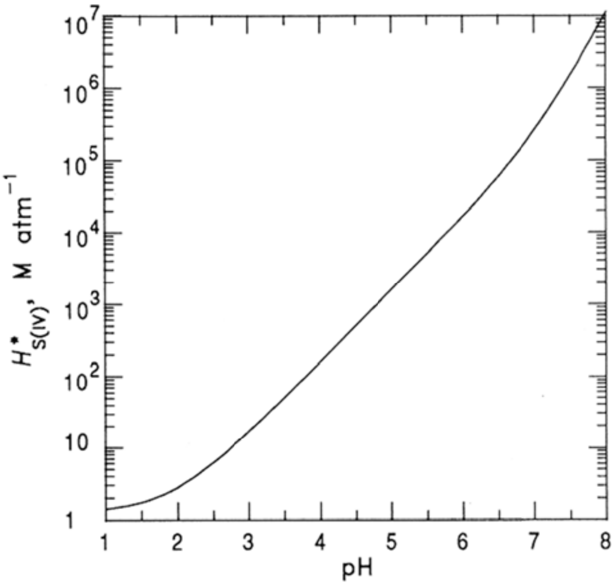


Figure 4. The effective Henry's law constant $H^*_{S(IV)}$ for dissolution of S(IV) in water as a function of the pH of the aqueous solution.

a) Explain why 5.6 can be considered to be "neutral" pH in the atmosphere. (1p)
b) Explain qualitatively what causes the increased solubility of S(IV). (1p)
c) Deduce an equation for the "effective" Henry's law constant $H^*_{S(IV)}$ for how gaseous S(IV) dissolves in water ($H^*_{S(IV)}$ = [S(IV)] / [$SO_2$(g)] ). This equilibrium constant should be able to qualitatively explain the pH dependence in Figure 4. (2p)
d) In which form is most S(IV) present in the aqueous solution at pH of atmospheric relevance (3-6)? (1p)
e) This phenomenon of strongly increased solubility of S(IV) is of utmost importance for the aqueous phase oxidation of S(IV) to S(VI) and thus also for the acidification of soils and waters. Explain why. (1p)

# Solutions to exam in Atmospheric Chemistry and Physics June 4, 2015

## 1. The Atmosphere

a) Fossil fuel combustion and deforestation, in particular in the tropics
b) The growth period consumes CO2, whereas biological decay increases the concentration
c) The residence time of CO2 is long compared to typical transport times in the atmosphere, implying that the concentration is similar everywhere, except close to strong sources.
d) $\Delta C = 398 - 280 = 118$ ppmv $= 118\ 10^{-6}$; $\Delta m_c = M_c \Delta n_c = M_c n_a \Delta C$
We need to calculate the number of moles of gas molecules in the atmosphere ($n_a$):
The weight of the overlying air causes the pressure at a given level: $m_a g = pA = 4\pi R^2 p$ =>
$n_a = m_a/M_a = 4\pi R^2 p/(gM_a)$ =>
$\Delta m_c = M_c n_a \Delta C = M_c \Delta C 4\pi R^2 p/(gM_a)$,
where R is the radius of the Earth ($6.37\ 10^6$ m), g the gravitation ($9.81$ m/s$^2$), $M_a$ the average molar mass of air (29.0 kg/kmol) and p the average pressure ate the surface of the Earth (984 hPa). Insert the numbers: $\Delta m_c = 2.5\ 10^{14}$ kg

## 2. Climate

a) The atmosphere absorbs radiation from the surface which then emits blackbody radiation at its temperature. The temperature decreases with altitude in the atmosphere, implying that less radiation is emitted to space at wavelengths where the atmosphere has strong absorption.
b) In Fig 2b we see that the absorption of terrestrial radiation is small in the "atmospheric window" 8 – 13 µm in wavelength. The estimated surface temperature by comparing with blackbody radiation is approximately 320 K (47° C; North Africa)
c) At the wavelengths where the atmosphere absorbs/emits radiation less radiation leaves the Earth. Therefore the temperature of the entire system is elevated to reach equilibrium with the incoming radiation from the sun.
d) When the absorption of the atmosphere exceeds 100%, the probability for double or multiple absorption increases. As a result, the last emission of radiation before leaving the Earth will on average be at a higher altitude. This is also a colder part of the atmosphere, thus implying that less radiation leaves the earth.

## 3. Aerosol-water interaction

a) Use the Köhler equation for the calculation. Result: 98.5%
b) The droplet will become larger due to the increase in relative humidity (RH). It will still be in equilibrium state, because the RH is still lower than the critical relative humidity.
c) Based on the Köhler equation, see Fig. 3 in Aerosol, Water and Clouds by Martinsson.
d) The droplet will follow the Köhler curve until it reaches the maximum level (=critical RH). Up to the critical value, the droplet will stay in the equilibrium state. If the RH increases further and exceed the critical RH, the droplet will leave the equilibrium state. This means that the droplet will grow without limitation, the droplet activates. This is the process for cloud droplet formation.

## 4. Stratospheric ozone

a) Photolysis of ozone (<320 nm) can proceed also in the UVB region where there is no photolysis of $O_2$ (<240 nm). The stratospheric ozone layer thus protects us from the hazardous UVB radiation (280 nm < $\lambda$ < 320 nm) which is not removed by ordinary oxygen $O_2$.

Answer b) The Chapman mechanism:

(1) $O_2 + h\nu \rightarrow O + O$
$O + O_2 + M \rightarrow O_3 + M$
(2) $O_3 + h\nu \rightarrow O_2 + O(^1D)$
$O(^1D) + M \rightarrow O + M$
$O_3 + O \rightarrow 2O_2$

c) Catalytic ozone loss via $HO_x$:
$OH + O_3 \rightarrow HO_2 + O_2$
$HO_2 + O_3 \rightarrow OH + 2O_2$
(the latter reation does not follow the general scheme for a catalyst X which is $XO + O \rightarrow$)

Catalytic ozone loss via $NO_x$:
$NO + O_3 \rightarrow NO_2 + O_2$
$NO_2 + O \rightarrow NO + O_2$ ($XO + O \rightarrow$)

Catalytic ozone loss via $ClO_x$:
$Cl + O_3 \rightarrow ClO + O_2$
$ClO + O \rightarrow Cl + O_2$ ($XO + O \rightarrow$)

d) Formation of $HO_x$:
$H_2O + O(^1D) \rightarrow 2OH$

Formation of $NO_x$:
$N_2O + O(^1D) \rightarrow 2NO$

$N_2O$ originates from soil decomposition processes and is stable in the troposphere.
NO is also emitted directly into the stratosphere by airplanes.

Formation of $ClO_x$:
Photolysis of chlorine-containing CFCs that are i stable in the troposphere.

e) Termination steps for catalytic ozone loss via $HO_x$:
$OH + HO_2 \rightarrow H_2O + O_2$
$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$

Termination steps for catalytic ozone loss via $NO_x$:
$NO_2 + OH + M \rightarrow HNO_3 + M$
$NO_2 + O_3 \rightarrow NO_3 + O_2$ and
$NO_3 + NO_2 + M \rightarrow N_2O_5 + M$

Termination steps for catalytic ozone loss via $ClO_x$:
$Cl + CH_4 \rightarrow HCl + CH_3$
$ClO + NO_2 + M \rightarrow ClNO_3 + M$

## 5. Acidification

a) Dissolution of $CO_2$ at present atmospheric levels (380 ppm) results in a "neutral" and non-acidified pH of 5.6 in cloud droplets and rain water. Only a pH below this value is a sign of acidification.

b) Dissolution of the gas $SO_2$ in water shifts the equilibrium for $SO_2(g)$ to push more S(IV) into the aqueous phase than would otherwise be the case.

The reactions are identical to those involving $CO_2$ (exchange $SO_2$ by $CO_2$), and are given in the "Equation Sheet".

(1) $SO_2(g) \Leftrightarrow SO_2 \cdot H_2O$ ($H_{SO2} = 1.23$ M·atm$^{-1}$, given)
(2) $SO_2(g) \cdot H_2O \Leftrightarrow HSO_3^- + H^+$ ($K_2 = 1.3 \cdot 10^{-2}$ M)
(3) $HSO_3^- \Leftrightarrow SO_3^{2-} + H^+$ ($K_3 = 6.3 \cdot 10^{-8}$ M)

The $K_i$ are equilibrium constants. $H_{SO2}$ is the ”traditional” Henry’s law constant for dissolution of S(IV) in water.

c) [S(IV)(aq)] = [$SO_2 \cdot H_2O$] + [$HSO_3^-$] + [$SO_3^{2-}$].

The ”effective” Henry’s law constant $H^*_{S(IV)}$ for dissolution of S(IV) in water is defined as $H^*_{S(IV)}$ = [S(IV)(aq)] / [$SO_2$(g)].

The equilibrium reactions in a) give

$$H_{SO2} = \frac{[SO_2 \cdot H_2O]}{[SO_2(g)]} = \frac{[SO_2 \cdot H_2O]}{p_{SO_2}} \Rightarrow [SO_2 \cdot H_2O] = H_{SO2} \cdot p_{SO_2}$$

$$K_2 = \frac{[HSO_3^-] \cdot [H^+]}{[SO_2(g) \cdot H_2O]} \Rightarrow [HSO_3^-] = \frac{K_2 \cdot [SO_2 \cdot H_2O]}{[H^+]} = \frac{K_2 \cdot H_{SO2} \cdot p_{SO_2}}{[H^+]}$$

$$K_3 = \frac{[SO_3^{2-}] \cdot [H^+]}{[HSO_3^-]} \Rightarrow [SO_3^{2-}] = \frac{K_3 \cdot [HSO_3^-]}{[H^+]} = \frac{H_{SO2} \cdot K_2 \cdot K_3 \cdot p_{SO_2}}{[H^+]^2}$$

$$[S(IV)] = [SO_2 \cdot H_2O] + [HSO_3^-] + [SO_3^{2-}] =$$

$$= H_{SO2} \cdot p_{SO_2} + \frac{K_2 \cdot H_{SO2} \cdot p_{SO_2}}{[H^+]} + \frac{H_{SO2} \cdot K_2 \cdot K_3 \cdot p_{SO_2}}{[H^+]^2} =$$

$$= H_{SO2} \cdot p_{SO_2} \left( 1 + \frac{K_2}{[H^+]} + \frac{K_2 \cdot K_3}{[H^+]^2} \right)$$

The ”effective” Henry’s law constant $H^*_{S(IV)}$ can thus be expressed as

$$H^*_{S(IV)} = \frac{[S(IV)(aq)]}{[SO_2(g)]} = \frac{[S(IV)(aq)]}{p_{SO_2}} = H_{SO2} \cdot \left( 1 + \frac{K_2}{[H^+]} + \frac{K_2 \cdot K_3}{[H^+]^2} \right)$$

The factor

$$\left( 1 + \frac{K_2}{[H^+]} + \frac{K_2 \cdot K_3}{[H^+]^2} \right)$$

that follows the ”traditional” Henry’s law constant $H_{SO2}$ explains how the pH of the aqueous solution affects the solubility of S(IV). Increased pH (lower [$H^+$]) causes this factor to increase considerably, and more S(IV) can be dissolved in water.

d) As $HSO_3^-$. Oxidation in the atmosphere need therefore proceed via $HSO_3^-$.

e) If the solubility of gas phase S(IV) in water would have been determined only by the ”traditional” Henry’s law constant $H_{SO2}$, then very little $SO_2$(g) would have been dissolved in water, for instance in cloud droplets.

As a result, nearly all oxidation of $SO_2$ would have taken place in the gas phase (via OH). The lifetime for $SO_2$(g) would have been considerably higher and the problems associated with acidification would have shifted further away from the source regions. Concentrations of $SO_2$(g) would also have been higher close to the sources with negative consequences for human health.

# Exam Atmospheric Chemistry and Physics

## June 4, 2016 at 8:00-13:00

You may use: Calculator, Table booklet (Tefyma or similar), Equation sheet of the course
Answer each question (1-5) on ***separate sheets.***

## 1. Geochemical cycles

a) Figure 1 shows the pre-industrial geochemical cycle of carbon. Calculate the residence time of carbon in the atmosphere from Figure 1. (1 p)

b) Form a combined ocean reservoir of the surface, middle and deep ocean reservoirs. Calculate the residence time of carbon in the new ocean reservoir. (1 p)

c) You find the carbon mass in the pre-industrial atmosphere in Figure 1. Calculate the pre-industrial concentration of $CO_2$ in the atmosphere as a mixing ratio, assuming that all carbon in the atmosphere is in the form $CO_2$ and that $CO_2$ is well mixed in the entire atmosphere. (1 p)

d) Discuss the validity of the two assumptions made in question 1c. (1 p)

e) Figure 2 shows how the $CO_2$ concentration has changed over the years at Mauna Loa, which can be assumed to be representative for global concentrations. Estimate the carbon mass in the atmosphere of today, making the same assumptions as in question 1c. Assume that we have first order (i.e. proportional) sink processes, and estimate the size of the sinks for atmospheric carbon. (1 p)

f) Increased atmospheric $CO_2$ concentration increases the carbon transport to the biosphere and the ocean. Briefly discuss the long-term capability of these to reservoirs to act as sinks for increasing atmospheric $CO_2$ concentrations. (1 p)

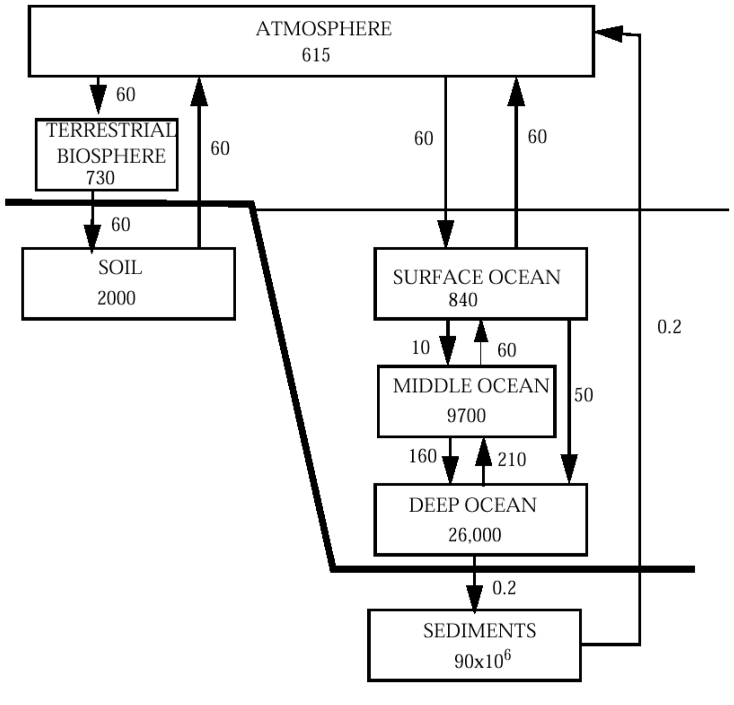


Figure 1. The pre-industrial geochemical cycle of carbon. The masses of carbon in the reservoirs are given in Pg ($10^{15}$ g) and the exchange in Pg per year.

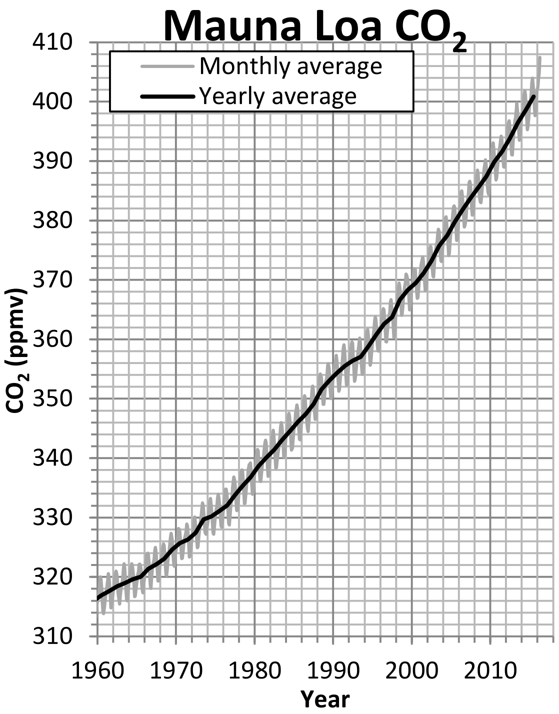


Figure 2. The $CO_2$ concentration in the air at Mauna Loa, Hawaii.

## 2. Climate effects of aerosols and clouds

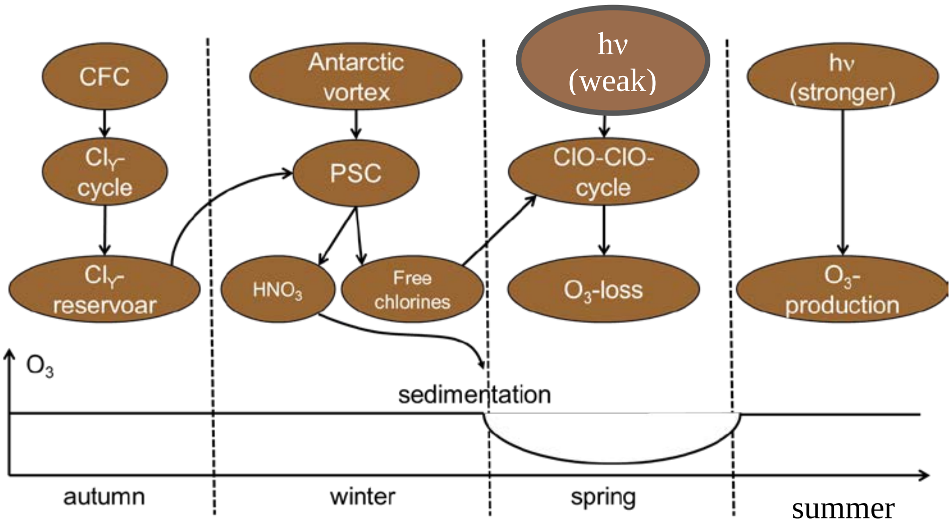
a) Compare in general terms the way in which aerosol particles and greenhouse gases interact with the climate. (1 p)
b) Describe the role and importance of clouds for the climate. (1 p)
c) Aerosol particles have two main effects on the climate, that can be subdivided further. Describe these main and sub-category effects. (3 p)
d) A cloud has the albedo $A_C=0.6$. Calculate the change in albedo for that cloud if the cloud droplet number increases by 40% due to increased number of aerosol particles. (1 p)

## 3. Stratospheric ozone

The following reactions take place in the stratosphere, participating in the destruction of ozone:

(1) $OH + O_3 \rightarrow HO_2 + O_2$
(2) $OH + HO_2 \rightarrow H_2O + O_2$
(3) $HO_2 + O_3 \rightarrow OH + 2O_2$
(4) $HO_2 + O(^3P) \rightarrow OH + O_2$
(5) $N_2O + O(^1D) \rightarrow 2\ NO$
(6) $NO + O_3 \rightarrow NO_2 + O_2$
(7) $NO_2 + O(^3P) \rightarrow NO + O_2$
(8) $OH + NO_2 + M \rightarrow HNO_3 + M$
(9) $NO_2 + O_3 \rightarrow NO_3 + O_2$
(10) $NO_2 + NO_3 + M \rightarrow N_2O_5 + M$
(11) $NO_2 + h\nu \rightarrow NO + O(^3P)$
(12) $O(^3P) + O_2 + M \rightarrow O_3 + M$

(a) Please choose either the $HO_X$ or $NO_Y$ family to construct a catalytic ozone destruction mechanism from two of these reactions. Write out the net reaction for this odd oxygen destruction. (1 p)
(b) Which of the above reactions is an initiation step for the $NO_Y$ ozone destruction process? (1 p)
(c) Select two of the above reactions as the termination steps for the $NO_Y$ cycle creating two different reservoir species, and name the reservoir species. (1 p)
(d) With the help of the figure below, please explain how the ozone hole is created. You must include an explanation of the role of the $Cl_Y$ reservoir, the role of PSC clouds, why sedimentation of $HNO_3$ is needed, and finally the role of the ClO-ClO cycle and the low intensity solar light. No reactions needed to explain what happens. (3 p)



## 4. Acidification

a. Why is “neutral” pH of rainwater approximately 5.6 and not 7? (1 p)

b. The pH in rainwater in Southern Sweden has changed from approximately 4.3 to 4.8 during the last 35 years. Explain the main reason why this is the case. Is acidification still a problem in Sweden today (motivate your answer) (1 p)

c. What is the oxidation number of sulfur (S) in $SO_2$, $H_2SO_4$, $H_2SO_3$, $HSO_4^-$, $HSO_3^-$, $SO_3^{2-}$ and $SO_4^{2-}$? (1 p)

Sulfur dioxide ($SO_2$) is dissolved in water (R1) and dissociates to $HSO_3^-$ (R2) and $SO_3^{2-}$ (R3).

$SO_2(g) \leftrightarrow SO_2(aq)$ ($K_1 = 1.2$ mol kg$^{-1}$ atm$^{-1}$) (R1)
$SO_2(aq) \leftrightarrow HSO_3^- + H^+$ ($K_2 = 1.3\text{x}10^{-2}$ mol kg$^{-1}$) (R2)
$HSO_3^- \leftrightarrow SO_3^{2-} + H^+$ ($K_3 = 6.3\text{x}10^{-8}$ mol kg$^{-1}$) (R3)

At a pH typical for most rain- and cloud droplets, $HSO_3^-$ is the dominant species of all S species involved in R1-R3. $HSO_3^-$ reacts rapidly with dissolved hydrogen peroxide ($H_2O_2$) (R4-R5)

$H_2O_2(g) \leftrightarrow H_2O_2(aq)$ ($K_4 = 7.45\text{x}10^4$ mol kg$^{-1}$ atm$^{-1}$) (R4)
$H_2O_2(aq) + HSO_3^- + H^+ \rightarrow SO_4^{2-} + H_2O + 2H^+$ ($k_5 = 7.45\text{x}10^7$ mol$^{-2}$ kg$^2$ s$^{-1}$) (R5)

Assume that a cloud is formed in an air mass which at the time of cloud formation has a $SO_2(g)$ concentration of 1 ppb$_v$, and a $H_2O_2$ (g) concentration of 0.5 ppb$_v$. The pH of the cloud water is 5. The pressure of the air mass is 900 hPa.
(1 atm = 1013.25 hPa)

d. Calculate the equilibrium $HSO_3^-$ concentration in the cloud water if the pH = 5 and $[SO_2(g)]$ = 1 ppb$_v$ (1 p)

e. Calculate the equilibrium $H_2O_2(aq)$ concentration in the liquid cloud water and the rate of $SO_4^{2-}$ formation $d[SO_4^{2-}]/dt$ (mol kg$^{-1}$ s$^{-1}$) if $[SO_2(g)]$ = 1 ppb$_v$ and $[H_2O_2(g)]$ = 0.5 ppb$_v$. What would the rate of $SO_4^{2-}$ formation be if the pH = 4 instead of 5? (1 p)

f. If the cloud has a relatively long lifetime, approximately what $H_2O_2(g)$ and $SO_2(g)$ concentration will eventually be reached in the air mass after the cloud has dissipated. (1 p)

## 5. Tropospheric ozone

The reactions given below (in random order) are very important for the tropospheric chemistry. They also describe how methane ($CH_4$) is oxidized in the troposphere to formaldehyde (HCHO).

(1) $NO_2 + OH + M \rightarrow HNO_3 + M$
(2) $O(^1D) + H_2O \rightarrow 2OH$
(3) $CH_3O + O_2 \rightarrow HCHO + HO_2$
(4) $NO + O_3 \rightarrow NO_2 + O_2$
(5) $CH_3 + O_2 + M \rightarrow CH_3O_2 + M$
(6) $O_3 + h\nu \rightarrow O_2 + O(^1D)$
(7) $2HO_2 \rightarrow H_2O_2 + O_2$
(8) $CH_3O_2 + NO \rightarrow CH_3O + NO_2$
(9) $HO_2 + NO \rightarrow OH + NO_2$
(10) $NO_2 + h\nu \rightarrow NO + O(^3P)$
(11) $CH_4 + OH \rightarrow CH_3 + H_2O$
(12) $O(^3P) + O_2 + M \rightarrow O_3 + M$

a) What is M that appears on both sides in some of the reactions and why is it needed to complete the reactions? (1p)

b) Which of the reactions are radical initiation, propagation, or termination steps? (1 p)

c) Write an expression for the life time of OH based on the reactions above. Typical OH lifetimes are around 1 s in the troposphere. (1 p)

d) Assuming steady state for both OH and the even more short-lived $O(^1D)$, write an expression for [OH], the concentration of OH, based on the reactions above. (1 p)

e) Combine a selection of the reactions above into a net reaction for the photo-stationary equilibrium that determines the concentration of tropospheric ozone in the absence of hydrocarbons. Give the reactions involved as well as the net reaction. (You don´t have to give an expression for the ozone concentration.) (1 p)

f) Why is the presence of $NO_X$ required in order to maintain the oxidizing capacity of the troposphere and thus facilitate the cleansing of harmful tropospheric trace gases? There are multiple steps in this chain of events. You may use the reactions above as an example of the removal of methane, a strong greenhouse gas. (1 p)

# Exam in Atmospheric Chemistry and Physics June 4, 2016 – Solutions

## 1. Geochemical cycles

a) The residence time is given by $\tau = m/F_{out}$; where m is the mass in the reservoir and $F_{out}$ are the sum of sinks: $\tau = 615/(60 + 60) = 5.1$ years
b) All flows between ocean reservoirs becomes internal in the combined ocean reservoir, and the new reservoir contains the sum of the masses of the three original reservoirs:
$\tau = m/F_{out} = (26\,000 + 9\,700 + 840)/(60 + 0.2) = 607$ years
c) Average molar mass of air: $M_a = 0.78\ m_{N2} + 0.21\ m_{O2} + 0.01\ m_{Ar} = 28.97$ kg/kmole
Mass of the atmosphere: $m_a g = pA$; $m_a = 4\pi R^2 p/g = 4\pi{*}(6.37\ 10^6)^2{*}98400/9.81 = 5.12\ 10^{18}$ kg
Mixing ratio $C = n_{CO2}/n_a = (m_C/M_C)/(m_a/M_a)$ = [note that the mass of carbon ($m_C$ not $m_{CO2}$) is given in Fig. 1] = $(615\ 10^{12}/12.01)/(5.12\ 10^{18}/28.97) = 2.91\ 10^{-4}$ = 291 ppmv
d) $CO_2$ is the most common carbon-containing gas in the atmosphere because it is the final stable oxidation product of the oxidation ongoing in the atmosphere. As a result of the chemical stability of $CO_2$ the residence time is long. As a result, $CO_2$ is well mixed in the atmosphere.
e) From Fig. 2 C = 401 ppmv; $m_C = n_C M_C = C\ n_a M_C = C\ m_a M_C / M_a$ =
$= 401\ 10^{-6}{*}5.12\ 10^{18}{*}12.01 / 28.97 = 849$ Pg carbon
First order sink processes: $F_{out} = km$; Pre-industrial: $k = m/F_{out} = 615/(60 + 60)$ =166 Pg/year
f) Biosphere: In order to preserve the loss rate constant of the biosphere the Net Primary Productivity (NPP) must increase proportionally to the atmospheric increase. There are some results pointing to increased growth-rate with increasing $CO_2$ concentration, but that concentration is not the only limiting factor for the growth. In addition, land use, e.g. deforestation in the tropics, has a large impact on the NPP.
Oceans: Increased $CO_2$ concentration in the air increases the dissolution and concentration of compounds originating in $CO_2$. This causes acidification of the oceans, which shifts the air-sea equilibrium towards increased fraction of $CO_2$ in the atmosphere implying that the loss-rate constant decreases.
Greenhouse gases also induces warming which could enhance or decrease NPP and that would lower the dissolution in the oceans.

## 2. Climate effects of aerosols and clouds

**2a)** Aerosol particles mainly interact with the incoming solar radiation. Aerosols scatter and absorb solar radiation. Greenhouse gases mainly interact with the outgoing terrestrial radiation, by absorbing radiation.
**2b)** Clouds make up around 2/3 (~0.19) of the global average (planetary) albedo of the Earth (~0.28). Changes in cloud coverage and cloud albedo (cloud optical properties) thus have large impact on the Earth's energy balance and climate. This is the major effect.
Clouds have a complex impact on climate. Clouds interact both with incoming solar radiation and outgoing terrestrial radiation. During daytime low clouds reflect solar radiation and increase the Earth's albedo (major effect), and cools the Earth's surface. During night time low clouds absorb outgoing terrestrial radiation, and warms the Earth's surface. High (cold) clouds mainly have impact on the outgoing terrestrial radiation, and thus mainly warms the Earth's surface.
Clouds are also of great importance for the hydrological cycle, for atmospheric chemistry, for energy transport in the atmosphere, etc.

**2c) Direct effect:** Direct interaction with incoming solar radiation. Most aerosols reflect the solar radiation, and thus coole the Earth. Some aerosols absorb solar radiation, and thus heat the Earth. **Indirect effect:** Aerosols act as cloud condensation nuclei (CCN) to form cloud droplets. Increasing aerosol concentrations lead to increased cloud droplet number concentrations, which affects the optical properties of the cloud (albedo) (first indirect effect). A higher number of cloud droplets in a cloud also leads to that the formed cloud droplets will be smaller in size. This affects precipitation formation, and can influence the cloud life time (second indirect effect).

**2d)**

$$\Delta A = \frac{A\cdot(1-A)}{3}\cdot\frac{\Delta N}{N}$$

$$A = 0.6 \qquad \frac{\Delta N}{N} = \frac{1.4\cdot N - N}{N} = 0.4$$

=> $$\Delta A = \frac{0.6\cdot(1-0.6)}{3}\cdot 0.4 = 0.032$$

Answer: The cloud albedo will increase by 0.032, and the new albedo will be 0.632

**3. Stratospheric ozone**

(a) Answer: (1)+(3), or (1)+(4), or (6)+(7).

(b) Answer: (5). OBS: reaction (11) is not an initiation reaction, since it does not bring new nitrogen containing compounds into the stratosphere due to the short lifetime of NO2 in the troposphere.

(c) Answer: (8) and (10).

(d) Answer: The Cly reservoir is formed during the autumn, and due to the week radiation at the end of the autumn, it stays in the reservoir. It provides the chlorine compounds needed for ozone destruction at a later time in the winter. At winter, PSC ice clouds are formed, which provide a surface for the reactions of the reservoir species with each other forming chlorine and HNO3. HNO3 needs to be sedimented by gravitation on top of the ice particles down to the troposphere, otherwise it can contribute to a disruption of the ozone destroying mechanism. As we have some low intensity solar light in spring, we feed the ozone destroying catalytic mechanism with the ClO-ClO cycle. As the solar intensity becomes too high later in the spring or towards the summer, the Chapman mechanism will start to take over, reproducing ozone.

(Point calculation: There are four factors needed for ozone depletion: -0.5p for each factor missed. So, at least 1p if you get one factor right, but if you are completely wrong on the remaining factors, you can get 0p or 0.5p even if one factor is correct).

## 4. Acidification

a. The neutral pH of rainwater is 5.6 and not 7 because of the $CO_2$ dissolution and dissociation of $H_2CO_3$ that adds $H^+$ ions to the aqueous phase:

$CO2(g) \leftrightarrow H_2CO_3(aq)$
$H_2CO_3(aq) \leftrightarrow HCO_3^- + \mathbf{H^+}$
$HCO_3^- \leftrightarrow CO_3^{2-} + \mathbf{H^+}$

b. The main reason why the pH in rainwater in Southern Sweden has increased during the last 35 years is a significant reduction of the anthropogenic emissions of $SO_2$ that mainly originated from coal power plants in Europe (e.g. Great Britain). Acidification of lakes and soil is still a substantial problem in parts of Sweden because the historically large deposition of sulfur has depleted the buffering capacity of the ecosystems. Therefore, even small amount of sulfur deposition is harmful for these ecosystems. It will take at least 100 years for these ecosystems to recover completely.

c. S(IV): $SO_2$, $H_2SO_3$, $HSO_3^-$, $SO_3^{2-}$
S(VI): $H_2SO_4$, $HSO_4^-$, $SO_4^{2-}$

d. The $SO_2(g)$ concentration expressed in atmospheres is:
$p_{SO2} = 90000/101325 \text{ x } 10^{-9}$ atm $= 8.88 \text{ x } 10^{-10}$ atm
$[H^+] = 10^{-pH}$ mol dm$^{-3}$ = $10^{-5}$ mol dm$^{-3} \approx 10^{-5}$ mol kg$^{-1}$ (Density of water ≈ 1 kg dm$^{-3}$)
Based on R1 and R2 we get:
$[SO_2(aq)] = K1 \text{ x } p_{SO2}$; $[HSO_3^-] = K2 \text{ x } [SO_2(aq)] / [H^+]$
$[HSO_3^-] = K1 \text{ x } K2 \text{ x } p_{SO2} / [H^+] = (1.2 \text{ x } 1.3 \text{ x } 10^{-2} \text{ x } 8.88 \text{ x } 10^{-10}) / 10^{-5} = \underline{1.39 \text{ x } 10^{-6} \text{ mol kg}^{-1}}$

e. The $H_2O_2(g)$ concentration expressed in atmospheres is:
$p_{H2O2} = 90000/101325 \text{ x } 0.5 \text{ x } 10^{-9}$ atm $= 4.44 \text{ x } 10^{-10}$ atm
The $H_2O_2(aq)$ we get from R4:
$[H_2O_2(aq)] = K4 \text{ x } p_{H2O2} = 7.45\text{x}10^4 \text{ x } 4.44 \text{ x } 10^{-10} = \underline{3.31 \text{ x } 10^{-5} \text{ mol kg}^{-1}}$
The rate of $SO_4^{2-}$ formation is according to R5 given by:
$d[SO_4^{2-}]/dt = k_5 \text{ x } [H_2O_2(aq)] \text{ x } [HSO_3^-] \text{ x } [H^+]$

Combining this with R1, R2 and R4 we get:
$d[SO_4^{2-}]/dt = k_5 \text{ x } K4 \text{ x } p_{H2O2} \text{ x } K1 \text{ x } K2 \text{ x } p_{SO2} / [H^+] \text{ x } [H^+]$

The two $[H^+]$ terms cancel out and we get a $SO_4^{2-}$ formation rate which is pH independent:
$^{(*)}d[SO_4^{2-}]/dt = \underline{k_5 \text{ x } K4 \text{ x } K1 \text{ x } K2 \text{ x } p_{H2O2} \text{ x } p_{SO2}} =$
$7.45\text{x}10^7 \text{ x } 7.45\text{x}10^4 \text{ x } 1.2 \text{ x } 1.3 \text{ x } 10^{-2} \text{ x } 4.44 \text{ x } 10^{-10} \text{ x } 8.88 \text{ x } 10^{-10}$ mol kg$^{-1}$ s$^{-1}$ =
$\underline{3.41 \text{ x } 10^{-8} \text{ mol kg}^{-1} \text{ s}^{-1}}$
According to the derived expression $^{(*)}$ the rate of $SO_4^{2-}$ formation does not depend on the $H^+$ concentration. Therefore $SO_4^{2-}$ formation is the same at pH = 4 as pH = 5.

f. After some time inside the cloud (the exact time will depend on the cloud water content) either all $H_2O_2$ or $SO_2$ will be removed. According to the expression $^{(*)}$ one $SO_2$ molecule is removed for each $H_2O_2$. Thus we get:
$[SO_2(g)] = \max([SO_2(g)]_{t=0} - [H_2O_2(g)]_{t=0}, 0) = \max(1-0.5, 0) \text{ ppb}_v = \underline{0.5 \text{ ppb}_v}$
$[H_2O_2(g)] = \max([H_2O_2(g)]_{t=0} - [SO_2(g)]_{t=0}, 0) = \max(0.5-1, 0) \text{ ppb}_v = \underline{0 \text{ ppb}_v}$
In principle all $H_2O_2$ (g) will be lost and 0.5 ppb$_v$ $SO_2(g)$ will remain.

## 5. Tropospheric ozone

a) Answer: M is used to denote a molecule that receives some of the excess energy released by the reaction and thus stabilizes the product, but which is not otherwise involved in the reaction. M is often one of the main components of air (N2, O2 eller Ar). All reactions are exothermic, otherwise they would not proceed. Without the presence of M, the single product would not be stable, since the system cannot conserve both momentum and energy (including the excess energy created in the exothermic reaction) with only one product. In all reactions with only one product, M is therefore needed (on each side). If not, the product would disintegrate back to the reactants. In reactions with two or more products, the excess energy can be shared and “wasted” in the form of kinetic energy (heat).

b) Answer:

radical initiation
(6) $O_3 + h\nu \rightarrow O_2 + O(^1D)$
(10) $NO_2 + h\nu \rightarrow NO + O(^3P)$ (and NOx propagation)

radical propagation
(2) $O(^1D) + H_2O \rightarrow 2OH$
(3) $CH_3O + O_2 \rightarrow HCHO + HO_2$
(4) $NO + O_3 \rightarrow NO_2 + O_2$
(5) $CH_3 + O_2 + M \rightarrow CH_3O_2 + M$
(8) $CH_3O_2 + NO \rightarrow CH_3O + NO_2$
(9) $HO_2 + NO \rightarrow OH + NO_2$
(11) $CH_4 + OH \rightarrow CH_3 + H_2O$

radical termination
(1) $NO_2 + OH + M \rightarrow HNO_3 + M$
(7) $2HO_2 \rightarrow H_2O_2 + O_2$
(12) $O(^3P) + O_2 + M \rightarrow O_3 + M$

c) Answer:

$$\tau_{OH} = \frac{M_{OH}}{L_{OH}} = \frac{[OH]}{k_{11}[NO_2][OH] + k_3[CH_4][OH]} = \frac{1}{k_{11}[NO_2] + k_3[CH_4]}$$

$L_{OH}$ is the loss rate of OH. $L_{OH} = \left.\frac{d[OH]}{dt}\right|_{loss}$ which proceeds through reactions (11) and (3).

d) Answer:
Steady state conditions mean that the production rate $P_{OH}$ of OH equals the loss rate $L_{OH}$ of OH. The same holds for $O(^1D)$.

$$P_{O(^1D)} = \left.\frac{d\left[O(^1D)\right]}{dt}\right|_{prod} = k_3\left[O_3\right]$$

$$L_{O(^1D)} = \left.\frac{d\left[O(^1D)\right]}{dt}\right|_{loss} = k_2\left[O(^1D)\right]\left[H_2O\right]$$

$$\left.\frac{d\left[O(^1D)\right]}{dt}\right| = 0 \Rightarrow P_{O(^1D)} = L_{O(^1D)} \Rightarrow k_3\left[O_3\right] = k_2\left[O(^1D)\right]\left[H_2O\right] \Rightarrow \left[O(^1D)\right] = \frac{k_3\left[O_3\right]}{k_2\left[H_2O\right]}$$

$$P_{OH} = \left.\frac{d\left[OH\right]}{dt}\right|_{prod} = 2k_2\left[O(^1D)\right]\left[H_2O\right] + k_7\left[HO_2\right]\left[NO\right]$$

$$L_{OH} = \left.\frac{d\left[OH\right]}{dt}\right|_{loss} = k_{11}\left[NO_2\right]\left[OH\right] + k_3\left[CH_4\right]\left[OH\right]$$

$$\left.\frac{d\left[OH\right]}{dt}\right| = 0 \Rightarrow P_{OH} = L_{OH} \Rightarrow 2k_2\left[O(^1D)\right]\left[H_2O\right] + k_7\left[HO_2\right]\left[NO\right] = k_{11}\left[NO_2\right]\left[OH\right] + k_3\left[CH_4\right]\left[OH\right] \Rightarrow$$

$$2k_2\frac{k_3\left[O_3\right]}{k_2\left[H_2O\right]}\left[H_2O\right] + k_7\left[HO_2\right]\left[NO\right] = \left[OH\right]\left(k_{11}\left[NO_2\right] + k_3\left[CH_4\right]\right) \Rightarrow$$

$$\left[OH\right] = \frac{2k_3\left[O_3\right] + k_7\left[HO_2\right]\left[NO\right]}{k_{11}\left[NO_2\right] + k_3\left[CH_4\right]}$$

e) Answer:
(10) $NO_2 + h\nu \rightarrow NO + O(^3P)$
(12) $O(^3P) + O_2 + M \rightarrow O_3 + M$
(4) $NO + O_3 \rightarrow NO_2 + O_2$

The photostationary equilibrium (in the absence of hydrocarbons) can be summarized by the net reaction:

$$NO_2 + O_2 \Leftrightarrow NO + O_3$$

f) Answer (more than needed):
Our atmosphere is an oxidizing medium. However, the two most abundant oxidants $O_2$ and $O_3$ do not contribute significantly to the oxidation of trace gases. Instead, gas-phase compounds found at exceedingly low concentrations, so called radicals, are responsible for the oxidation. Ozone ($O_3$) is needed for the formation of such radicals. In turn, nitrogen oxides ($NO_2$) are required for net production of $O_3$ in the troposphere:

$$NO_2 \xrightarrow{(1)} O_3 \xrightarrow{(2)} \text{Radicals} \rightarrow \text{Oxidation of harmful trace gases}$$

(10) $NO_2 + h\nu \rightarrow NO + O(^3P)$

This reaction initiates the formation of $O(^3P)$, which is very important for the tropospheric chemistry as it constitutes <u>the only way to produce ozone in the troposphere</u> through

(6) $O_3 + h\nu \rightarrow O_2 + O(^1D)$

In the stratosphere, $O(^3P)$ can be formed also via photolysis of $O_2$ at $\lambda<240$ nm. This UVc radiation is fortunately unable to penetrate into the troposphere. The oxygen atom $O(^3P)$ is a bi-radical and has two unpaired electrons. Without nitrogen oxides ($NO_X$), there would be no net production of $O_3$ in the troposphere. Instead, there would be a net ozone destruction since OH radicals are not recycled though (9) $HO_2 + NO \rightarrow OH + NO_2$. OH would then rather be terminated via reactions such as (1) $NO_2 + OH + M \rightarrow HNO_3 + M$.
Only the highly excited oxygen atom $O(^1D)$, but not $O(^3P)$, is able to break up the very stable water molecule $H_2O$ to produce OH radicals.

(2) $O(^1D) + H_2O \rightarrow 2OH$

The hydroxyl radical OH it the detergent of the atmosphere and is propagated further to form other $HO_x$ radicals ($HO_2$, RO, $RO_2$) in catalytic ozone production cycles. This boosts the oxidizing capacity of the troposphere and facilitates the cleansing of harmful tropospheric trace gases. Without this production of radicals in the troposphere in the multiple steps starting with $NO_X$, the concentrations of several harmful trace gases would reach levels that would have made life on Earth in its present form impossible. The entire tropospheric chemistry is driven by radicals.