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)

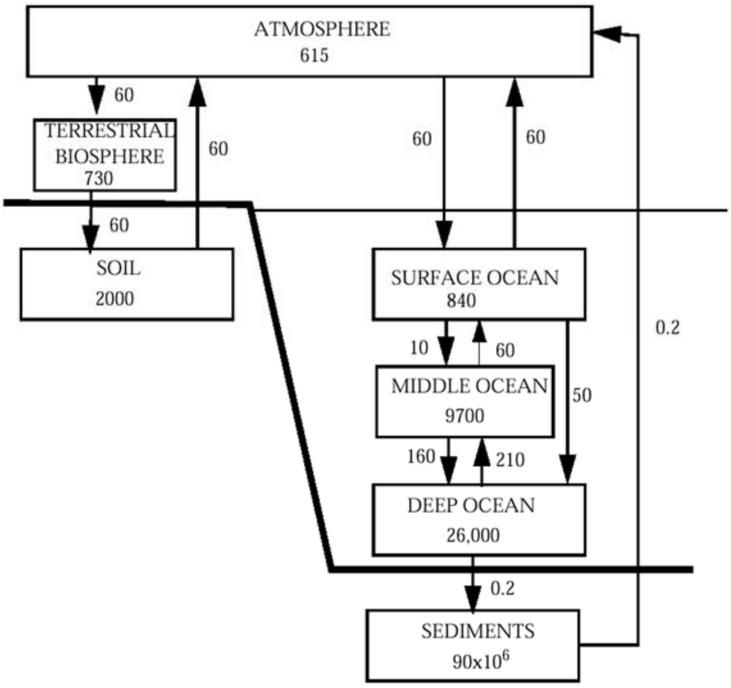


Figure 1. The pre-industrial geochemical cycle of carbon. The masses of carbon in the reservoirs are given in Pg (10^{15} g) and the exchange in Pg per year.

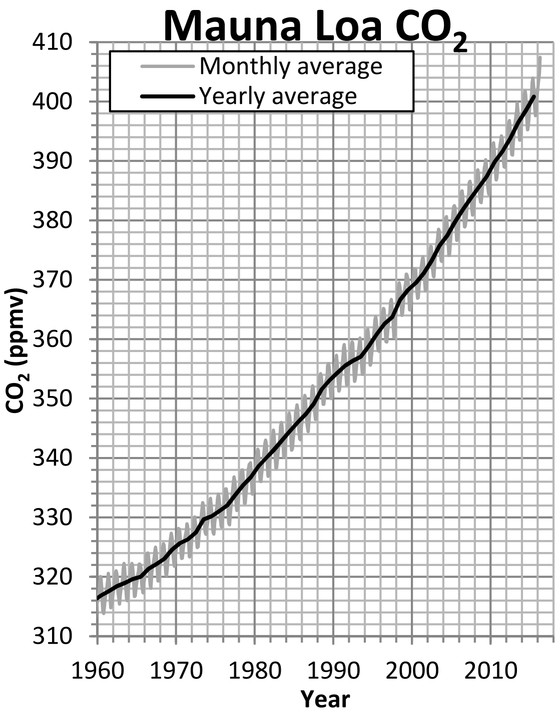


Figure 2. The CO_2 concentration in the air at Mauna Loa, Hawaii.

2. Climate effects of aerosols and clouds

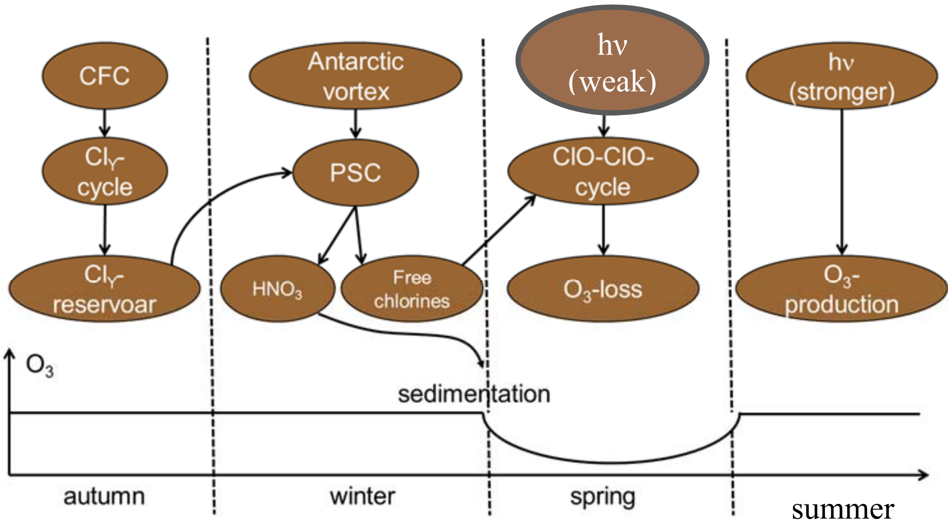
a) Compare in general terms the way in which aerosol particles and greenhouse gases interact with the climate. (1 p)
b) Describe the role and importance of clouds for the climate. (1 p)
c) Aerosol particles have two main effects on the climate, that can be subdivided further. Describe these main and 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)
$SO_2(aq) \leftrightarrow HSO_3^- + H^+$ ($K_2 = 1.3 \times 10^{-2}$ mol kg^{-1}) (R2)
$HSO_3^- \leftrightarrow SO_3^{2-} + H^+$ ($K_3 = 6.3 \times 10^{-8}$ 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)

$H_2O_2(g) \leftrightarrow H_2O_2(aq)$ ($K_4 = 7.45 \times 10^4$ mol kg^{-1} atm^{-1}) (R4)
$H_2O_2(aq) + HSO_3^- + H^+ \rightarrow SO_4^{2-} + H_2O + 2H^+$ ($k_5 = 7.45 \times 10^7$ 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:
$p_{SO2} = 90000/101325 \text{ x } 10^{-9} \text{ atm} = 8.88 \text{ x } 10^{-10} \text{ atm}$
$[H^+] = 10^{-pH} \text{ mol dm}^{-3} = 10^{-5} \text{ mol dm}^{-3} \approx 10^{-5} \text{ mol kg}^{-1}$ (Density of water $\approx 1 \text{ kg dm}^{-3}$)
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:
$p_{H2O2} = 90000/101325 \text{ x } 0.5 \text{ x } 10^{-9} \text{ atm} = 4.44 \text{ x } 10^{-10} \text{ atm}$
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:
$^{(*)}d[SO_4^{2-}]/dt = \underline{k_5 \text{ x } K4 \text{ x } K1 \text{ x } K2 \text{ x } p_{H2O2} \text{ x } p_{SO2}} =$
$7.45\text{x}10^7 \text{ x } 7.45\text{x}10^4 \text{ x } 1.2 \text{ x } 1.3 \text{ x } 10^{-2} \text{ x } 4.44 \text{ x } 10^{-10} \text{ x } 8.88 \text{ x } 10^{-10} \text{ mol kg}^{-1} \text{ s}^{-1} =$
$\underline{3.41 \text{ x } 10^{-8} \text{ mol kg}^{-1} \text{ s}^{-1}}$
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) $O_3 + hv \rightarrow O_2 + O(^1D)$
(10) $NO_2 + hv \rightarrow NO + O(^3P)$ (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(^{1}D).

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

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

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

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

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

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

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

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

e) Answer:

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

(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 the only way to produce ozone in the troposphere 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.

Exam Atmospheric Chemistry and Physics

May 29, 2017 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) What is meant by geostrophic flow? (1p)
b) Compare the winds around an atmospheric low pressure region at ground level with the winds several hundreds of meters up in the same region. Are there any differences? Explain! (1p)
c) Explain why the weather usually is fair when the atmospheric pressure is high, and why clouds and precipitation are connected with low pressure. (2p)
d) The temperature of a 1 km thick layer in contact with the ground decreases by 10 K/km. Above this layer the temperature does not change with altitude. How high can an air parcel in contact with the ground rise under these conditions? (2p)

2. Aerosols and clouds

a) Name two important natural sources of atmospheric aerosol and name their main chemical components (1p)
b) Name the most important category of atmospheric aerosol connected with human activity, and the main chemical constituents. (1p)
c) Roughly describe the particle sizes of the three sources you described in a) and b). (1p)
d) In cloud formation the particles "compete" for the water. Consider the following cases:

i) Two particles, 0.1 and 0.2 μm in diameter, and with the same chemical composition, participate in the in the same cloud formation. Which particle has the best chance to form a cloud drop? (0.5p)

ii) Two particles of the same size but with different chemical composition: one of them contains 70% water insoluble and 30% soluble material, and the other contains 100% of the same soluble material. Which particle has the best chance to form a cloud drop? (0.5p)

iii) Sketch the Köhler equation graphically (no calculations needed), and explain your answers to i) and ii). (2p)

3. Climate

In the textbook, Jacob presents a simple climate model of the Earth, where the atmosphere consists of an isothermal thin layer that absorbs the fraction f = 0.77 of the terrestrial radiation. The planetary albedo is 0.28.

a) Make a sketch over the radiation fluxes and derive an expression of the surface temperature of the Earth. (2 p)

b) Calculate the temperature increase induced by the natural greenhouse effect. (1 p)

In Fig1 IPCC lists the radiative forcing (RF) of different components relative to the year 1750.

c) Which of these components have warmed/cooled the climate, and what factors have largest influence on the uncertainty in the radiative forcing estimation. (1 p)

d) To reduce the health burden of air pollution many countries strive to reduce their emissions of aerosol particles. Are there any possible negative side-effects to such a reduction? (1 p)

e) Briefly explain the importance of feed-backs in the climate system. (1 p)

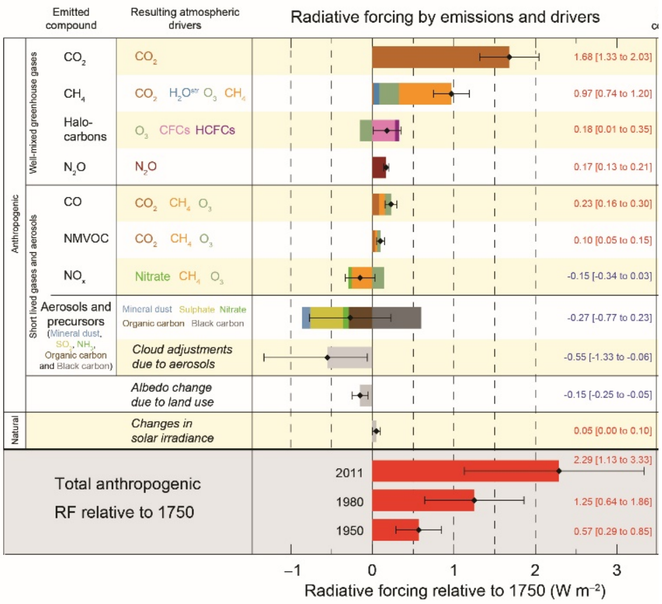


Fig 1. Radiative forcing estimates in 2011 relative to 1750 and aggregated uncertainties for the main drivers of climate change.

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

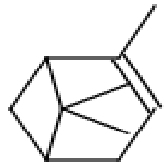
b) the Chapman mechanism for ozone production in the stratosphere (1p)

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 reactions above constitute termination steps for catalytic ozone loss propagated via the HO_x, NO_x and ClO_x radicals? (1p)

5. The oxidation power of the troposphere



α-pinene ($C_{10}H_{16}$)

The reactions given below are important for the OH, O_x and NO_x chemistry of the troposphere and the formation of secondary organic aerosol (SOA). SOA can be formed when α-pinene ($C_{10}H_{16}$), a so-called monoterpene, is oxidized in the atmosphere. α-pinene is emitted in large quantities from pine and spruce forests.

1. $NO + O_3 \rightarrow NO_2 + O_2$, $k_1 = 1.60\text{x}10^{-14}$ molec^{-1} cm^3 s^{-1}
2. $O + O_2 + M \rightarrow O_3 + M$, $k_2 = 6.0\text{x}10^{-34}$ molec^{-2} cm^6 s^{-1}
3. $NO_2 + O_3 \rightarrow NO_3 + O_2$, $k_3 = 3.1\text{x}10^{-17}$ molec^{-1} cm^3 s^{-1}
4. $O(^1D) + O_2 \rightarrow O + O_2$, $k_4 = 4\text{x}10^{-11}$ molec^{-1} cm^3 s^{-1}
5. $O(^1D) + N_2 \rightarrow O + N_2$, $k_5 = 3.1\text{x}10^{-11}$ molec^{-1} cm^3 s^{-1}
6. $O(^1D) + H_2O \rightarrow 2\,OH$, $k_6 = 2.14\text{x}10^{-10}$ molec^{-1} cm^3 s^{-1}
7. $C_{10}H_{16} + O_3 \rightarrow C_{10}H_{16}O_3$, $k_7 = 9.1 \text{ x } 10^{-17}$ molec^{-1} cm^3 s^{-1}
8. $C_{10}H_{16} + NO_3 \xrightarrow{+O_2} C_{10}H_{16}NO_5$, $k_8 = 6.4 \text{ x } 10^{-12}$ molec^{-1} cm^3 s^{-1}
9. $C_{10}H_{16} + OH \xrightarrow{+O_2} C_{10}H_{17}O_3$, $k_9 = 5.4 \text{ x } 10^{-11}$ molec^{-1} cm^3 s^{-1}
10. $NO_3 + NO_2 \rightarrow N_2O_5$, $k_{10} = 1.25\text{x}10^{-12}$ molec^{-1} cm^3 s^{-1}
11. $NO_2 + OH \rightarrow HNO_3$, $k_{11} = 1.2\text{x}10^{-11}$ molec^{-1} cm^3 s^{-1} [α]
12. $O_3 + h\nu \rightarrow O_2 + O(^1D)$
13. $NO_2 + h\nu \rightarrow NO + O$
14. $NO_3 + h\nu \rightarrow NO + O_2$
15. $NO_3 + h\nu \rightarrow NO_2 + O$
16. $HNO_3 + h\nu \rightarrow NO_2 + OH$

[α] Reaction 11 is a three-body reaction but the provided reaction rate k_{11} (unit: molec^{-1} cm^3 s^{-1}) already include the concentration of the inert air molecules (M).

a. From the reactions above, select one example of a radical initiation reaction, a radical propagation reaction, and a radical termination reaction. (**1 p**)

b. Write down the reactions that describes the minute time scale daytime NO_x null cycle with no net catalytic O_x (O_3 and O) or NO_x (NO and NO_2) losses (**1 p**)
(Hint: The reactions you need are included in the list above)

c. α-pinene has a carbon-carbon double bond and can therefore be efficiently oxidized by several oxidation agents. Write an expression for the lifetime of α-pinene (**1 p**)

d. Based on the reactions 1-16 given above, estimate the daytime lifetime of α-pinene for the following conditions:
$[OH] = 3.0\text{x}10^6$ molecules cm^{-3}, $[O_3]$ = 30 ppb$_v$, $[NO_x]$ = 0.5 ppb$_v$, $[C_{10}H_{16}]$ = 0.5 ppb$_v$, an atmospheric pressure (p) of 10^5 Pa and a temperature (T) of 293 K (**1 p**).
(Hint: Reaction 14 and 15 can be assumed to proceed fast during the daytime)

e. Based on the reactions 1-16 given above, estimate the nighttime lifetime of α-pinene for the following conditions:
$[O_3]$ = 30 ppb$_v$, $[NO_x]$ = 0.5 ppb$_v$, $[C_{10}H_{16}]$ = 0.5 ppb$_v$, an atmospheric pressure of 10^5 Pa and a temperature of 293 K.
(Hint: OH has a lifetime ~1 s. You can assume steady state conditions for NO_3). (**1 p**)

f. For the conditions specified in **d** and **e**, which oxidation agent is the single most important for the oxidation of α-pinene during daytime and which oxidation agent is the single most important for the oxidation α-pinene of during the night? (**1 p**)

Answers to exam in Atmospheric Chemistry and Physics May 29, 2017

1. The Atmosphere – Answer

a) Geostrophic flow: Balance between the horizontal gradient and Coriolis forces leading to winds along isobars.

b) Winds several hundred meters above the ground is affected by gradient horizontal gradient and Coriolis forces => Geostrophic winds parallel to the isobars around the low pressure. Winds close to the ground are affected by a friction force that induces a wind component that crosses isobars causing winds towards low pressure regions.

c) Low pressure: Winds close to the ground towards the centre of the low pressure, i.e. convergence, induce an upward wind. The atmospheric pressure decreases with altitude implying that the lifted air mass will expand and cool adiabatically, leading to reduced saturation vapour pressure of water. Eventually this can lead to formation of clouds and precipitation. High pressure: Friction against the ground induces divergence, causing a wind downwards. This means that air parcels are moving towards higher pressure with this wind => compression and warming of the air => higher saturation vapour pressure of water which counteracts cloud formation, and thus resulting in fair weather.

d) The layer close to the ground: $dT/dz = -10$ K/km => unstable air (close to neutral). The air above 1 km altitude: $dT/dz = 0$ K/km => stable air. An air mass at the ground can rise through the atmosphere until its temperature equals that of the isothermal layer, implying that the temperature change of the air mass can be the height h of the unstable layer times the temperature gradient, i.e. $\Delta T = h*dT/dz = 1*(-10) = -10$ K. The dry adiabatic lapse rate $\Gamma = -dT/dz$ of the rising air mass = 9.8 K/km. The maximum altitude that the air mass can reach is found when the temperature change becomes ΔT, i.e. $-\Gamma z = \Delta T \Rightarrow z = -\Delta T/\Gamma = 10/9.8 = 1.02$ km ≈ 1 km. (Proper handling of wet adiabatic lapse rate also gave max points).

2. Aerosols and clouds – Answer

a) Sea spray (sodium chloride and several other minor constituents) from the oceans and windblown dust (minerals)

b) Various combustion processes (sulphates, nitrates, organic material, soot)

c) Sea spray and windblown dust are both mechanically generated => large particles ($D > 1$ µm typically). Combustion particles are formed from hot vapours and atmospheric processing of gaseous effluents => small particles ($D < 1$ µm typically).

d) 0.2 µm; ii) 100% soluble; iii) Draw two schematic Köhler curves, one for each particle. The chance of forming cloud drops is decided by the critical saturation ratio (the maximum of the Köhler curve). In i) the larger particle requires lower cloud super-saturation because of a lower critical saturation ratio due to less curvature and hence less influence from the Kelvin effect. In ii) the insoluble part of one of the particles does not bind any water, whereas soluble material induces vapour pressure depression => less grow than the 100% soluble particle. A smaller drop will be more affected by the Kelvin effect due to stronger curvature => The particle with 100% soluble material has a lower critical saturation ratio and will thus have a better chance to form a cloud drop.

3. Climate – Answer

a) The expression can be derived using radiation balance equations (Chapter 7.3.2 in the textbook)

i. Incoming – Outgoing radiation for the Earth (incl. the atmosphere)

$F_s(1-A)/4 = f\sigma T_1^4 + (1-f)\,\sigma T_0^4$

ii. Incoming – Outgoing radiation for the atmosphere

$f\sigma T_0^4 = 2f\sigma T_1^4$

which leads to

$T_0 = 2^{¼}\, T_1$

replacement and rearrangement results in the expression

$$T_0 = \left[\frac{Fs(1-A)}{4\sigma(1-\frac{f}{2})}\right]^{¼}$$

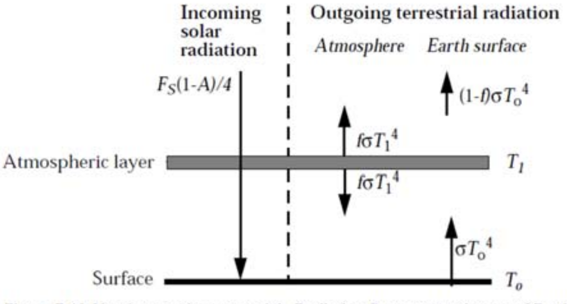


Figure 7-12 Simple greenhouse model. Radiation fluxes per unit area of Earth's surface are shown.

b) The temperature increase by the natural greenhouse warming (GHG) can be calculated by computing the temperature difference between the cases with (f = 0.77) and without greenhouse warming (f = 0).

$\Delta T = T_{0,GHW} - T_{0,NoGHW}$

$$\Delta T = \left[\frac{Fs(1-A)}{4\sigma(1-\frac{0.77}{2})}\right]^{¼} - \left[\frac{Fs(1-A)}{4\sigma(1-\frac{0}{2})}\right]^{¼} = 33°\mathrm{C}$$

c) The radiative forcing (RF) for a component is a measure of how much that component perturbs the energy balance of the Earth. (The difference between the solar insolation absorbed by the Earth and the energy that gets radiated out of the Earth-atmosphere (back to space)). Positive RF warms, and negative RF cools the surface of the Earth.

In the figure from IPCC we can see that the cooling mainly comes from aerosol particles. They induce an increased albedo by scattering more sunlight back to space, and via particle-cloud-interactions they are estimated to also alter the net albedo of the clouds, inducing further warming. The warming has mostly been from GHGs, and most warming has been induced by CO_2 and CH_4. Aerosol particles that absorb sunlight (such as soot) have also added to the warming.

The uncertainties in the estimations for each component are marked by error bars. Based on the length of the error bars we find the RF from aerosol particles (and their influence on clouds) to hold the largest uncertainties. Those uncertainties are propagated to the sum of the components, i.e. to the 'Total anthropogenic RF'. Thus, most of the uncertainties in the estimations in the red bars come from uncertainties in the RF of aerosols.

d) Aerosol particles have a net cooling effect on climate. Removing a component that cools climate would result in further warming of the Earth. Decreased particle emissions may result in a rapid warming, since aerosol particles have short residence times in the atmosphere (generally less than a month in the troposphere).

e) Feed-back systems can attenuate or amplify the temperature effects of changes in the Earth's radiation budget. Hence, climate change feed-backs can strongly influence the climate sensitivity. An example is that a temperature increase in the Arctic may lead to less snow cover, resulting in a decrease in the albedo of the Earth.

4. Stratospheric ozone – Answer

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 < λ < 320 nm) which is not removed by ordinary oxygen O_2.

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. The oxidation power of the troposphere – Answer

a. Radical initiation: 12, 16, 7*; Radical propagation: 1, 3, 8, 9; Radical termination: 2, 10, 11
Reactions 4, 5 and 6: $O(^1D)$ is not a radical but extremely reactive and thus 4,5 and 6 can be considered be similar to radical propagation reactions because all form radicals.
*In reaction 7 two non-radicals ($C_{10}H_{16}$ and O_3) reacts and form very reactive Criegee' biradicals $C_{10}H_{16}O_3$ that rapidly decompose and form different peroxy radicals ($C_{10}H_{15}O_4$).

b. 1. $NO + O_3 \rightarrow NO_2 + O_2$
11. $NO_2 + hv \rightarrow NO + O$
2. $O + O_2 + M \rightarrow O_3 + M$

c.

$$\tau_{C_{10}H_{16}} = \frac{M_{C_{10}H_{16}}}{L_{C_{10}H_{16}}} = \frac{[C_{10}H_{16}]}{(k_7[O_3] + k_8[NO_3] + k_9[OH])[C_{10}H_{16}]} = \frac{1}{(k_7[O_3] + k_8[NO_3] + k_9[OH])}$$

d. Because reaction 14 and 15 proceeds fast during the daytime very little NO_3 will be present and we can neglect the loss of α-pinene due to the reaction with NO_3. We when get:

$$\tau_{\mathrm{C_{10}H_{16}}} \approx \frac{1}{(k_7[\mathrm{O_3}] + k_9[\mathrm{OH}])}$$

$$[\mathrm{O_3}] = \frac{30\cdot 10^{-9}\cdot pN_{av}}{RT} = \frac{30\cdot 10^{-9}\cdot 10^5\cdot 6.023\cdot 10^{23}}{8.3145\cdot 293} = 7.4\cdot 10^{11}\ \text{molec cm}^{-3}$$

$$\tau_{\mathrm{C_{10}H_{16}}} \approx \frac{1}{(k_7[\mathrm{O_3}]+k_9[\mathrm{OH}])} = \frac{1}{(9.1\cdot 10^{-17}\cdot 7.4\cdot 10^{11}+5.4\cdot 10^{-11}\cdot 3.0\cdot 10^{6})} = 4360\ \text{s} \approx 1.2\ \text{h}$$

e. Because of the very short lifetime and the lack of major OH sources (no photolysis reactions during the night) we get:

$$\tau_{\mathrm{C_{10}H_{16}}} \approx \frac{1}{(k_7[\mathrm{O_3}] + k_8[\mathrm{NO_3}])}$$

$$\frac{d[\mathrm{NO_3}]}{dt} = k_3[\mathrm{NO_2}][\mathrm{O_3}] - k_{10}[\mathrm{NO_2}][\mathrm{NO_3}] - k_8[\mathrm{C_{10}H_{16}}][\mathrm{NO_3}] = 0$$

$$\Rightarrow [\mathrm{NO_3}] = \frac{k_3[\mathrm{NO_2}][\mathrm{O_3}]}{k_{10}[\mathrm{NO_2}] - k_8[\mathrm{C_{10}H_{16}}]}$$

Further, during night in principle all NO_x are in the form of NO_2 ($[NO_2] \approx [NO_x]$).

$$[\mathrm{NO_3}] \approx \frac{k_3[\mathrm{NO}_x][\mathrm{O_3}]}{k_{10}[\mathrm{NO}_x] - k_8[\mathrm{C_{10}H_{16}}]} = 3.0\cdot 10^6\ \text{molec cm}^{-3}$$

$$\tau_{\mathrm{C_{10}H_{16}}} \approx \frac{1}{(k_7[\mathrm{O_3}]+k_8[\mathrm{NO_3}])} = \frac{1}{(9.1\cdot 10^{-17}\cdot 7.4\cdot 10^{11}+6.4\cdot 10^{-12}\cdot 3.0\cdot 10^{6})} = 11555\ \text{s} \approx 3.2\ \text{h}$$

f. During the day we have:

$$k_9[\mathrm{OH}] = 1.6\cdot 10^{-4}\ \text{s}^{-1} > k_7[\mathrm{O_3}] = 6.7\cdot 10^{-5}\ \text{s}^{-1} > k_8[\mathrm{NO_3}]$$

During the night we have:

$$k_7[\mathrm{O_3}] = 6.7\cdot 10^{-5}\ \text{s}^{-1} > k_8[\mathrm{NO_3}] = 1.9\cdot 10^{-5}\ \text{s}^{-1} > k_9[\mathrm{OH}]$$

Thus, in this example OH is the main oxidation agent that oxidizes α-pinene during the day and O_3 is the main oxidation agent that oxidizes α-pinene during the night.