

# Atmospheric Chemistry and Physics

## Calculation Exercises

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*Note that approximately 40% of the written exam deals with calculations. The remainder is about understanding of the theory.*

**Exercises marked with an asterisk (\*) are for the most interested students. These exercises are more comprehensive and/or difficult than questions appearing in the written exam.**

## Atmospheric Chemistry and Physics – Exercise A, chap. 1 – 3

**Recommended activity before exercise:** Try to solve 1:1 – 1:5, 2:1 – 2:2 and 3:1 – 3:2.

Summary:

Concentration	Example	Advantage
<b>Number density</b>	No. molecules/m <sup>3</sup> , kmol/m <sup>3</sup>	Useful for calculations of reaction rates in the gas phase
<b>Partial pressure</b>		Useful measure on the amount of a substance that easily can be converted to mixing ratio
<b>Mixing ratio</b>	<b>ppmv</b> can mean e.g. mole/mole or partial pressure/total pressure	Concentration relative to the concentration of air molecules. Very useful because air is compressible.

Ideal gas law:  $PV = nRT$   
 Molar mass:  $M = m/n$   
 Density:  $\rho = m/V = PM/RT$ ; (from the two equations above)  
 Mixing ratio (vol):  $C_x = n_x/n_a = P_x/P_a \neq m_x/m_a$   
 Number density:  $C_{vol} = nN_{av}/V$   
 Avogadro's number:  $N_{av} = 6,023 \cdot 10^{26} \text{ kmol}^{-1}$   
 Gas constant:  $R = 8314.3 \text{ J/(kmol K)}$

Relative humidity:  $RH = 100P_{H_2O}/P_{SAT} (\%)$   
 Saturation vapour pressure [*Mättnadsångtryck*]:  $p_{SAT}$  can be obtained from tables over vapour pressure or diagram (strongly dependent on temperature)

Barometric law:  $P = P_0 \exp(-z/H)$   
 Scale height:  $H = RT/M_a g$   
 Relation between pressure and mass:  $PA = mg$ ; (pressure x surface area = (mass of the air column) x gravitation)

**Mass balance equation:**  $dm/dt = F_{in} - F_{out} + E - D + P - L$

Box model: Fixed, well mixed box  
 Two-box model: Two boxes with exchange in both directions  
 Puff model: The model travels with the air parcel  $\Rightarrow F_{in} = F_{out} = 0$

*Important concepts:*

First order process: the sinks proportional to the concentration  
 Steady state [*stationärt tillstånd*]:  $dm/dt = 0$   
 Quasi steady state: = dynamic equilibrium  $\Rightarrow$  concentration changes slowly compared with production and loss rates  $\Rightarrow dm/dt \approx 0$

Residence time:  $\tau = m/(F_{out} + D + L)$   
 Loss rate constant:  $k = 1/\tau = F_{out}/m + D/m + L/m$   
 $F_{out} + D + L = (k_{out} + k_d + k_c)m$  (first order process)

## Exercises, chapter 1

1:1) The dry atmosphere consists mainly of nitrogen ( $N_2$ : 0.78 mol/mol), oxygen ( $O_2$ : 0.21 mol/mol) and argon (Ar: 0.01 mol/mol). Calculate the average molar mass of the dry atmosphere. (Molar masses of N, O and Ar are 14.007, 15.999 and 39.948 kg/kmol)

1:2) Calculate the density of a dry air mass of temperature 253 K and pressure 300 hPa.

1:3) a: Which is the saturation vapour pressure [*mättnadsångtryck*] for water vapour at  $+10^\circ\text{C}$ ?

b: An air mass of temperature  $+10^\circ\text{C}$  and pressure 101300 Pa contains 0.01 mol/mol water vapour. Calculate the relative humidity. (Use the printed answer to 1:3a for this calculation.)

1:4) Assume that an air mass at the tropopause ( $P = 250\text{ hPa}$ ,  $T = -40^\circ\text{C}$ ) has the volume  $1\text{ m}^3$ . If we move this air mass to ground level ( $P = 984\text{ hPa}$ ;  $T = +18^\circ\text{C}$ ), which volume would it require?

1:5) Calculate the number density of  $\text{CO}_2$  (365 ppmv) in the atmosphere at ground level ( $P = 984\text{ hPa}$ ,  $T = +18^\circ\text{C}$ ).

1:6) Fig. 1-1 shows the typical vertical profile of ozone ( $\text{O}_3$ ). Ozone is formed in the stratosphere by photolysis of  $\text{O}_2$ , which is important for our protection from harmful UV radiation. Ozone is harmful for humans and vegetation, and an air quality standard [*gränsvärde*] is needed. At present surface air concentration of  $\text{O}_3$  may not exceed 80 ppbv in the USA.

a: Calculate the mixing ratio of ozone at the maximum of the curve ( $z = 25\text{ km}$ ), where the pressure and temperature are 35 hPa and 220 K. Compare with the air quality standard for surface air!

b: Calculate the mixing ratio of ozone in surface air ( $z = 0\text{ km}$ ,  $P = 1000\text{ hPa}$ ,  $T = 290\text{ K}$ ). Compare with the air quality standard!

c: Why is the ratio between the concentrations at 0 and 25 km altitude larger expressed in mixing ratio than in number density (like in fig. 1-1)?

d: The  $\text{O}_3$  column expresses the total number of ozone molecules per surface area and determines the efficiency of the air in filtering UV radiation. Estimate the  $\text{O}_3$  column by approximating

the  $\text{O}_3$  profile with the triangle according to fig. 1-1!

e: To illustrate how thin this stratospheric  $\text{O}_3$  layer actually is, imagine that all of the  $\text{O}_3$  in the atmospheric column were brought down to sea level as a layer of pure  $\text{O}_3$  gas ( $P = 1000\text{ hPa}$ ,  $T = 290\text{ K}$ ). Calculate the thickness of this layer.

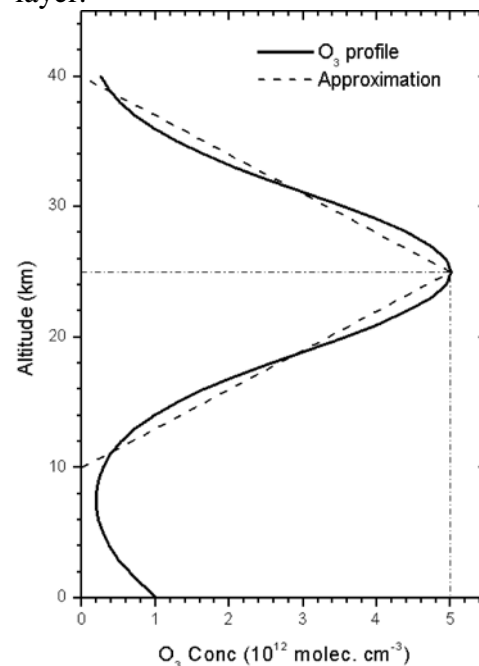


Figure 1-1.

## Exercises, chapter 2

2:1) Calculate the mass of the earth's atmosphere. The average pressure at the surface is 984 hPa and the radius of the earth is 6370 km.

2:2) The atmosphere contains 0.0093 mol/mol of argon. Calculate the total mass of argon in the atmosphere.

2:3) Calculate the altitude of the middle of the atmosphere with respect to mass, assuming constant temperature ( $T = 260 \text{ K}$ ).

2:4) Calculate the altitude of the middle of the atmosphere with respect to volume.

## Exercises, chapter 3

3:1) A chemical compound is removed from the atmosphere by deposition (0.2 %/day) and chemical transformation (1.2 %/day). Calculate the residence time in the atmosphere with respect to a: deposition, b: transformation and c: total residence time.

3:2) A power plant emits a chemical compound with the rate  $E$  (kg/s) starting at time 0 ( $m(0) = 0$ ). The compound is removed from the atmosphere by first order processes with the loss rate constant  $k$  ( $\text{s}^{-1}$ ).

a: Deduce an expression for the mass of the compound as a function of time.

b: Which is the steady state [*stationärt tillstånd*] mass of the compound?

3:3) A village emits ( $E$ )  $2 \mu\text{g}/(\text{m}^2 \text{ s})$  of the chemical compound X. The wind speed ( $w$ ) is 2 m/s and the compound is mixed up to 500 m altitude ( $h$ ) in the atmosphere. The village extends 1000 m in the wind direction ( $r$ ). Calculate the concentration in the air ( $C_{\text{vol}}$ ) after the passage of the village. The concentration before the air reached the village was  $0.1 \mu\text{g}/\text{m}^3$ . (Assume  $P = L = D = 0$ .)

\*3:4) The rate of exchange of air between the troposphere and the stratosphere is critical for determining the potential of various pollutants emitted from the surface to reach the stratosphere and affect the stratospheric ozone layer. One of the first estimates of this rate was made in the early 1960s using measurements of strontium-90 ( $^{90}\text{Sr}$ ) in the stratosphere. Strontium-90 is a radioactive isotope (half-life 28 years) produced in nuclear explosions. It has no natural sources. Large amounts of  $^{90}\text{Sr}$  were injected into the stratosphere in the 1950s by above-ground nuclear tests. These tests were banned in international treaty in 1962. Following the test ban the stratospheric concentrations of  $^{90}\text{Sr}$  began to decrease as the  $^{90}\text{Sr}$  was transferred to the troposphere. In the troposphere,  $^{90}\text{Sr}$  is removed by wet deposition with a residence time of 10 days (by contrast there is no rain, and hence no wet deposition, in the stratosphere). An intensive stratospheric measurement network was operated in the 1960s to monitor the decay of  $^{90}\text{Sr}$  in the stratosphere. We interpret these observations here using a two-box model for stratosphere-troposphere exchange with transfer rate constants  $k_{\text{TS}}$  and  $k_{\text{ST}}$  ( $\text{yr}^{-1}$ ) between the

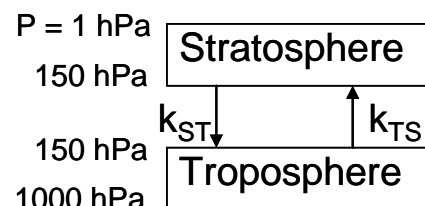


Figure 3-1. Two-box model of stratosphere-troposphere exchange.

tropospheric and stratospheric reservoirs. The reservoirs are assumed to be individually well mixed (Figure 3-1).

Let  $m_S$  and  $m_T$  represent the masses of  $^{90}\text{Sr}$  in the stratosphere and the troposphere respectively. Observations of the decrease in the stratospheric inventory for the period 1963 – 1967 can be fitted to an exponential  $m_S(t) = m_S(0) e^{-kt}$  where  $k = 0.77 \text{ yr}^{-1}$ .

- a: Write the mass balance equation for  $m_S$  and  $m_T$  in the 1963 – 1967 period.
- b: Assuming that the transfer of  $^{90}\text{Sr}$  from the troposphere to the stratosphere is negligible (we will verify this assumption later), show that the residence time of air in the stratosphere is  $\tau_S = 1/k_{ST} = 1.3$  years.
- c: Let  $m'_S$  and  $m'_T$  represent the total masses of air in the stratosphere and the troposphere, respectively. Show that the residence time of air in the troposphere is  $\tau_T = \tau_S(m'_T/m'_S) = 7.4$  years.
- d: Conclude to the validity of your assumption in question b.
- e: CFCs were banned by the Montreal protocol because of their harmful effect on the stratospheric ozone layer. HCFCs are used as replacement products. In contrast to CFCs, the HCFCs can be oxidised in the troposphere, and the oxidation products washed out by precipitation, so that most of the HCFCs do not penetrate into the stratosphere to destroy ozone. Two common HCFCs have trade names HCFC-123 and HCFC-124. Their life-time against oxidation in the troposphere is 1.4 and 5.9 years, respectively. There are no other sinks of these species in the troposphere. Using our two-box model, determine what fraction of the emitted HCFC-123 and HCFC-124 penetrate into the stratosphere.

3:5) The 1987 Montreal protocol was the first international agreement to control emissions of chlorofluorocarbons (CFCs) harmful to the ozone layer. It was subsequently amended (London 1990, Copenhagen 1992) to respond to the increased urgency created by the discovery of the Antarctic ozone hole. In this problem we compare the effectiveness of the original and amended protocols. We focus on CFC-12, which has an atmospheric lifetime of 100 years against loss by photolysis in the stratosphere. We start our analysis in 1989 when the Montreal protocol entered into force. In 1989 the mass of CFC-12 in the atmosphere was  $m = 1.0 \times 10^{10}$  kg and the emission rate was  $E = 4 \times 10^8$  kg/yr.

- a: The initial Montreal protocol called for a 50% reduction of CFC emissions by 1999 and a stabilization of emissions henceforth. Consider a future scenario where CFC-12 emissions are held constant at 50% of the 1989 values. Show that the mass of CFC-12 in the atmosphere would eventually approach a steady state value  $m = 2 \times 10^{10}$  kg, higher than the 1989 value. Explain briefly why the CFC-12 abundance would increase even though its emission decreases.
- b: The subsequent amendments to the Montreal protocol banned CFC production completely as of 1996. Consider a scenario where CFC-12 emissions are held constant from 1989 to 1996 and then drop to zero as of 1996. Calculate the masses of CFC-12 in the atmosphere in years 2050 and 2100. Compare with the 1989 value.

# Atmospheric Chemistry and Physics – Exercise B, chap. 4 and 6

**Recommended activity before exercise:** Try to solve 4:1 – 4:3 and 6:1 – 6:2.

*Summary:*

Buoyant acceleration:  $\gamma_b = (\rho' - \rho)g/\rho = (T - T')g/T'$ ; causes vertical transport  
Dry adiabatic lapse rate: [torradiabatisk temperaturprofil]  $\Gamma = -dT/dz = g/C_p = 9,8 \text{ K/km}$   
Wet adiabatic lapse rate: [fuktadiabatisk temperaturprofil]  $\Gamma_w = 2 - 7 \text{ K/km}$  (due to heat of condensation by clouds)

Atmospheric stability:

Unstable: -  $dT/dz > \Gamma$ ; (Unusual. Strong turbulence makes atmosphere neutral)  
Neutral: -  $dT/dz = \Gamma$ ; (Common due the fate of unstable air; characterized by strong vertical motions.)  
Stable conditional:  $\Gamma > -dT/dz > 2 \text{ K/km}$ ; (Can be unstable due to cloud formation)  
Stable: -  $dT/dz < 2 \text{ K/km}$   
Stable, inversion: -  $dT/dz < 0$  (Temperature increase with altitude. Very stable.)

Planetary boundary layer [Gränsskiktet] A layer from the ground up to 2 – 3 km altitude. Often topped by a small inversion caused by subsidence [nervindar] in anti-cyclonic [högtryck] systems and precipitation history of the air mass.

Mixed layer [Blandningsskiktet] Part of the planetary boundary layer in contact with the ground. The height of the mixed layer varies over the day and the layer is characterized by strong turbulence.

Mass balance equation (Chap. 3)

Definition of residence time (Chap. 3)

Loss rate constant (Chap. 3)

Henry's law: Equilibrium gas – dissolution in liquid,  $K_H$ . Unit: M/atm

Dissociation: Equilibrium in liquid described by equilibrium constant  $k_i$ . Unit: M

Geochemical cycle: [Kretslopp] Reservoirs containing mass (inventory) and mass flows between the reservoirs. Useful technique when evaluating geochemical cycles: Summing of reservoirs, i.e. sum inventories of reservoirs to a new large reservoir and sum the flows to/from external reservoirs exchanging with the new large reservoir.

## Exercises, chapter 4

4:1) Atmospheric stability with respect to vertical air motions strongly depends on the temperature gradient of the atmosphere. Due to the weight of the atmosphere, the pressure decreases with altitude. As a consequence, air expands when moving upwards. This expansion is approximately adiabatic, and causes cooling of the upward moving air mass by 9.8 K/km (dry adiabatic lapse rate). An air mass moving downwards is compressed and is therefore heated at the same rate, i.e. 9.8 K/km. Expansion and compression rapidly adjusts the pressure of a vertically moving air mass to the surrounding air pressure. Temperature exchange is much slower. The density of air is dependent on the temperature. Depending on the atmospheric lapse rate a vertically moving air mass can either obtain higher, equal or lower density than the surrounding air at the same altitude. The outcome depends on the atmospheric lapse rate. When the atmospheric temperature decreases slower with altitude than the adiabatic lapse rate, the surrounding air will be warmer than an air mass that has moved upwards. The moving air mass thus will have a higher density and the gravity will bring it back towards its original altitude, i.e. the atmospheric lapse rate in this case counteracts vertical motion. In the same way, when we have motion downwards the air mass becomes warmer than the surrounding air. The density is lower and hence the air mass is brought back towards its original position. To conclude, *vertical motions are counteracted by atmospheric temperature decreases with altitude that are smaller than the adiabatic lapse rate. When the atmospheric temperature decrease with altitude is larger than or equal to the adiabatic lapse rate, the counteraction against vertical motions from gravity disappears.*

With this background, examine the temperature profiles A – D in Figure 4-1 and conclude to which of the smoke plumes 1 to 4 that appeared in the four profiles. Assume that the smoke has the same temperature as the surrounding air when it enters the atmosphere.

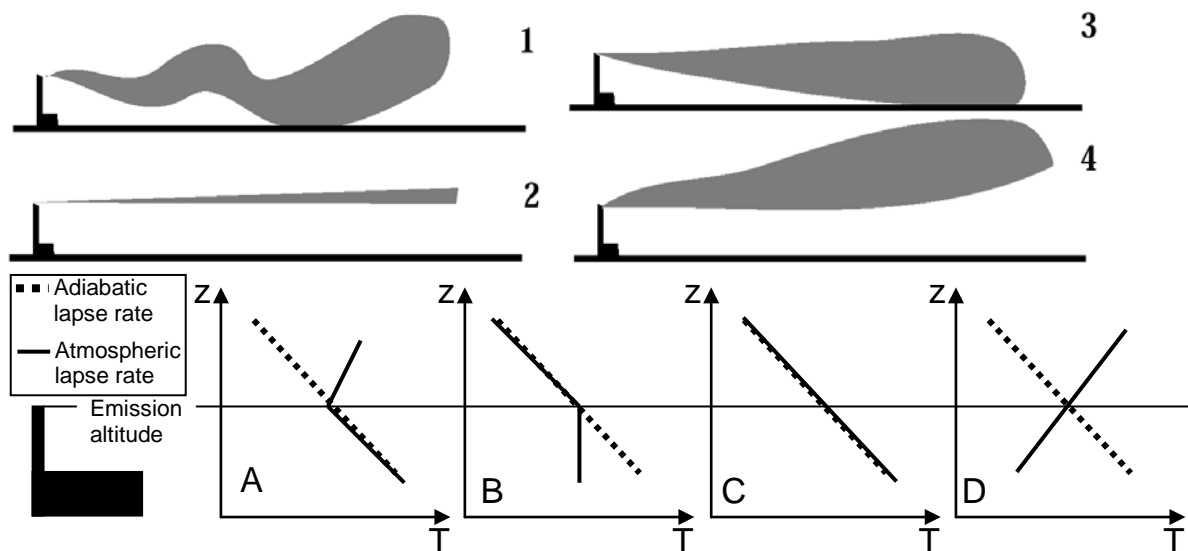


Figure 4-1.

4:2) In an atmospheric layer in contact with the ground and of 1 km height, the temperature *decreases* by 12 K/km. The temperature is independent of altitude above that layer. To which altitude can an air mass be lifted if it starts from the ground? Assume that the air is dry during the ascent.

4:3) In an atmospheric layer in contact with the ground and of 1 km height, the temperature *increases* by 12 K/km. The temperature is independent of altitude above that layer. To which altitude can an air mass be lifted if it starts from the ground? Assume that the air is dry during the ascent.

4:4) Figure 4-2 shows a simplified model over the variation of the planetary boundary layer (PBL) [*gränsskiktet*] during day and night, where the boundary layer is divided into two parts. In contact with the ground we have the mixed layer [*blandnings-skiktet*] and the remainder of the boundary layer is the remnant PBL. The two layers are separated by an inversion. The right part of Figure 4-2 shows the atmospheric temperature profile at noon, according to the model. Assume that the two layers are well mixed and that no exchange takes place across the inversions.

a: Provide a brief justification for this model, and for the diurnal variation in the sizes of the two domains. Why is there a mixed layer during night? (*Hint*: buoyancy is not the only source of vertical turbulent mixing.)

b: Consider an inert pollutant X emitted from the surface with a constant emission flux E (kg/s) beginning at t = 0 (midnight). Plot the change in the concentration of X from t = 0 to t = 24 hours in the mixed layer and in the remnant PBL, starting from zero concentrations at t = 0 in both domains.

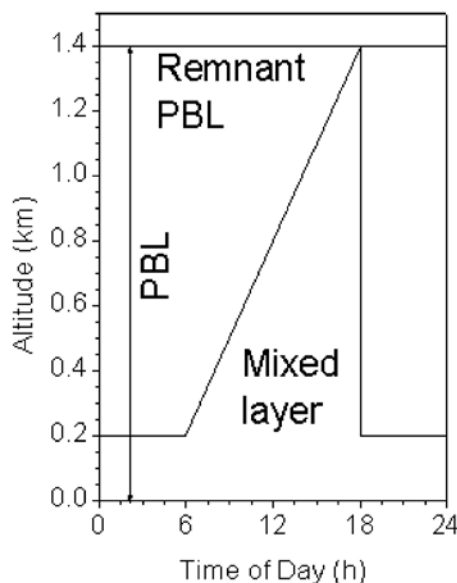


Figure 4-2.

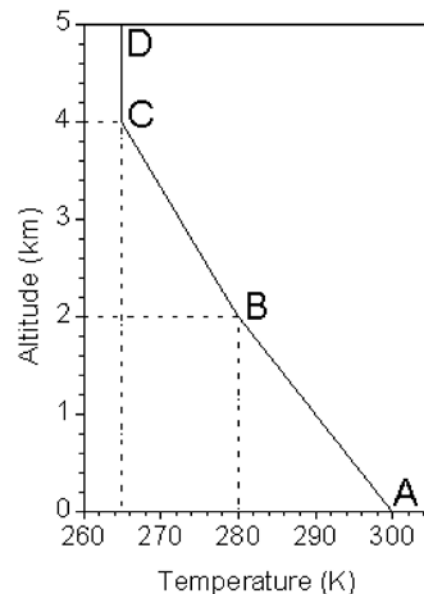


Figure 4-3.

4:5) Consider the vertical temperature profile shown in Figure 4-3.

a: Classify sections AB, BC and CD with respect to stability.

b: Consider an air parcel rising from A to B and forming a cloud at B. Assume that the wet adiabatic lapse rate in the cloud is  $\Gamma_w = 6$  K/km. To which altitude can the air parcel rise before it becomes stable relative to the surrounding atmosphere?

c: Conclude as to the effect of cloud formation for the ventilation of pollution released at the surface.



## Exercises, chapter 6

6:1) Figure 6-1 shows the trend in atmospheric CO<sub>2</sub> concentration from 1958 at the Mauna Loa observatory. Assume that this trend is valid over the entire earth.

a: Calculate the average rate of increase during 1983 to 1993 expressed in Pg C/year.

b: Is it reasonable to assume that the measurements in Figure 6-1 are representative of the entire earth?

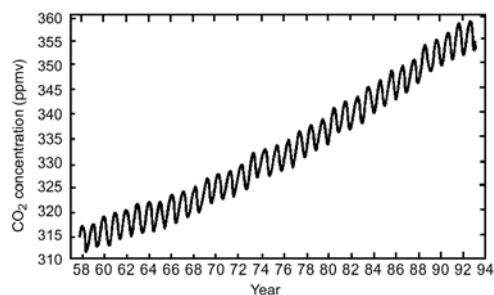


Figure 6-1.

6:2) Figure 6-2 shows the oceanic circulation in a box model. The inventories are given as 10<sup>15</sup> m<sup>3</sup> and the flows as 10<sup>15</sup> m<sup>3</sup>/year. Calculate the residence time of water in the warm and cold surface reservoirs.

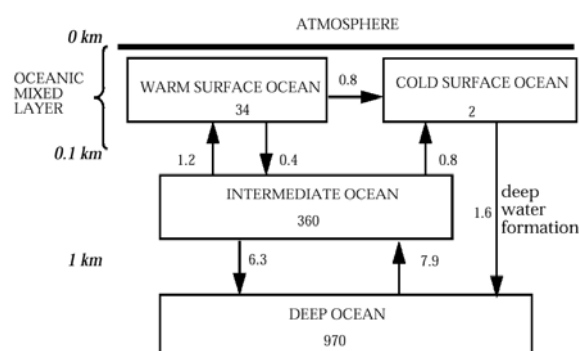
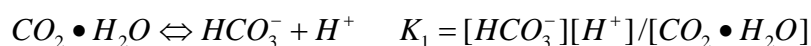


Figure 6-2.

6:3) The use of fossil fuels for transportation and energy production has significantly increased the atmospheric concentration of the greenhouse gas CO<sub>2</sub>. The ocean is an important sink for CO<sub>2</sub>. The equilibrium between atmosphere and ocean is described by:



a: Calculate the concentration in the oceans of dissolved CO<sub>2</sub>, i.e. the sum of carbonic acid [*kolsyra*], bi-carbonate [*vätekarbonat*] and carbonate ions, assuming that the atmosphere is at equilibrium with the entire oceans.

b: Calculate the fraction of CO<sub>2</sub> in the atmosphere, assuming that the atmosphere is at equilibrium with the entire oceans. Hint: Use the total number of moles of CO<sub>2</sub> in the atmosphere and dissolved in the oceans for the calculations.

c: The result obtained in (b) is an incorrect description of the oceanic uptake of CO<sub>2</sub> from fossil fuels. One reason is that the assumption of equilibrium with the entire oceans overestimates the uptake. There is also another important effect that was not accounted for in the calculations. Which effect was omitted?

*Useful constants:*  $K_H = 0.03 \text{ M/atm}$ ,  $K_1 = 9 \times 10^{-7} \text{ M}$ ,  $K_2 = 7 \times 10^{-10} \text{ M}$ ,

*Ocean volume:*  $1.4 \times 10^{18} \text{ m}^3$ , *Ocean pH:* 8.2 ( $[\text{H}^+] = 6.3 \times 10^{-9} \text{ M}$ ),

*Partial pressure of CO<sub>2</sub> at sea level:*  $3.6 \times 10^{-4} \text{ atm}$

6:4) Figure 6-3 shows the part of the geochemical cycle of carbon dealing with vegetation (units Pg C and Pg C/year). The three reservoirs “ground vegetation”, “tree leaves” and “tree wood” represent collectively the “terrestrial vegetation reservoir”. The flow rate of atmospheric CO<sub>2</sub> into this terrestrial vegetation reservoir represents the net primary productivity (NPP) of the terrestrial biosphere.

a: Calculate the residence time of carbon in the terrestrial vegetation reservoir against transfer to the litter and soil.

b: Tree leaves eventually fall to produce litter. What is the dominant fate of carbon in the litter? What fraction is incorporated into the soil?

c: Acid rain causes a decrease of microbial activity in the litter and in the soil. How is atmospheric CO<sub>2</sub> affected by acidification?

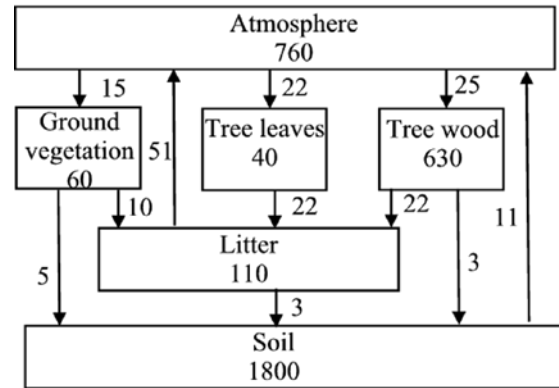


Figure 6-3.

\*6:5) High-precision measurements of the long-term trend in the O<sub>2</sub> concentration show a decrease of 8.9 ppmv during the three years 1991 – 1994. We will use this result in this exercise to estimate the sinks of CO<sub>2</sub> from fossil fuels. We start by examining the stoichiometric relations in terms of O<sub>2</sub>:CO<sub>2</sub> of sources and sinks.

a: The composition of fossil fuel is on average CH<sub>1.6</sub>. The combustion process consumes O<sub>2</sub> and forms CO<sub>2</sub> and H<sub>2</sub>O. How many moles of O<sub>2</sub> are consumed for each mole of CO<sub>2</sub> produced?

b: How many moles of O<sub>2</sub> are produced per mole CO<sub>2</sub> taken up by the biosphere?

c: Does dissolution of CO<sub>2</sub> in the oceans produce or consume O<sub>2</sub>?

Make use of these stoichiometric relations and the measured change of the O<sub>2</sub> concentration together with the facts that the CO<sub>2</sub> concentration in atmosphere increased by 3.2 ppmv during years 1991 – 1994 (3 years) and the global combustion of fossil fuels (P<sub>C</sub>) was 6.3x10<sup>12</sup> kg C/year, to calculate:

d: Consider a scenario where none of the sinks affect the atmospheric concentrations of O<sub>2</sub> and CO<sub>2</sub>. How much would the concentration these gases change due to fossil fuel combustion 1991 – 1994?

e: Estimate the fraction of the CO<sub>2</sub> emissions accumulated in the atmosphere and the fractions that are taken up by the biosphere and the oceans.

# Atmospheric Chemistry and Physics – Exercise C, chap. 7 – 8

(+ lecture notes on aerosols&clouds and booklets by Heintzenberg and by Martinsson)

**Recommended activity before exercise:** Try to solve 7:1 – 7:2 and 8:1 – 8:3.

Total radiation flux from a blackbody:	$\Phi = \sigma T^4$ ; $\sigma = 5.67 \times 10^{-8} \text{ W}/(\text{m}^2 \text{ K}^4)$
Planck's law:	$d\Phi/d\lambda = 2\pi hc^2/[\lambda^5(\exp(hc/kT\lambda) - 1)]$
Kirchhoff's radiation law:	An object absorbing fraction $\varepsilon$ [0 – 1] at wavelength $\lambda \Rightarrow$ emission of the same fraction of the blackbody radiation at that wavelength and object temperature
Solar constant:	$F_S = \sigma T^4 R^2/d^2 = 1370 \text{ W}/\text{m}^2$
Planetary albedo:	Fraction of the incoming solar radiation that is reflected back to space. The earth: $A = 0.28$ .
Absorbed flux:	$\Phi = F_S(1 - A)/4$
Radiation balance:	The radiation out from earth equals the incoming solar radiation.
Effective temperature:	$\sigma T_E^4 = F_S(1 - A)/4$ ; $T_E = -18^\circ \text{ C}$
Simple radiation model:	The atmosphere is approximated by a thin, isothermal layer that is transparent for solar radiation and absorbs fraction $f$ of the terrestrial radiation.
Radiative forcing	
[“Strålningsstörning”]:	$\Delta F = F_{\text{out, equilibrium}} - F_{\text{out, perturbed}}$
Climate sensitivity param.:	$\Delta T_j = \lambda \Delta F$ ; Without feedbacks: $\lambda = 1/[4(1 - 1/2f)\sigma T_j^3]$
Aerosol:	Definition, upper and lower size limit of aerosol particles, size modes, sources of aerosol particles and typical size distribution, primary and secondary particles, aerosol deposition, global distribution over the earth, typical number and mass concentrations over the oceans and in the urban environments
Relative humidity:	$RH = 100 p/p_0$ ;
Kelvin effect:	Increase of vapour pressure at droplet surface due to curvature
Vapour pressure depression [ångtryckssänkning]:	Raoult's law
Köhler equation:	Describes the equilibrium size of a droplet and the limit between condensation and evaporation as a function of RH; $p/p_0 = (\text{vapour pressure depression}) \times (\text{Kelvin effect})$
Critical supersaturation:	The supersaturation required for a droplet to activate and form a cloud droplet. The critical supersaturation depends strongly on the amount of soluble matter in the droplet.
Cloud condensation nuclei:	Clouds form in supersaturation by condensation of water vapour on aerosol particles, which acts as cloud condensation nuclei (CCN).
Direct effect:	Aerosol particles efficiently scatter solar radiation. A fraction is scattered back to space thus increasing the albedo. This is called the direct effect of aerosol particles.
Indirect effect:	Increased concentration of aerosol particles increases the number of CCN and hence the cloud droplet number concentration, increasing the reflectivity of the cloud and possibly the cloud lifetime. (Increased cloud albedo)

## Exercises, chapter 7

7:1) The sun with radius  $6.96 \times 10^8$  m emits like a blackbody with the temperature 5780 K.

a: Calculate the total power [*effekt*] emitted by the sun.

b: Calculate the solar radiation flux (power per surface area) at the earth. The earth is at the distance (d) of  $1.496 \times 10^{11}$  m from the sun.

c: Calculate the solar radiation flux averaged over the surface area of the earth.

7:2) a: What is meant by the planetary albedo?

b: The planet H has on average  $8 \times 10^7$  km distance to the sun and the planetary albedo is 0.85. The same quantities of the earth are  $1.5 \times 10^8$  km and  $A = 0.28$ . The solar constant at the earth is  $1370 \text{ W/m}^2$ . Calculate the effective temperature of the two planets.

c: Based on the given properties of the two planets, can anything be concluded on the surface temperature of planet H in comparison with the earth? Explain!

7:3) A simple greenhouse model approximates the atmosphere with a thin, isothermal layer that is transparent to solar radiation and absorbs a fraction f of the terrestrial radiation.

a: Make sketch of the simple model.

b: Calculate the temperature at the earth's surface and the isothermal atmosphere, assuming that  $f = 0.77$  and the planetary albedo  $A = 0.28$ .

c: The unperturbed atmosphere of planet H, having the properties described in exercise 7:2b, absorbs 40% of the long wave radiation. Calculate the change of temperature at the surface of planet H induced by the greenhouse effect.

d: The earth's atmospheric concentration of greenhouse gases like  $\text{CO}_2$  has changed due to emissions. Calculate the radiative forcing caused by these emissions which increased the atmospheric absorption to  $f' = 0.78$ . Use the results in exercise (b) as the reference scenario.

e: Calculate the temperature change induced by the radiative forcing according to exercise (d), assuming that no feedbacks affect the temperature. The climate sensitivity parameter is given by  $\lambda = 1/[4(1 - \frac{1}{2}f)\sigma T_j^3]$ .

7:4) In a technical report from the climate panel of UN (IPCC) the following relations between changed concentration of greenhouse gases and radiative forcing are given:

$$\text{CO}_2: \Delta F = \frac{4,37}{\ln 2} \ln \frac{C(t)}{C_0}$$

$$\text{CH}_4: \Delta F = 0.036(\sqrt{C(t)} - \sqrt{C_0})$$

$$\text{N}_2\text{O}: \Delta F = 0.14(\sqrt{C(t)} - \sqrt{C_0})$$

where  $C(t)$  and  $C_0$  are the concentrations at time t and the reference scenario in ppbv. Radiative forcing  $\Delta F$  is given in  $\text{W/m}^2$ .

a: Calculate the present time radiative forcing of the three gases related to year

1750 (Fig. 7-1). Compare with Fig. 7-15 in the text book.

b: Assuming that there are no feedback mechanisms to a temperature change, how much would the temperature at ground change as the result of a doubling of the  $\text{CO}_2$  concentration?

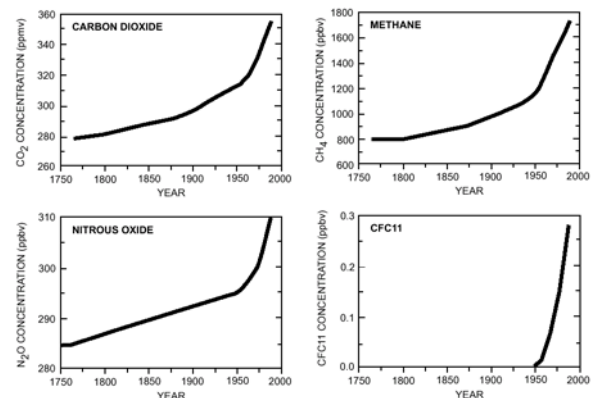


Figure 7-1.

7:5) Figure 7-2 shows terrestrial emission spectra (full line) measured from a satellite over northern Africa, the Mediterranean and Antarctica. The broken lines indicate the emission from blackbodies at different temperatures. The spectra are reported as a function of wave number [*vågta*], which is the inverse of the wavelength, the latter being shown at the upper X axis.

a: Why do the measured spectra differ in shape from blackbody radiation?

b: Estimate from the spectra the surface temperature of each region.

c: Why does the dip at 15  $\mu\text{m}$  wavelength become a bump in the emission spectrum for Antarctica?

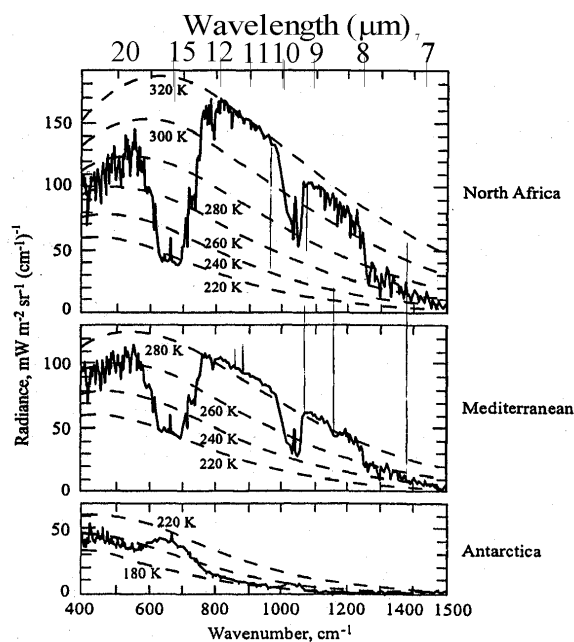


Figure 7-2.

7:6) Sedimentary deposits in rocks show that liquid water was present on earth as early as 3.8 billion [*miljarder*] years ago, when solar radiation was 25% less than today according to current models of the evolution of the sun. Consider the simple greenhouse model where the atmosphere is represented as a thin layer transparent to solar radiation and absorbing a fraction  $f$  of the terrestrial radiation. Assume throughout this problem a constant planetary albedo  $A = 0.28$  for the earth.

a: If the greenhouse effect 3.8 billion years ago were the same as today ( $f = 0.77$ ), what would be the surface temperature of the earth? Would liquid water be present?

b: Current thinking is that a stronger greenhouse effect offset the weaker sun. Let us try to simulate this stronger greenhouse effect by keeping our one-layer model for the atmosphere but assuming that the atmospheric layer absorbs 100% of terrestrial radiation. Calculate the resulting surface temperature. What do you conclude?

c: We can modify our model to produce a warmer surface temperature by representing the atmosphere as two superimposed layers ( $a_1$  and  $a_2$ ), both transparent to solar radiation and both absorbing 100% of terrestrial radiation. Provide a physical justification for this two-layer model. Calculate the resulting surface temperature.

d: It has been proposed that the strong greenhouse effect in the early earth could have resulted from accumulation in the atmosphere of  $\text{CO}_2$  emitted by volcanoes. Imagine an earth initially covered by ice. Explain why volcanic  $\text{CO}_2$  would accumulate in the atmosphere under such conditions, eventually thawing the earth.

### Exercises, chapter 8 + lecture notes on aerosols and booklet by Heintzenberg

8:1) Visibility [*siktbarhet*].

a: Looking to the southwest from a high position in Lund you sometimes can see Lomma clearly and other days it can disappear in haze. Which are the most important causes of the varying visibility? Explain!

b: Calculate the mass of a 1  $\text{m}^2$  cross-section tube of air from Lund to Lomma (distance 9 km). The pressure and temperature are 984 hPa and 290 K. Compare with the

mass of a vertical column of air through the entire atmosphere of cross-section  $1 \text{ m}^2$ . What do you conclude (qualitatively) on the potential of aerosol particles to disturb the climate?

c: The optical depth is on average 0.25 between  $30$  to  $60^\circ$  latitude in the northern hemisphere. The backscattered fraction is 0.2, resulting in the albedo of the aerosol layer  $A_a = 0.25 \times 0.2 = 0.05$ . Calculate the radiative forcing (with sign) induced by the aerosol layer in the latitude interval given. The solar constant is  $1370 \text{ W/m}^2$  and the earth's albedo  $A_0 = 0.28$ . *Hint:* The total albedo can be obtained from  $A_T \approx A_0 + A_a(1-A_0)^2$ .

8:2) Water uptake by aerosol particles.

a: A pure water droplet of diameter  $D = 0.01 \text{ }\mu\text{m}$  is situated in air with relative humidity of 103% ( $\text{RH} = 100 \text{ p/p}_0$ ). The temperature is  $20^\circ \text{ C}$ . Will the droplet grow, remain unchanged or evaporate? Explain your answer. *Hint:* The fate of pure droplets is determined by the Kelvin effect. The surface tension of water is  $0.073 \text{ N/m}$ .

b: Figure 8-1 shows the saturation ratio as a function of droplet diameter for droplets that have formed on a particle of given size and chemical composition. The Figure includes five points (A, B, C, D, E) indicating droplets formed on the same kind of particle. Assume that the saturation ratio remains constant for a long time. How large are droplets A, B, C, D and E after this time has passed?

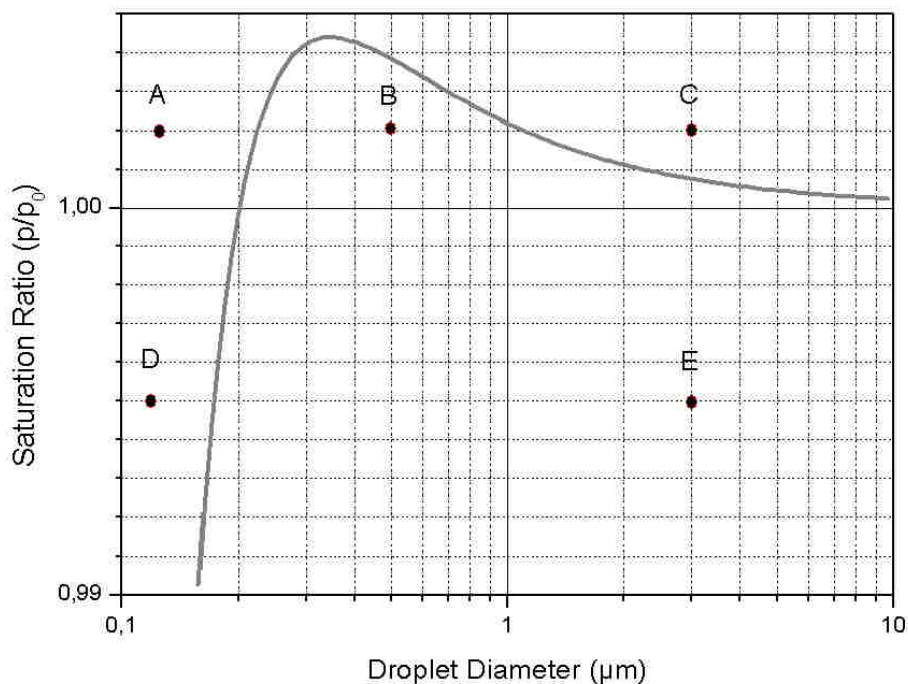


Figure 8-1.

8:3) A given droplet has curvature that induces increase of the vapour pressure at the droplet surface by 0.4%. Salt dissolved in the droplet cause a vapour pressure depression by 1.2%. Will the droplet size increase or decrease when the relative humidity is 99%?

\*8:4) The radioactive isotope  $^{210}\text{Pb}$  is formed from decay of  $^{222}\text{Rn}$ , and condenses immediately on existing aerosol particles.  $^{222}\text{Rn}$  is emitted from the ground in land areas with the flux ( $e$ ) of  $1.0 \text{ atoms}/(\text{cm}^2\text{s})$ , whereas the emissions from the sea are zero. Land covers 30% ( $f_A$ ) of the earth's surface. The radioactive decay forming  $^{210}\text{Pb}$  is the only sink of  $^{222}\text{Rn}$

(half-life 3.8 days).  $^{210}\text{Pb}$  is removed from the atmosphere by radioactive decay (half-life 23 years) and aerosol deposition. The total mass of  $^{210}\text{Pb}$  in the troposphere is 380 g.

a: Calculate the residence time with respect to deposition of  $^{210}\text{Pb}$ -containing aerosol particles in the troposphere. Assume steady state.

b: Interpret the results of exercise (a) in terms of temporal and geographical variation in the concentration of aerosol particles in the troposphere.

8:5) The total albedo of two overlaid albedo layers can be obtained from:

$$A_T = A_M + A_0(1 - A_M)^2 + A_0^2 A_M (1 - A_M)^2 + \sum_{n=2}^{\infty} A_0^{n+1} A_M^n (1 - A_M)^2 \quad (1)$$

where  $A_T$  is the total albedo and  $A_M$  and  $A_0$  are the albedos of the upper and lower layer, respectively. Assume that the earth without clouds has the albedo  $A_0 = 0.13$  and that 30% of the earth is covered by clouds having the albedo  $A_M = 0.6$ .

a: Calculate the total planetary albedo  $A_T$ . (Truncate the calculations in eqn 1 at  $n = 2$ )

b: The radiative properties of clouds are affected by the droplet number concentration.

The change of the cloud albedo following a change in the droplet number concentration can be approximated:

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

where  $N$  is the number concentration of cloud droplets. Make the assumption that the number of cloud droplets increases globally by 40% as the result of increased emissions of aerosol particles. Calculate the radiative forcing induced by the changed droplet number concentration. Assume that the cloud cover of the earth remains unchanged (30%).

8:6) A typical particle size distribution of the atmospheric aerosol is shown by the full line in Figure 8-2. Usually the distribution can be described by four log-normal distributions, namely ultra-fine mode (A), Aitken mode (B), accumulation mode (C) and the coarse mode (D). These modes are the results of different sources contributing primary particles and by aerosol-dynamical processes ongoing in the atmosphere.

a: To which mode (A – D) do the following sources primarily contribute: sea-spray (1), formation of new particles in the atmosphere (2), windblown dust (3), combustion (4) and aged particles smaller than  $1 \mu\text{m}$  in diameter (5).

b: The bars in Figure 8-2 shows the number of particles in each mode (right Y axis: 200, 300, 100 and 0.005 particles per  $\text{cm}^3$ ) at the maximum of each mode ( $d_i = 0.008, 0.05, 0.15$  and  $5 \mu\text{m}$  diameter). Approximate the number distribution ( $C_{ai}$ )

by these discrete values and calculate mass concentration ( $C_{mi}$ ) of each mode assuming that the density of the particles is  $1.5 \text{ g/cm}^3$ .

c: Discuss the sources in exercise (a) with respect to their importance in terms of number concentration and mass of particulate matter in the atmosphere.

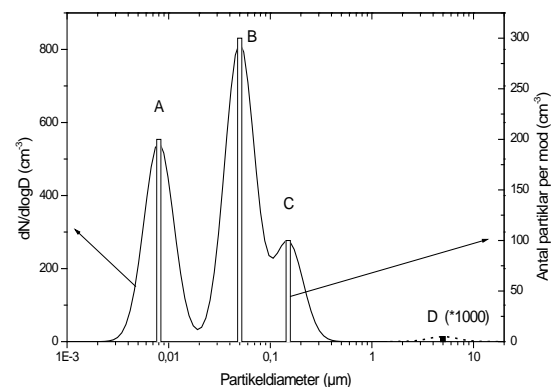


Figure 8-2 (Mode D multiplied by 1000)

## Atmospheric Chemistry and Physics – Exercise D, chap. 9

**Recommended activity before exercise:** Read and understand the tips given below. Try also to solve 9-1 and 9-3.

1. Be careful to distinguish between chemical equilibria (with equilibrium constants  $K$ ) and reactions that proceed primarily from reactants towards products (with reaction rate constants  $k$ ). Chemical equilibria are simply reversible chemical reactions that proceed with equal rates in both directions, that is  $A+B \rightarrow C+D$  and the reverse reaction  $C+D \rightarrow A+B$  have equal rates.

The reaction rate constant  $k$  multiplied with the concentrations of all reactants gives the reaction rate for the reaction in question:



$$(2) \quad \frac{d[C]}{dt} = \frac{d[D]}{dt} = -\frac{d[A]}{dt} = -\frac{d[B]}{dt} = k[A][B]$$

(production rate of C and D, loss rate for A and B).

The concentration of molecule X is denoted  $[X]$ , and is often expressed in units of molecules of X per  $\text{cm}^3$  of air in atmospheric chemistry. Note that one can not use the concentrations expressed as partial pressures (for instance in ppmv, ppbv) since the factor  $[A][B]$  should be proportional to the number of collisions between A and B per unit time. The derivative  $d[X]/dt$  can also be written  $\Delta[X]/\Delta t$  and denote how much of molecule X ( $\Delta[X]$ ) that is produced ( $\Delta X/\Delta t > 0$ ) or consumed ( $\Delta X/\Delta t < 0$ ) in each small time interval  $\Delta t$ . As  $\Delta t$  becomes infinitely small ( $\Delta t \rightarrow 0$ ) one should write the derivative  $dX/dt$  instead of  $\Delta X/\Delta t$ .

The equilibrium constant  $K$  is the ratio between the rate constants,  $k_1$  and  $k_2$  for a reversible equilibrium reaction:



$$(4) \quad \frac{dC}{dt} = k_1[A][B] \quad (\text{production rate of C and D})$$

$$(5) \quad \frac{dA}{dt} = k_2[C][D] \quad (\text{production rate of A and B})$$

At equilibrium  $\frac{dC}{dt} = -\frac{dA}{dt}$  and the equilibrium constant  $K$  is defined as;

$$(6) \quad K = k_1/k_2.$$

$K$  **can not** be calculated for an irreversible reaction, while  $k$  **can** be estimated for all reactions.

2. Note that the units for the various reaction rate constants may be different, and sometimes they may even summarize the rates of several reactions.

3. **Photolysis** reactions are extremely important in the atmosphere, since they mark the start of nearly all chemical activities in the atmosphere. The reaction rate constant for photolysis (photolysis rate constant) always has the unit  $\text{time}^{-1}$ , when the photolysis rate is integrated



over a certain wavelength interval (the wavelength-dependent photolysis rate constants are given in units of  $s^{-1}nm^{-1}$ , or similar).

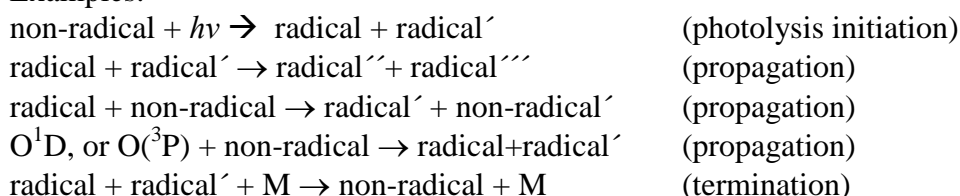
4. Make a habit of **identifying which molecules that are radicals**. Count electrons. An odd number of electrons reveals that the molecule has an unpaired electron and therefore is a radical.

Exception:  $O(^3P)$  has two unpaired electrons and is a biradical.  $O(^1D)$  has no unpaired electrons but is in a highly excited state, and is therefore, like a radical, very reactive. Ozone is no radical and is thus actually fairly stable.

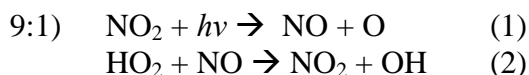
5. Learn to see which reactions that are **radical initiation** (most often via photolysis), **radical propagation**, and **termination**.

In a photolysis reaction, electron pairs are split and radicals are formed (**radical initiation**). In a **propagation** step, the radicals on the left side in the reaction (LS) must have the same number of unpaired electrons as on the right side (RS). In a **termination** step, two radicals on the LS form two non-radicals on the RS. The exceptions in this course are  $O(^3P)$  and  $O(^1D)$ .

Examples:



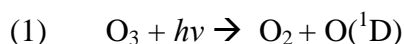
## Exercises, chapter 9



The reaction rate constants can be denoted as  $k_1$  (a photolysis reaction) and  $k_2$  respectively. Note that these are not equilibrium reactions. First consider reactions (1) and (2) separately. Write an expression for

- the production rate of NO in reaction (1) and the loss rate of NO in (2),
- the production rate of  $NO_2$  in reaction (2) and the loss rate of  $NO_2$  in (1).
- Then write expressions for the production rates of both NO and  $NO_2$  when both reactions (1) and (2) occur in the same air mass.

9:2) The reactions given below describe how methane ( $CH_4$ ) is oxidized in the troposphere to formaldehyde (HCHO). Apart from being the main sink for the greenhouse gas methane, this chain of reactions is also important for the production of ozone in the troposphere (ground-level ozone). Each reaction involves at least one radical. Name all radicals in these reactions. Which of the radical reactions are initiation steps, propagation steps, or termination steps? What are the termination products (the non-radicals that are formed in the termination reactions)? 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 ( $N_2$ ,  $O_2$  or Ar).



- (2)  $\text{O}(^1\text{D}) + \text{H}_2\text{O} \rightarrow 2\text{OH}$
- (3)  $\text{CH}_4 + \text{OH} \rightarrow \text{CH}_3 + \text{H}_2\text{O}$
- (4)  $\text{CH}_3 + \text{O}_2 + \text{M} \rightarrow \text{CH}_3\text{O}_2 + \text{M}$
- (5)  $\text{CH}_3\text{O}_2 + \text{NO} \rightarrow \text{CH}_3\text{O} + \text{NO}_2$
- (6)  $\text{CH}_3\text{O} + \text{O}_2 \rightarrow \text{HCHO} + \text{HO}_2$
- (7)  $\text{HO}_2 + \text{NO} \rightarrow \text{OH} + \text{NO}_2$
- (8)  $\text{NO}_2 + h\nu \rightarrow \text{NO} + \text{O}(^3\text{P})$
- (9)  $\text{O}(^3\text{P}) + \text{O}_2 + \text{M} \rightarrow \text{O}_3 + \text{M}$
- (10)  $2\text{HO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{O}_2$
- (11)  $\text{NO}_2 + \text{OH} + \text{M} \rightarrow \text{HNO}_3 + \text{M}$

9:3) The concentration of formaldehyde (HCHO) is  $1.2 \cdot 10^{11}$  molecules $\cdot\text{cm}^{-3}$  at the summer solstice, an altitude of 1 km and 40°N latitude. At this altitude, the incident light intensity is  $I=2.7 \cdot 10^{13}$  photons $\cdot\text{cm}^{-2}\cdot\text{s}^{-1}$  in the wavelength interval 295-305 nm. The HCHO photolysis cross section is  $\sigma=2.62 \cdot 10^{-20}$  cm<sup>2</sup> $\cdot\text{molecules}^{-1}$  at these conditions. The quantum yield  $q$  describes how many molecules that are photolyzed for each photon that interacts with a HCHO molecule. The unit for  $q$  can therefore be written as molecules $\cdot\text{photon}^{-1}$ , but since both "molecules" and "photon" denote numbers, the quantum yield is dimensionless. For HCHO the probability that the absorption of a photon leads to a photolysis reaction (the quantum yield) is 0.79. The photolysis reaction is:



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

9:4) In exercise 9:3 above you have calculated the photolysis rate only within a specific wavelength interval. Here you will examine the wavelength dependence of photolysis rate reactions.

The photolysis reaction

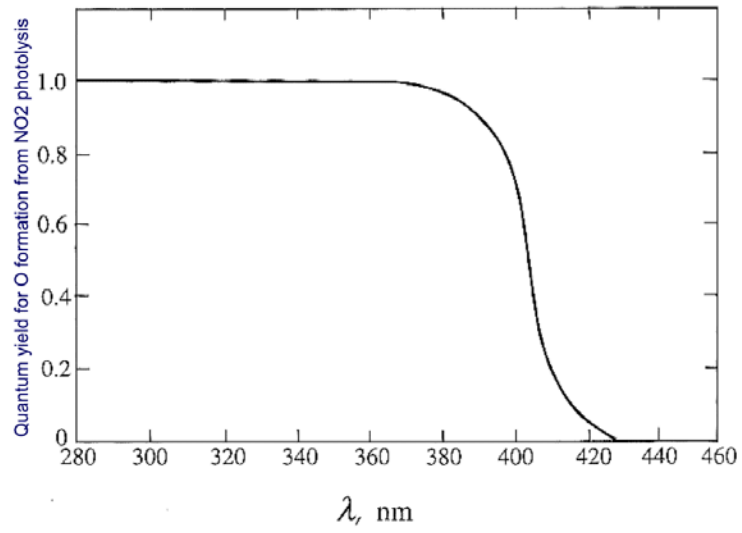
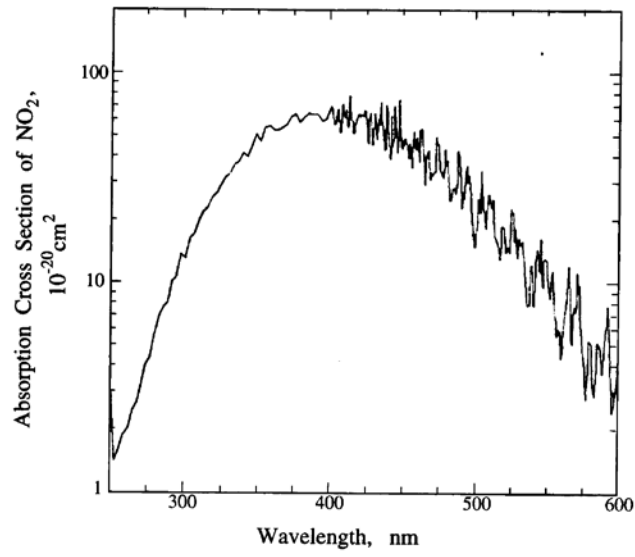
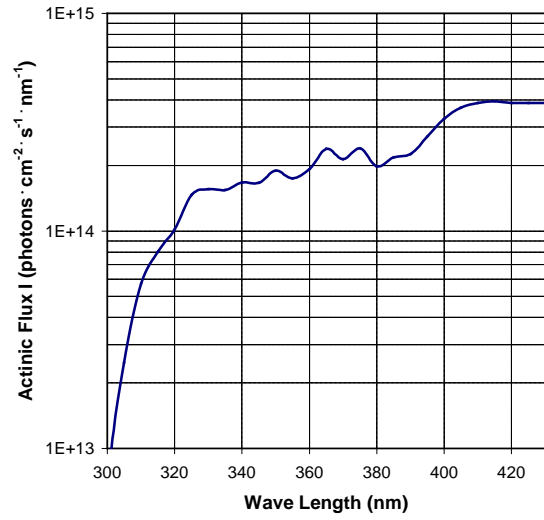


where O is O(<sup>3</sup>P), is very important for the tropospheric chemistry as it constitutes the only way to produce ozone in the troposphere (through  $\text{O}_2 + \text{O} \rightarrow \text{O}_3$ ; chapters 11, 12). In the stratosphere, O(<sup>3</sup>P) can be formed also via photolysis of O<sub>2</sub> at  $\lambda < 240$  nm (chapter 10 and the Chapman reaction). This UVc radiation is fortunately unable to penetrate into the troposphere. The oxygen atom O(<sup>3</sup>P) is a bi-radical and has two unpaired electrons.

Among other things, the photolysis of NO<sub>2</sub> depends on the wavelength of the incident light, as shown in the figures below.

a) Using the figures below, calculate approximate values for the photolysis rate constant  $k$  for photolysis of NO<sub>2</sub> at wavelengths 320, 380, 420 and 430 nm, and draw a diagram showing this wavelength dependence. Note that you should calculate the values at these four wavelengths, and not for a broader wavelength interval.

b) The photolysis rate constants for NO<sub>2</sub> photolysis are wavelength dependent. Describe how to continue if you were to calculate also the total photolysis rate constant for photolysis NO<sub>2</sub>. You don't have to perform these calculations, only describe the procedure. What is the unit for this (and all other) photolysis rate constants?



## Atmospheric Chemistry and Physics – Exercise E, chap. 10

Concepts and things to consider in preparation for the exercise in Atmospheric Chemistry, chapter 10, Jacobs and for the exam.

**Recommended activity before exercise:** Read and understand the tips given below.

- **The Chapman mechanism.** Memorize this mechanism. It is the ozone that absorbs the dangerous UVB radiation ( $\lambda < 320$  nm). Even shorter wavelengths ( $\lambda < 240$  nm) are absorbed by ordinary oxygen ( $O_2$ ) and therefore does not constitute a problem.
- Why is the stratospheric ozone layer concentrated around 15-30 km altitude? What factors govern this behaviour?
- Grouping chemical compounds into various chemical "**families**" facilitates the understanding of the reaction schemes. Radicals can be prevented from working catalytically if they are bound in the radical family **reservoirs**. What characterizes such a reservoir? Which molecules and radicals are part of the chemical families  $O_x$ ,  $HO_x$ ,  $NO_x$  and  $ClO_x$  and which compounds are part of the  $NO_x$  and  $ClO_x$  family reservoirs?
- **Catalytic reaction chains** are very important. **Catalytic ozone loss** is treated in this chapter. Consider what we mean by the word "catalytic".
- Memorize the reaction schemes for the **catalytic ozone loss** for the various radical families ( $X = OH, NO, Cl$ ).
- Make a habit of **identifying which molecules that are radicals**. Count electrons. An odd number of electrons reveals that the molecule has an unpaired electron and therefore is a radical. Exception:  $O(^3P)$  has two unpaired electrons and is a biradical.  $O(^1D)$  has no unpaired electrons but is in a highly excited state, and is therefore, like a radical, very reactive. Ozone is no radical and is thus actually fairly stable. (Repetition of chapter 9).
- Learn how to see which reactions that are **radical initiation** (most often via photolysis), **radical propagation**, and **termination** (Repetition of chapter 9).
- If one can assume that one or more of the molecules that take part in the reactions are in **steady-state** (*stationärt tillstånd*) then the calculations are often very much simplified. How can one determine that **steady-state** conditions prevail (chapter 3)? Often one can start by estimating the lifetime ( $\tau$ ) for molecule X as the mass in the reservoir (M) divided by the loss rate (L) of X. In atmospheric chemistry we often work with open systems (a given part of the atmosphere), which is why we replace the mass of X with the concentration  $[X]$  expressed in units of molecules/cm<sup>3</sup>. Similarly, we replace the loss rate of X with the rate of change in concentration  $\Delta[X]/\Delta t$  (or  $d[X]/dt$ ) in units of molecules·cm<sup>-3</sup>·s<sup>-1</sup>.
- If the lifetime thus calculated is short compared to the processes that govern the rates of formation (P) and loss (L) of X, then we can assume steady-state. In that case, the rates of formation and loss of the molecule are in balance, meaning that  $d[X]/dt = P - L = 0$ .
- The underlying mechanisms of the so called ozone hole that appears in early spring over Antarctica are rather complex. Important concepts are heterogeneous reactions, polar stratospheric clouds and the Antarctic polar vortex. Study figure 10-13 in Jacob.

## Exercises, chapter 10

10:1) Stratospheric ozone can be consumed catalytically, where the compound that destroys ozone is regenerated and thus not consumed. This discovery was rewarded with the Nobel Prize in Chemistry in 1995 for Paul Crutzen, Mario Molina and Sherwood Rowland.

- Name the reactions (one photolysis plus two additional) that together describe the catalytic ozone destruction by a catalyst X, and sum up these reactions to a net reaction.
- Name four molecules or atoms that can work as catalysts X (all X are radicals).

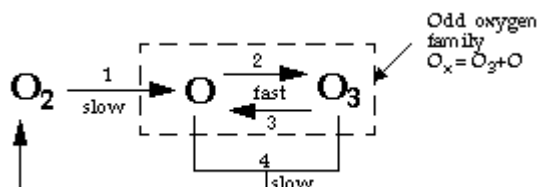
10:2) The radicals belonging to the HO<sub>x</sub> family (H, OH, HO<sub>2</sub>) destroy ozone in catalytic chain reactions. The most important reactions are given in Jacob, section 10.2.1. There are more ways. Below, a number of reactions are given that are important in various parts of the stratosphere. O denotes O(<sup>3</sup>P).

- $\text{OH} + \text{O} \rightarrow \text{O}_2 + \text{H}$
- $\text{OH} + \text{HO}_2 \rightarrow \text{H}_2\text{O} + \text{O}_2$
- $\text{OH} + \text{O}_3 \rightarrow \text{HO}_2 + \text{O}_2$
- $\text{H} + \text{O}_2 + \text{M} \rightarrow \text{HO}_2 + \text{M}$
- $\text{H} + \text{O}_3 \rightarrow \text{O}_2 + \text{OH}$
- $\text{HO}_2 + \text{O} \rightarrow \text{OH} + \text{O}_2$
- $\text{HO}_2 + \text{O}_3 \rightarrow \text{OH} + 2\text{O}_2$
- $\text{HO}_2 + \text{HO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{O}_2$

- How are HO<sub>x</sub> radicals formed in the stratosphere (initiation steps)?
- For each reaction, name the molecules that are radicals.
- Which of the reactions are propagation steps for HO<sub>x</sub> radicals?
- Which of the reactions are sinks for HO<sub>x</sub> radicals (termination steps)?
- Using these reactions, find five different cycles for HO<sub>x</sub>-catalyzed ozone destruction that each start with a reaction with OH.

10:3) The Chapman mechanism for stratospheric ozone can be written:

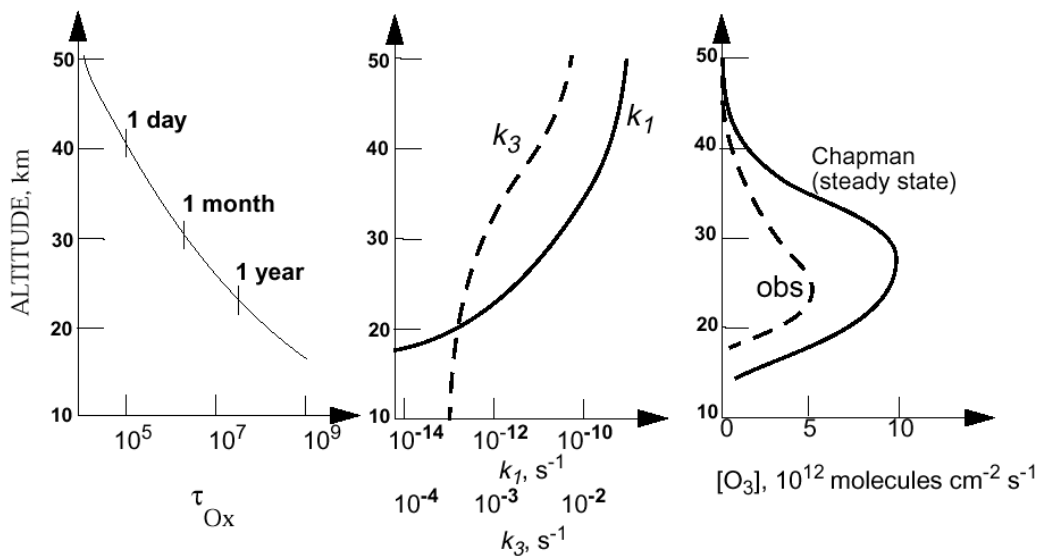
- $\text{O}_2 + h\nu \rightarrow \text{O} + \text{O} \quad (\lambda < 240 \text{ nm})$
- $\text{O} + \text{O}_2 + \text{M} \rightarrow \text{O}_3 + \text{M} \quad (2x) \quad (k_2 = 1 \cdot 10^{-33} \text{ cm}^6 \text{ molecule}^{-2} \cdot \text{s}^{-1})$
- $\text{O}_3 + h\nu \rightarrow \text{O}_2 + \text{O} \quad (k_3, \text{ see Jacob, Figure 10-5, } \lambda < 320 \text{ nm})$
- $\text{O}_3 + \text{O} \rightarrow 2\text{O}_2 \quad (k_4 = 8.0 \cdot 10^{-12} \cdot \exp(-2060/T) \text{ cm}^3 \cdot \text{molecule}^{-1} \cdot \text{s}^{-1})$



Here,  $k_i$  are reaction rate constants and T the temperature in Kelvin ( $k_1$  and  $k_3$  are photolysis rate constants). Reactions 1 and 4 are much slower than reactions 2 and 3. The temperature at 20 km altitude is 200 K and at 45 km 270 K. The air molecule number concentration is  $1.8 \cdot 10^{18} \text{ molecules} \cdot \text{cm}^{-3}$  at 20 km and  $4.1 \cdot 10^{16} \text{ molecules} \cdot \text{cm}^{-3}$  at 45 km.

- Write an expression for the lifetime of the O atom and calculate the lifetimes at 20 and 45 km altitude. Can we assume steady state conditions for the O atom in the stratosphere? Motivate your answer.

- b) Assuming steady-state conditions for the O atom in the stratosphere, and further considering that reactions (2) and (3) are much faster than reactions (1) and (4), calculate the ratio  $[O]/[O_3]$  at the altitudes 20 and 45 km. Show that  $[O_X] = [O_3] + [O] \approx [O_3]$  throughout the stratosphere. This means that  $[O_3]$  is controlled by reactions (1) and (4), and that the lifetime of ozone is defined by the lifetime of  $O_X$ .
- c) At least in the upper stratosphere one can assume steady-state conditions also for  $O_X$  (Jacob, left part of figure 10-5). Give an expression for  $[O_3]$  under the assumption that steady-state conditions prevail throughout the entire stratosphere (see Jacob, section 10.1.2).
- d) Calculate  $[O_3]$  at the altitudes 20 and 45 km using the expression derived above ( $k_1$  and  $k_3$ , see Jacob, figure 10-5). Draw your calculated  $[O_3]$  values in the right hand figure below. Also calculate  $[O_3]$  in the unit ppmv.



\*10:4) An air parcel at 30 km altitude ( $30^\circ$  N, at noon) has the following concentrations:

$$[O_3] = 3.0 \cdot 10^{12} \text{ molecules} \cdot \text{cm}^{-3}$$

$$[O] = 3.0 \cdot 10^7 \text{ atoms} \cdot \text{cm}^{-3}$$

$$[NO] = 7 \cdot 10^8 \text{ molecules} \cdot \text{cm}^{-3}$$

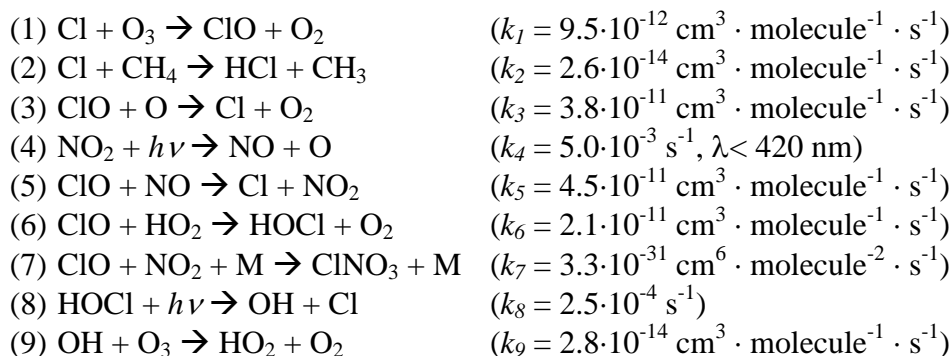
$$[NO_2] = 2.2 \cdot 10^9 \text{ molecules} \cdot \text{cm}^{-3}$$

$$[HO_2] = 8.5 \cdot 10^6 \text{ molecules} \cdot \text{cm}^{-3}$$

$$[CH_4] = 2.8 \cdot 10^{11} \text{ molecules} \cdot \text{cm}^{-3}$$

The air molecule number concentration is  $3.9 \cdot 10^{17}$  molecules  $\cdot \text{cm}^{-3}$  at 30 km altitude.

We examine the Cl-catalyzed mechanism for  $O_3$  loss in this air parcel on the basis of the following reactions:



- a) Calculate the lifetimes of Cl and ClO. Which reactions are the main sinks for these molecules?
- b) Based on your answer above, explain why reaction (3) is the rate limiting step for the catalyzed O<sub>3</sub> loss.
- (1)  $\text{Cl} + \text{O}_3 \rightarrow \text{ClO} + \text{O}_2$
- (3)  $\text{ClO} + \text{O} \rightarrow \text{Cl} + \text{O}_2$
- c) If ClO reacts with NO instead of with O, do we still get a catalyzed O<sub>3</sub> loss?
- d) Provide a catalytic cycle for O<sub>3</sub> loss based on the formation of HOCl via reaction (6). How important is this path for catalyzed O<sub>3</sub> loss compared to that in question b) above?
- e) (*Rather tricky to solve*) Calculate the lifetime for the chemical family ClO<sub>x</sub> containing Cl and ClO. Compare with the lifetime of ClO only. What is your conclusion?

## Atmospheric Chemistry and Physics – Exercise F, chap. 11-13

Concepts and things to consider in preparation for the exercise in Atmospheric Chemistry, chapters 11-13, Jacobs and for the exam.

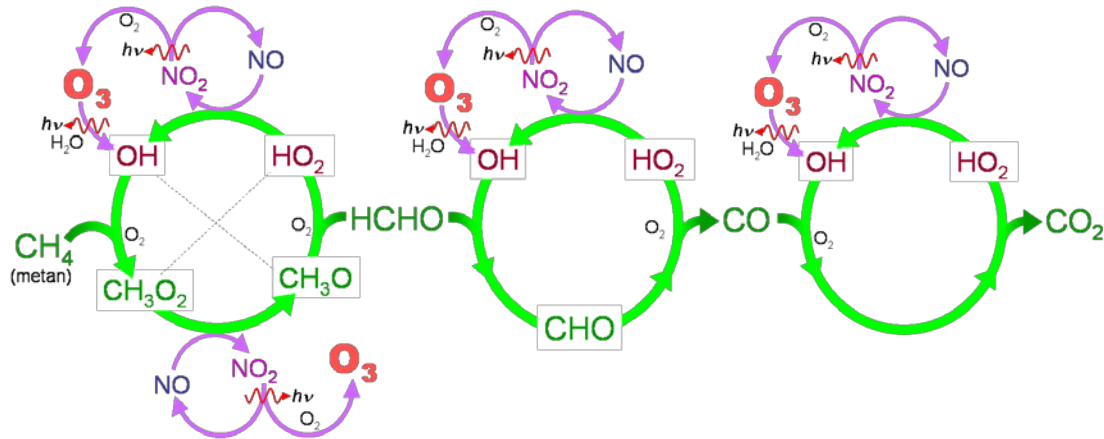
**Recommended activity before exercise:** Try to solve 11:1 and 13:1.

- $\text{NO}_x$  catalyzes ozone destruction in the stratosphere but favours ozone production in the troposphere. Why? (Jacob, pp. 209-210).
- Photolysis of  $\text{NO}_2$  :  
$$\text{NO}_2 + h\nu \rightarrow \text{NO} + \text{O} \quad (\lambda < 420 \text{ nm})$$
followed by  
$$\text{O} + \text{O}_2 + \text{M} \rightarrow \text{O}_3 + \text{M}$$
is **the only way to produce ozone in the troposphere**, since photolysis of  $\text{O}_2$  by  $\lambda < 240$  nm will not occur here. If we write only O then we mean  $\text{O}({}^3\text{P})$ .
- $\text{NO}_2 + \text{O}_2 \rightleftharpoons \text{NO} + \text{O}_3$   
Memorize this reaction since it summarizes tropospheric ozone production in a simplified way. The reaction is shifted towards the right side (ozone net production) via photolysis of  $\text{NO}_2$  ( $\lambda < 420$  nm) and more importantly since hydrocarbons consume NO while simultaneously forming  $\text{NO}_2$ .
- Make sure to distinguish between  $\text{O}({}^3\text{P})$  and  $\text{O}({}^1\text{D})$ .  $\text{O}({}^3\text{P})$  is formed in the troposphere via photolysis of  $\text{NO}_2$  while  $\text{O}({}^1\text{D})$  is formed via photolysis of  $\text{O}_3$ .  $\text{O}({}^3\text{P})$  is needed for  $\text{O}_3$  to form.  $\text{O}_3$  in turn is photolyzed to form  $\text{O}({}^1\text{D})$ , which is needed to produce OH radicals, since only  $\text{O}({}^1\text{D})$  is able to break up the very stable water molecule  $\text{H}_2\text{O}$ .
- The oxidizing capacity of the troposphere, and thus also the ability of the troposphere to cleanse itself from hazardous trace gases, hinges on a series of reactions. Note the importance of the nitrogen oxides for the production of ozone and  $\text{HO}_x$ -radicals:  
$$\text{NO}_x \rightarrow \text{O}_3 \rightarrow \text{HO}_x \rightarrow \text{Oxidizing capacity of the troposphere} \rightarrow \text{Cleansing from hazardous trace gases.}$$
- Learn how to determine the oxidation number of the various atoms (mainly S, C, and N) in the different molecules. Oxidation results in an increase in oxidation number.
- As we now treat the interaction between the gaseous and aqueous phases, it is of particular importance to distinguish between chemical equilibria (with equilibrium constant  $K$ ) and reactions that proceed mainly from reactants to products (with reaction rate constant  $k$ ). For equilibrium reactions we use a double-sided arrow ( $\rightleftharpoons$ ) to signify that the reactions are fully reversible and proceed in both directions, while a single arrow ( $\rightarrow$ ) clearly indicates which way the irreversible reaction proceeds (repetition from chapter 9).
- Note that both  $\text{SO}_2$  and  $\text{CO}_2$  are dissolved in the aqueous phase by completely analogous equilibrium reactions (simply replace S with C). If you learn one reaction scheme, then you also learn the other. Also note that the oxidation numbers of  $\text{SO}_2$  and  $\text{CO}_2$  are left unchanged when they dissolve in the aqueous phase. No chemical oxidation has therefore taken place for S and C, which also means that the reactions are fully reversible (equilibria).
- Neutral pH in pure water is 7. In the atmosphere, however, "neutral" pH=5.6. This is the pH of a cloud droplet even if has not been acidified by sulphur or nitrogen compounds. Why is this? (Jacob 13.1.1)



## Exercises, chapter 11

11:1) The figure below describes schematically how the hydrocarbon methane  $\text{CH}_4$  is oxidized in the atmosphere via formaldehyde  $\text{HCHO}$  and  $\text{CO}$  into carbon dioxide  $\text{CO}_2$ . The reactions can be found in Jacob, exercise 11-2.



In the atmosphere, the largest sinks for  $\text{CO}$  and  $\text{CH}_4$  are via reactions with the hydroxyl radical  $\text{OH}$ .  $\text{HCHO}$  is a significant sink for  $\text{OH}$ .

The reaction rate constants at 298 K are given below

- (1)  $\text{CO} + \text{OH} \rightarrow \text{CO}_2 + \text{H}$  ( $k_1 = 1.5 \cdot 10^{-13} \text{ cm}^3 \cdot \text{molecule}^{-1} \cdot \text{s}^{-1}$ )
- (2)  $\text{CH}_4 + \text{OH} \rightarrow \text{CH}_3 + \text{H}_2\text{O}$  ( $k_2 = 6.3 \cdot 10^{-15} \text{ cm}^3 \cdot \text{molecule}^{-1} \cdot \text{s}^{-1}$ )
- (3)  $\text{HCHO} + \text{OH} \rightarrow \text{CHO} + \text{H}_2\text{O}$  (followed by  $\text{CHO} + \text{O}_2 \rightarrow \text{CO} + \text{HO}_2$ )  
( $k_3 = 9.4 \cdot 10^{-12} \text{ cm}^3 \cdot \text{molecule}^{-1} \cdot \text{s}^{-1}$ )

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

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

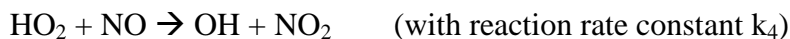
$$[\text{CH}_4] = 5.3 \cdot 10^{13} \text{ molecules} \cdot \text{cm}^{-3} \text{ (2000 ppb),}$$

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

a) Calculate the lifetime of the  $\text{OH}$  radical in this air mass, considering reactions 1-3. Which is the dominant sink?

b) Can we assume a steady state for  $[\text{OH}]$ ? Motivate your answer.

c) The main source of  $\text{OH}$  radicals in this air mass is the reaction



Give an expression for  $[\text{OH}]$ .

d) Calculate  $[\text{OH}]$  when  $k_4 = 8.6 \cdot 10^{-12} \text{ cm}^3 \cdot \text{molecule}^{-1} \cdot \text{s}^{-1}$ , and

$$[\text{HO}_2] = 8.2 \cdot 10^7 \text{ molecules} \cdot \text{cm}^{-3} \text{ (0.003 ppb).}$$

$$[\text{NO}] = 1.0 \cdot 10^{10} \text{ molecules} \cdot \text{cm}^{-3} \text{ (0.38 ppb).}$$

e) Other important sinks for  $\text{HO}_x$ -radicals ( $\text{OH}$  and  $\text{HO}_2$ ) are termination steps in the radical chain. Give examples of two such termination steps.

11:2) Considering that the hydroxyl radical OH is absolutely essential for the ability of the troposphere to cleanse itself from harmful trace gases (such as for instance SO<sub>2</sub>, NO<sub>x</sub> and CO) it is of great interest to examine to what extent human activities have affected the global OH concentrations. If, at the same time as we emit huge quantities of air pollutants, we also cause [OH] to decrease, then we are in real trouble. Ice cores drilled in the ice sheets of Greenland and Antarctica have shown to be useful for constraining historic [OH]. Scientists are able to measure the concentration of certain stable gases such as methane CH<sub>4</sub> and formaldehyde HCHO in bubbles of gas captured in the ice as it formed. The ratios between various hydrogen and oxygen isotopes reveal even the temperature of the snow that once fell. Dating can be made using different methods, including <sup>14</sup>C.

The main sink for formaldehyde HCHO in the Arctic is photolysis, with an average reaction rate constant  $k_1 = 1.0 \cdot 10^{-5} \text{ s}^{-1}$ . Oxidation of methane CH<sub>4</sub> via OH is the only HCHO source of importance in the Arctic. The temperature dependent rate constant for this reaction is  $k_2 = 2.0 \cdot 10^{-12} \cdot \exp(-1700/T) \text{ cm}^3 \cdot \text{molecule}^{-1} \cdot \text{s}^{-1}$ , where T is the temperature in K.

a) Show that  $[HCHO] = \frac{k_2}{k_1} [CH_4] \cdot [OH]$ .

The table below shows the results of measurements made on Greenland ice cores that are representative of various time periods: present, pre-industrial (year 1600) and the latest ice age 18000 years B.C.

	[CH <sub>4</sub> ] ppbv	[HCHO] ppbv	T (K)
Present	1700	0.10	260
Pre-industrial	740	0.05	260
Glacial	410	0.01	250

b) Calculate [OH] (molecules · cm<sup>-3</sup>) over Greenland during each time period. Compare the value obtained for "present" with the [OH] in exercise 11:1 above. Discuss the difference.

c) How do you interpret the difference in [OH] between pre-industrial time and present?

d) A possible explanation for the difference in [OH] between the glacial and pre-industrial time could be that stratospheric O<sub>3</sub> concentrations were higher during the ice age. Why could this be? And if so, how can the stratospheric O<sub>3</sub> concentrations affect [OH] in the troposphere?

### Exercises, chapter 13

13:1) Give the oxidation number for C, S and N in the various compounds below. The ions are in aqueous phase.

Carbon: CO(g), CO<sub>2</sub>(g), HCO<sub>3</sub><sup>-</sup>, CO<sub>3</sub><sup>2-</sup>

Nitrogen: NO(g), NO<sub>2</sub>(g), N<sub>2</sub>O(g), NO<sub>3</sub>(g), N<sub>2</sub>O<sub>5</sub>(g), HNO<sub>2</sub>(g), HNO<sub>3</sub>(g), NO<sub>3</sub><sup>-</sup>

Sulphur: H<sub>2</sub>S(g), SO<sub>2</sub>(g), HSO<sub>3</sub><sup>-</sup>, SO<sub>3</sub><sup>2-</sup>, H<sub>2</sub>SO<sub>4</sub>(g), SO<sub>4</sub><sup>2-</sup>

13:2) Nitric acid  $\text{HNO}_3(\text{g})$  is a strong acid that is of increasing importance for acidification since the  $\text{SO}_2$  emissions are decreasing (at least in Europe and North America) while emissions of nitrogen oxides ( $\text{NO}_x$ ) tend to increase instead, primarily as a result of increasing traffic.

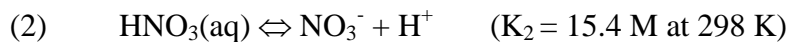
a) How is  $\text{HNO}_3$  formed in the gas phase?

b) What is the oxidation number of N in  $\text{HNO}_3$  as well as in the gas that reacts to form  $\text{HNO}_3$ ?

$\text{HNO}_3(\text{g})$  is a very water-soluble gas:



$K_H$  is the Henry's law constant for  $\text{HNO}_3$ .  $\text{HNO}_3(\text{aq})$  is a strong acid and dissociates efficiently in the aqueous phase:



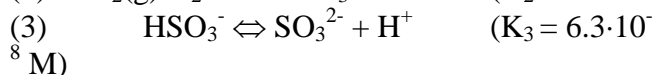
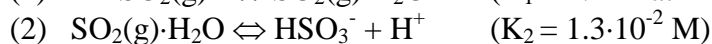
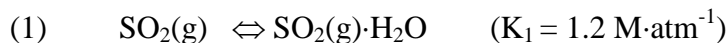
c) Typical values of pH in cloud and rain drops lie in the range 3-6. Calculate the ratio  $[\text{NO}_3^-]/[\text{HNO}_3(\text{aq})]$  at pH = 3 and pH = 6. In what form ( $\text{HNO}_3(\text{aq})$  or  $\text{NO}_3^-$ ) is most of the nitrogen found in these drops?

d) Henry's law constant  $K_H$  describes how much a gas (here  $\text{HNO}_3(\text{g})$ ) dissolves in the aqueous phase. But  $K_H$  only considers the first step in the chain of equilibrium reactions. Since  $\text{HNO}_3(\text{aq})$  dissociates efficiently in the aqueous phase, the equilibrium reaction (1) is shifted towards the right side to compensate for the loss of  $\text{HNO}_3(\text{aq})$ .

Give an expression for an "effective" Henry's law constant  $K^*_H$  that shows how much  $\text{HNO}_3(\text{g})$  that is actually dissolved in water at various values of pH. ( $K^*_H = [\text{total-N}(\text{aq})] / [\text{HNO}_3(\text{g})]$ ). Here  $[\text{total-N}(\text{aq})]$  denotes the total aqueous phase concentration of all molecules and ions that contain N. Let  $p_{\text{HNO}_3}$  denote the partial pressure of  $\text{HNO}_3$  in the gas phase ( $p_{\text{HNO}_3} = [\text{HNO}_3(\text{g})]$ , unit: atm).

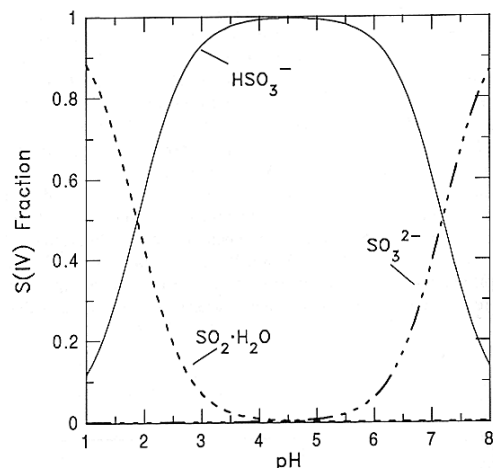
e) Calculate  $[\text{total-N}(\text{aq})]$  at pH = 4.3 (rain water in southern Sweden) and  $P_{\text{HNO}_3} = 0.1$  ppb, using the "effective" Henry's law constant  $K^*_H$  and the "ordinary" Henry's law constant  $K_H$ . Compare the solubility and discuss the implications of these results.

13:3) The gas  $\text{SO}_2$  dissolves in water in several steps according to the reaction scheme below.

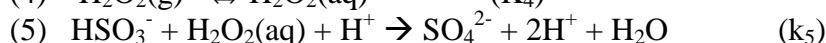
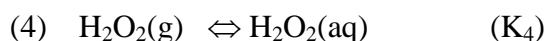


Here the  $K_i$  are equilibrium constants.

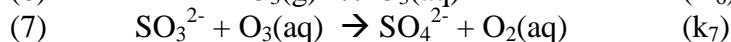
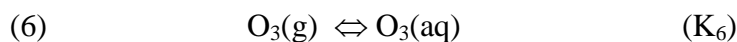
- Give the oxidation numbers of sulphur in the various compounds above.
- In which form is most of the sulphur in reactions (1)-(3) found at typical values of pH in rain and cloud drops (3-6) and qualitatively explain why.



Sulphur is oxidized in aqueous solution mainly via hydrogen peroxide:



or ozone:



Here the  $k_i$  are reaction rate constants.

- Which is the oxidation number for S in sulphate ( $\text{SO}_4^{2-}$ )?
- Using the reactions above, show how the oxidation rates of sulphur via  $\text{H}_2\text{O}_2$  and  $\text{O}_3$  depend on pH. Use  $P_{\text{SO}_2}$ ,  $P_{\text{O}_3}$  and  $P_{\text{H}_2\text{O}_2}$  to denote the partial pressures (in units of atm) of  $\text{SO}_2(\text{g})$ ,  $\text{O}_3(\text{g})$  and  $\text{H}_2\text{O}_2(\text{g})$ .
- What are the implications of this pH dependence for the oxidation of S via  $\text{H}_2\text{O}_2$  for the acidification of soils, waters and ecosystems?
- How is hydrogen peroxide  $\text{H}_2\text{O}_2(\text{g})$  formed?

## Answers and Solutions

- 1:1) 28.97 kg/kmol  $M_a = C_{N_2}M_{N_2} + C_{O_2}M_{O_2} + C_{Ar}M_{Ar}$   
 1:2) 0.413 kg/m<sup>3</sup>  $PV = nRT = m/MRT$ ;  $\rho = m/V = PM/(RT)$   
 1:3) a: 12.28 hPa From Jacob fig. 1-3 or table (more exact)  
 b: 82.5 %  $P_{H_2O} = C_{H_2O}P$ ;  $RH = 100 P_{H_2O}/P_{sat}$   
 1:4) 0.317 m<sup>3</sup>  $V = nRT/P$  (R and, in this case, n constant);  $V_2 = T_2P_1V_1/(T_1P_2)$   
 1:5)  $8.94 \times 10^{21}$  molecules/m<sup>3</sup>  $P_{CO_2} = C_{CO_2}P$ ;  $C_{vol} = N_{av}n_{CO_2}/V = N_{av}P_{CO_2}/(RT)$   
 1:6) a: 4340 ppbv; More than 50 times the air quality standard of surface air!  
 $C = n_{O_3}/n = P_{O_3}/P$ ;  $P_{O_3} = n_{O_3}RT/V = RTC_{vol}/N_{av}$ ;  
 $C = (RTC_{vol}/N_{av})/P$   
 b: 40 ppbv; half of the air quality standard of surface air. (Solution: see 1:6a)  
 c: The ratio of the two concentrations is larger when using mixing ratio because this unit expresses relative concentration and thus takes into account that stratospheric air contains fewer air molecules per volume unit than surface air.  
 d:  $7.5 \times 10^{22}$  molecules/m<sup>2</sup>

$$Col_{O_3} = \int_{z_1}^{z_2} C_{vol}(z) dz; \quad \text{Triangle distribution} \Rightarrow$$

$$Col_{O_3} = \text{base} \cdot \text{height} / 2 = (z_2 - z_1) C_{vol}^{max} / 2$$

- e: 3.0 mm Ideal gas law  $\Rightarrow$  equal amount of molecules of two different gases of the same pressure and temperature have the same volume;  $d = (\text{No. moles } O_3/\text{m}^2)/(\text{No. moles air}/\text{m}^3)$ ; (Regard d as the height of pure  $O_3$  in a jar with area 1 m<sup>2</sup>)  
 $n_{O_3}/V = (Col_{O_3}/N_{av})/d = P_{O_3}/(RT) = P/(RT)$ ;  
 $[P_{O_3} = P] \quad d = Col_{O_3}RT/(N_{av}P)$

- 2:1)  $5.12 \times 10^{18}$  kg  $PA = m_a g$ ;  $m_a = PA/g = 4\pi R_j^2 P/g$   
 2:2)  $6.56 \times 10^{16}$  kg  $m_{Ar} = n_{Ar}M_{Ar} = C_{Ar}n_a M_{Ar} = C_{Ar}M_{Ar}m_a/M_a$   
 2:3) 5.27 km  $m_a = PA/g \sim P$ ;  $\Rightarrow m_a/2$  at  $P/2$ ;  $P(z) = P(0) e^{-z/H}$ ;  
 $H = RT/(M_a g)$ ; Find  $P(z)/P(0) = 0.5 = e^{-z/H}$ ;  
 Logarithm of both sides:  $\ln(0.5) = -z/H$ ;  $z = -H \ln(0.5)$   
 2:4) Not possible, because the atmosphere has no well defined outer limit.

- 3:1) a: 500 days  $\tau_D = m/D$ ;  $d = 0.2 \%$ /day;  $d = 100D/m$ ;  $\tau_D = 100/d$   
 b: 83.3 days  $\tau_L = m/L$ ;  $l = 1.2 \%$ /day;  $l = 100L/m$ ;  $\tau_L = 100/l$   
 c: 71.4 days total:  $t = d + l$ ;  $\tau_t = 100/(d + l)$   
 3:2) a:  $m = E/k(1 - e^{-kt})$   $dm/dt = E + P + F_{in} - D - L - F_{ut} = E - km$ ;  
 $m(t) = m(0)e^{-kt} + E/k(1 - e^{-kt})$ ; see text book for solution of the differential equation  
 b:  $m(\infty) = E/k$  ( $e^{-kt}$  approaches 0 for large t)

- 3:3)  $2.1 \mu\text{g}/\text{m}^3$   
 $\frac{dC_{vol}}{dt} = \frac{E}{h} + P - L - D = \frac{E}{h}$ ;  $\frac{dC_{vol}}{dt} = \frac{dC_{vol}}{dx} \frac{dx}{dt} = w \frac{dC_{vol}}{dx}$ ;  $\Rightarrow$   
 $\frac{dC_{vol}}{dx} = \frac{E}{wh}$ ;  $C_{vol}(r) = C_{vol}(0) + \int_0^r \frac{dC_{vol}}{dx} dx = C_{vol}(0) + \frac{Er}{wh}$

- 3:4) a:  $dm_S/dt = k_{TS}m_T - k_r m_S - k_{ST}m_S$ ;  $k_r = \ln 2/t_{1/2}$   
 $dm_T/dt = k_{ST}m_S - k_r m_T - k_D m_T - k_{TS}m_T$ ;  $k_D$ : deposition  
b:  $dm_S/dt = -k_r m_S - k_{ST}m_S = -km_S$ ;  $k_{ST} = k - k_r = (0.77 - 0.025) \text{ year}^{-1}$   
 $\tau_S = m_S / k_{ST}m_S = 1/k_{ST} = 1.3 \text{ year}$   
c:  $dm'_T/dt = k_{ST}m'_S - k_{TS}m'_T = m'_S/\tau_S - m'_T/\tau_T = 0$   
 $\tau_T = \tau_S m'_T/m'_S = 1.3 \times (1000 - 150)/(150 - 1) = 7.6 \text{ year}$  (See fig. 3-1)  
d:  $\tau_D = 10 \text{ days} \ll \tau_T$ ;  $\Rightarrow$   $^{90}\text{Sr}$  disappears by deposition in the troposphere before the air returns to the stratosphere.  
e:  $f = k_{TS}/(k_{TS} + k_{ox})$ ; HCFC-123:  $f = 0.16$ ; HCFC-124:  $f = 0.44$
- 3:5) a:  $dm/dt = E - km$ ;  $m = m(0)e^{-kt} + E/k(1 - e^{-kt})$ ;  $m_\infty = E/k = 2 \times 10^{10} \text{ kg}$   
Fast increase in the CFC emissions up to 1989 compared with the residence time, i.e.  $m_\infty$  was not reached year 1989.  
b: 1989 – 1996 (7 y):  $m = m_0 e^{-kt} + E/k(1 - e^{-kt})$ ;  $m(1996) = 1.2 \times 10^{10} \text{ kg}$   
1997 – 2050 (53 y):  $m = m(1996)e^{-kt} = 7.1 \times 10^9 \text{ kg}$  (71 % of  $m(1989)$ )  
1997 – 2100 (103 y):  $m = m(1996)e^{-kt} = 4.3 \times 10^9 \text{ kg}$  (43 % of  $m(1989)$ )
- 4:1) A – 3: Neutral downwards, inversion upwards  $\Rightarrow$  Smoke mixes only downwards  
B – 4: Neutral upwards, stable downwards  $\Rightarrow$  Smoke mixes only upwards  
C – 1: Unstable or neutral over the entire profile  $\Rightarrow$  Air moves both up and down  
D – 2: Inversion over the entire profile  $\Rightarrow$  Air does not move vertically
- 4:2) 1.22 km;  $dT/dz = -12 \text{ K/km}$ ; In the 1 km layer:  $\Delta T = h dT/dz = -12 \text{ K}$ ;  $\Delta z = -\Delta T/\Gamma$
- 4:3) Air does not move vertically due to the inversion, i.e. the atmosphere is stable.
- 4:4) a: Subsidence causes inversion that tops the planetary boundary layer (PBL). At night, cooling of the surface produces a second inversion close to the surface; a shallow mixed layer persists because of wind-induced turbulence. In the daytime, heating of the surface gradually erodes the nighttime inversion and the mixed layer deepens as the day progresses. At sunset, surface cooling causes the mixed layer to collapse rapidly. The greatest weakness of this model is the assumption of a well-mixed remnant PBL (in fact, the remnant PBL is stable and would not be well mixed).  
b: Used parameters:  $m_0 = Et_0$ ; where  $t_0 = 3600 \text{ s}$ ;  $V_0 =$  mixed layer volume at  $t = 0$ .  
C =  $m/V =$  concentration; B = mixed layer; R = remnant PBL
- |         |   |                           |
|---------|---|---------------------------|
| At 0:   | $C_B = 0$ ;                                 | $C_R = 0$                 |
| At 6:   | $C_B = 6 m_0/V_0$ ;                         | $C_R = 0$                 |
| At 9:   | $C_B = 9m_0/2.5V_0 = 3.6 m_0/V_0$ ;         | $C_R = 0$                 |
| At 12:  | $C_B = 12m_0/4V_0 = 3 m_0/V_0$ ;            | $C_R = 0$                 |
| At 15:  | $C_B = 15m_0/5.5V_0 = 2.7 m_0/V_0$ ;        | $C_R = 0$                 |
| At 18-: | $C_B = 18m_0/7V_0 = 2.6 m_0/V_0$ ;          | $C_R = 0$                 |
| At 18+: | $C_B = 18m_0/7V_0 = 2.6 m_0/V_0$ ;          | $C_R = C_B = 2.6 m_0/V_0$ |
| At 24:  | $C_B = C_B(18) + 6 m_0/V_0 = 8.6 m_0/V_0$ ; | $C_R = 2.6 m_0/V_0$       |
- 4:5) a: AB:  $dT/dz = -10 \text{ K/km}$ ; unstable (neutral)  
BC:  $dT/dz = -7.5 \text{ K/km}$ ; conditionally stable      CD:  $dT/dz = 0$ ; stable  
b:  $\Gamma_w < -dT/dz_{BC} \Rightarrow$  The air parcel can rise until  $T = T_C \Rightarrow$   
 $\Delta T_{\text{air parcel}} = T_C - T_B = -15 \text{ K} \Rightarrow \Delta z = \Delta T_{\text{air parcel}}/(-\Gamma_w) = 2.5 \text{ km}$   
 $z = z_B + \Delta z = 4.5 \text{ km}$   
c: Cloud formation increases vertical transport because  $\Gamma_w$  is smaller than  $\Gamma$ . This causes increased ventilation of the air closest to ground.
- 6:1) a:  $\Delta m_C/\Delta t = +3.6 \text{ Pg C/y}$        $\Delta C_C = 17 \text{ ppmv}$ ;  $\Delta m_C/\Delta t = \Delta C_{Cn_a} M_C/\Delta t$

- b: Shows approximately the global trend, because the residence time of CO<sub>2</sub> is long compared with typical transport times.
- 6:2)  $\tau_{\text{WSO}} = 34/(0.8 + 0.4) \text{ y} = 28.3 \text{ y}$ ;  $\tau_{\text{CSO}} = 2/1.6 \text{ y} = 1.25 \text{ y}$
- 6:3) a:  $[\text{CO}_2(\text{aq})] = 0,00173 \text{ M}$ ;  $[\text{CO}_2(\text{aq})] = [\text{CO}_2 \cdot \text{H}_2\text{O}] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}]$   
 $[\text{CO}_2 \cdot \text{H}_2\text{O}] = K_{\text{H}} \cdot P_{\text{CO}_2}$ ;  $[\text{HCO}_3^-] = K_1[\text{CO}_2 \cdot \text{H}_2\text{O}]/[\text{H}^+] = K_1 K_{\text{H}} \cdot P_{\text{CO}_2}/[\text{H}^+]$ ;  
 $[\text{CO}_3^{2-}] = K_2[\text{HCO}_3^-]/[\text{H}^+] = K_1 K_2[\text{CO}_2 \cdot \text{H}_2\text{O}]/[\text{H}^+]^2 = K_1 K_2 K_{\text{H}} \cdot P_{\text{CO}_2}/[\text{H}^+]^2$ ;  
 $[\text{CO}_2(\text{aq})] = K_{\text{H}} P_{\text{CO}_2} (1 + K_1/[\text{H}^+] + K_1 K_2/[\text{H}^+]^2)$
- b:  $F = 0.026$ ;  $F = n_{\text{atm}}/(n_{\text{atm}} + n_{\text{oc}})$ ;  $n_{\text{oc}} = V_{\text{oc}} \cdot [\text{CO}_2(\text{aq})]$ ;  
 $n_{\text{atm}} = C_{\text{CO}_2} n_{\text{a}} = n_{\text{a}} P_{\text{CO}_2}/P$ ; Enter of  $n_{\text{atm}}$  and  $n_{\text{oc}}$  to obtain F.
- c: Dissolution of CO<sub>2</sub> lower the oceanic pH, causing a shift in the equilibrium.
- 6:4) a:  $m = 60 + 40 + 630 = 730 \text{ Pg}$ ;  $L = 10 + 22 + 22 + 5 + 3 = 62 \text{ Pg C/y}$ ;  $\tau = 11.8 \text{ y}$
- b: Forms CO<sub>2</sub> that accumulates in the atmosphere;  $f = 3/(3 + 51) = 5.6 \%$
- c: Reduced production of CO<sub>2</sub>  $\Rightarrow$  Lower atmospheric concentration
- 6:5) a:  $\text{CH}_{1.6} + y\text{O}_2 \rightarrow z\text{H}_2\text{O} + \text{CO}_2$ ;  $z = 1,6/2 = 0.8$ ;  $y = z/2 + 1 = 1.4$   
i.e combustion consumes 1.4 mole O<sub>2</sub> to produce 1 mole CO<sub>2</sub>.
- b:  $n\text{CO}_2 + n\text{H}_2\text{O} \xrightarrow{\text{h}\nu} (\text{CH}_2\text{O})_n + n\text{O}_2$ ; 1 O<sub>2</sub> formed per consumed CO<sub>2</sub>.
- c: Dissolution of CO<sub>2</sub> in the ocean does not affect the O<sub>2</sub> concentration.
- d:  $\Delta C_{\text{CO}_2} = (P_{\text{ct}}/M_{\text{C}})/n_{\text{a}} = 8.8 \text{ ppmv}$ ;  $\Delta C_{\text{O}_2} = -1.4\Delta C_{\text{CO}_2} = -12.3 \text{ ppmv}$
- e: Atmosphere (measured):  $\Delta C_{\text{CO}_2} = 3.2 \text{ ppmv (36\%)}$   
Biosphere (O<sub>2</sub> production):  $\Delta C_{\text{CO}_2} = 12.3 - 8.9 = 3.4 \text{ ppmv (39\%)}$   
Oceans (remaining CO<sub>2</sub>):  $\Delta C_{\text{CO}_2} = 8.8 - 3.2 - 3.4 = 2.2 \text{ ppmv (25\%)}$
- 7:1) a:  $3.85 \times 10^{26} \text{ W}$ ;  $P = 4\pi R_{\text{S}}^2 \sigma T_{\text{S}}^4$  (*Radiating surface area x radiative flux*)
- b:  $1370 \text{ W/m}^2$ ;  $F_{\text{S}} = P/(4\pi d^2) = R_{\text{S}}^2 \sigma T_{\text{S}}^4/d^2$  (At distance d the radiation is distributed over the surface area  $4\pi d^2$ )
- c:  $342 \text{ W/m}^2$ ;  $F_{\text{S}} \pi R_{\text{j}}^2/(4\pi R_{\text{j}}^2) = F_{\text{S}}/4$  (The earth “cuts out” a disk of radiation that is then averaged over the surface area of a sphere)
- 7:2) a: The fraction of the incoming solar radiation that is reflected back to space by e.g. clouds and ice.
- b: Planet H: 238 K; Earth: 257 K  
 $F_{\text{S}}(1 - A)/4 = \sigma T^4 \Rightarrow T_{\text{E}} = [F_{\text{S}}(1 - A)/(4\sigma)]^{0.25}$ ;  $F_{\text{S,H}} = F_{\text{S,jorden}}(d_{\text{j}}/d_{\text{H}})^2$ ;
- c: No. We have no information about the atmosphere of planet H, implying that we cannot estimate its greenhouse effect.
- 7:3) a: See the text book, p 129.
- b:  $T_{\text{j}} = 290 \text{ K}$ ;  $T_{\text{a}} = 244 \text{ K}$ ; Radiation balance atm:  $f\sigma T_{\text{j}}^4 = 2f\sigma T_{\text{a}}^4$ ;  $T_{\text{j}} = 2^{1/4} T_{\text{a}}$ ;  
[The earth has only one surface, the atmosphere has two.]  
Radiation balance entire earth:  $F_{\text{S}}(1 - A)/4 = (1 - f)\sigma T_{\text{j}}^4 + f\sigma T_{\text{a}}^4$ ; Use the atmospheric radiation balance to eliminate T<sub>a</sub>:  $F_{\text{S}}(1 - A)/4 = (1 - f/2)\sigma T_{\text{j}}^4 \Rightarrow$   
 $T_{\text{j}} = [F_{\text{S}}(1 - A)/(4\sigma(1 - f/2))]^{1/4}$
- c:  $\Delta T = T_{\text{surface}} - T_{\text{effective}} = 13.6 \text{ K}$ ;  $T_{\text{surface}} = [F_{\text{S,H}}(1 - A_{\text{H}})/(4\sigma(1 - f_{\text{H}}/2))]^{1/4}$
- d:  $\Delta F = 2.0 \text{ W/m}^2$ ; Reference:  $F_{\text{S}}(1 - A)/4 = (1 - f/2)\sigma T_{\text{j}}^4$ ; “Freeze” temp:  
 $\Delta F = F_{\text{out,ref}} - F_{\text{out,perturbed}} = F_{\text{S}}A/4 + (1 - f/2)\sigma T_{\text{j}}^4 - F_{\text{S}}A/4 - (1 - f'/2)\sigma T_{\text{j}}^4 =$   
 $= 0.5\Delta f\sigma T_{\text{j}}^4$
- e:  $\Delta T = +0.59 \text{ K}$ ;  $\Delta T = \lambda\Delta F$ ;  $\lambda = 1/[4(1 - 1/2f)\sigma T_{\text{j}}^3] = 0.29 \text{ K/(W/m}^2)$
- 7:4) a: CO<sub>2</sub>:  $1.50 \text{ W/m}^2$ ; CH<sub>4</sub>:  $0.47 \text{ W/m}^2$ ; N<sub>2</sub>O:  $0.10 \text{ W/m}^2$
- b:  $\Delta T = +1.3 \text{ K}$ ;  $\Delta T = \lambda\Delta F$ ;  $\Delta F = 4.37 \text{ W/m}^2$ ;  $\lambda = 1/[4(1 - 1/2f)\sigma T_{\text{j}}^3]$
- 7:5) a: The atmosphere absorbs at some wavelengths. The re-emission of radiation from the atmosphere takes place at a lower temperature, causing reduced intensity.

b: The atmospheric window at 8 – 13 μm wavelength can be used to estimate the surface temperature, because the atmospheric absorption is small in that range (with the exception of 9 – 10 μm)

North Afrika: 320 K; Mediterranean: 285 K; Antarctica: 180 K

c: The radiation at 14 – 16 μm corresponds to 220 – 230 K at all three locations. CO<sub>2</sub> has the effective absorption height in the atmosphere of approx. 10 km, at around the tropopause. The “bump” appearing in the Antarctic radiation spectrum is caused by that the ground there is colder than the tropopause.

7:6) a:  $T_j = 270$  K; Too cold for liquid water;  $T_j = [F_s(1 - A)/(4\sigma(1 - f/2))]^{1/4}$

b:  $T_j = 284$  K; Water is liquid;  $T_j = [F_s(1 - A)/(4\sigma(1 - f/2))]^{1/4}$

c: In a strongly absorbing atmosphere radiation can be emitted and re-absorbed by a layer higher up in the atmosphere, causing emission at still lower temperature. This can be represented in the model by adding an atmospheric layer.

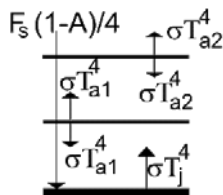
Balance entire earth:  $F_s(1-A)/4 = \sigma T_{a2}^4$ ; (1)

Balance layer a2:  $\sigma T_{a1}^4 = 2\sigma T_{a2}^4$ ; (2)

Balance layer a1:  $\sigma T_j^4 + \sigma T_{a2}^4 = 2\sigma T_{a1}^4$ ; (3)

Combine (2) and (3):  $\sigma T_j^4 = 3\sigma T_{a2}^4$ ; (4)

Insert (4) in (1):  $T_j = [3F_s(1 - A)/(4\sigma)]^{1/4} = 315$  K



The surface temperature increased when we added one more atmospheric layer to the model. The one-layer model is a simplification.  $f = 1$  does not correspond to the maximum greenhouse effect of the atmosphere, because we can obtain further heating of the surface when the effective emission altitude is moved further up to colder parts of the atmosphere.

d: Today the important sinks of atmospheric CO<sub>2</sub> are the oceans and the biosphere. These sinks would not be efficient on an ice-covered earth, which would cause accumulation of CO<sub>2</sub> in the atmosphere.

8:1) a: High concentration of aerosol particles and high relative humidity. The atmospheric scattering of light is mainly caused by particles. The water uptake by particles at high relative humidity causes increased scattering. As a result, the visibility is reduced. Depending on the degree of visibility reduction the state is referred to as haze [*dis*], mist or fog [*dimma*].

b: Lomma – Lund:  $m = 10\,600$  kg;  $m = PVM/(RT)$ ;  $V = A L$ ; ( $A=1$  m<sup>2</sup>,  $L=9$  km)  
Vertical column:  $m = 10\,000$  kg;  $m = P A/g$ ; ( $A = 1$  m<sup>2</sup>)

Since we know that the visibility over a horizontal distance can be significantly reduced, we can conclude that a similar effect works in the vertical causing scattering of radiation out to space. This is called the direct climate effect of aerosol.

c:  $\Delta F = -8,9$  W/m<sup>2</sup>;

$$\Delta F = F_{\text{out,ref}} - F_{\text{out,perturbed}} = F_s A_0 / 4 + (1 - f/2)\sigma T_j^4 - F_s A_T / 4 - (1 - f/2)\sigma T_j^4 = F_s(A_0 - A_T) / 4 = -\Delta A F_s / 4; \quad (A_T = 0.306; \Delta A = A_T - A_0 = 0.026)$$

8:2) a:  $100P^*/P_0 = 124 > 103\% \Rightarrow$  The drop is below the Kelvin curve, i.e. the drop will evaporate



- b: A: 0.22  $\mu\text{m}$ ; B: 0.22  $\mu\text{m}$ ;  
C: The drop outside the equilibrium region. It is growing.  
D: 0.18  $\mu\text{m}$ ; E: 0.18  $\mu\text{m}$
- 8:3)  $P/P_0 = 1.004 \cdot 0.988 = 0.992 > 0.99$ ; The vapour pressure at the drop surface is higher than the surrounding relative humidity  $\Rightarrow$  The drop will evaporate until its surface reaches  $P/P_0 = 0.99$ .
- 8:4) a: Stationary state  $\Rightarrow$  Number of  $^{222}\text{Rn}$  disintegrations equals the emission and  $dm/dt = 0$ , where  $m = m(^{210}\text{Pb})$ ;  $dm/dt = E - (\ln 2/t_{1/2} + k_D)m = 0$ ;  
 $t_{1/2}$  is the halflife of  $^{210}\text{Pb}$  ( $k = \ln 2/t_{1/2}$ )  
 $E = (e/N_{av})M_{\text{Pb}}f_A A = (1.0 \times 10^4 / 6.023 \times 10^{26}) \times 210 \times 0.3 \times 4\pi R^2 = 5.33 \times 10^{-7} \text{ kg/s}$ ;  
 $1/\tau_D = k_D = E/m - \ln 2/t_{1/2}$ ;  $\tau_D = 8.3 \text{ dygn}$
- b: The residence time of aerosol particles in the troposphere is significantly shorter than typical transport times (compare with figs. 4-12 and 4-24 in the textbook). A large fraction of the aerosol particles are deposited before they are mixed in the entire troposphere, with the result that the particle concentration varies in time and space with highest concentration close to source regions.
- 8:5) a: With cloud:  $A_1 = A_M + (A_0 + A_0^2 A_M + A_0^3 A_M^2)(1 - A_M)^2 = 0.623$ ;  
Without cloud:  $A_2 = 0.13$ ;  $A_T = 0.3A_1 + 0.7A_2 = 0.278$
- b:  $\Delta A_M = 0.032$ ; [Calculate  $A_1$  like in 8:5a but with  $A_M = 0.6 + 0.032$ ]  
 $A_T = 0.3 \times 0.651 + 0.7 \times 0.13 = 0.286$   
 $\Delta F = -\Delta A_T F_s / 4 = [\text{see answer of 8:1c}] = -1/4 \times 1370 \times (0.286 - 0.278) = -2.9 \text{ W/m}^2$
- 8:6) a: 1 - D, 2 - A, 3 - D, 4 - B, 5 - C
- b:  $C_{mi} = C_{ai} 4\pi(d_i/2)^3 \rho / 3$   
 $C_A = 8 \times 10^{-5} \mu\text{g/m}^3$ ;  $C_B = 0.029 \mu\text{g/m}^3$ ;  $C_C = 0.27 \mu\text{g/m}^3$ ;  $C_D = 0.49 \mu\text{g/m}^3$
- c: Type 1: mass; 2: number; 3: mass; 4: number; 5: mass and number

9:1) a):  $\frac{d[NO]}{dt} = k_1[NO_2]$  and  $-\frac{d[NO]}{dt} = k_2[HO_2][NO]$

b):  $\frac{d[NO_2]}{dt} = k_2[HO_2][NO]$  and  $-\frac{d[NO_2]}{dt} = k_1[NO_2]$

c):  $\frac{d[NO]}{dt} = k_1[NO_2] - k_2[HO_2][NO]$

$$\frac{d[NO_2]}{dt} = k_2[HO_2][NO] - k_1[NO_2]$$

9:2) Count the number of electrons. An odd number characterizes a radical. The following molecules are radicals in order of appearance: OH, CH<sub>3</sub>, CH<sub>3</sub>O<sub>2</sub>, NO, CH<sub>3</sub>O, NO<sub>2</sub> and HO<sub>2</sub>. The oxygen atom O(<sup>1</sup>D) is an exception from the rule that at least one electron should be unpaired, but since it is extremely reactive it is therefore considered a radical. O(<sup>3</sup>P) has two unpaired electrons and is a biradical. It is worth noting that O<sub>3</sub> is no radical, and it is not particularly reactive compared to most radicals.

1. initiation: (1) and (8)
2. propagation: (2), (3), (4), (5), (6), and (7)
3. termination: (9), (10) and (11)

Note that it is the propagation reactions, which convert one radical into another, that maintain the chain of reaction. The termination products are O<sub>3</sub> (9), hydrogen peroxide H<sub>2</sub>O<sub>2</sub> (10) and nitric acid HNO<sub>3</sub> (11).

9:3) The rate of HCHO photolysis is:

$$\frac{-d[\text{HCHO}]}{dt} = k[\text{HCHO}].$$

k is calculated as:

$$k = q \cdot \sigma \cdot I = 5.6 \cdot 10^{-7} \text{ s}^{-1}.$$

We then get:

$$\frac{-d[\text{HCHO}]}{dt} = 67 \cdot 10^3 \text{ molecules cm}^{-3} \text{ s}^{-1}.$$

9:4) a)  $k = q\sigma I$  where  $q$ ,  $\sigma$  and  $I$  all vary with the wavelength of light.

320 nm:  $q=1.0$ ,  $\sigma=25 \cdot 10^{-20} \text{ cm}^2 \cdot \text{molecules}^{-1}$ ,  $I=1 \cdot 10^{14} \text{ photons} \cdot \text{cm}^{-2} \cdot \text{s}^{-1} \cdot \text{nm}^{-1}$   
 $k \approx 2.5 \cdot 10^{-5} \text{ s}^{-1} \cdot \text{nm}^{-1}$ . Note that the unit is  $\text{s}^{-1} \cdot \text{nm}^{-1}$ , since this value only is valid only in a very small wavelength interval around 320 nm.

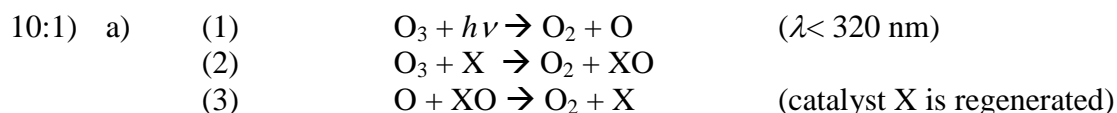
380 nm:  $q=0.96$ ,  $\sigma=60 \cdot 10^{-20} \text{ cm}^2 \cdot \text{molecules}^{-1}$ ,  $I=2 \cdot 10^{14} \text{ photons} \cdot \text{cm}^{-2} \cdot \text{s}^{-1} \cdot \text{nm}^{-1}$   
 $k \approx 1.2 \cdot 10^{-4} \text{ s}^{-1} \cdot \text{nm}^{-1}$ .

420 nm:  $q=0.05$ ,  $\sigma=60 \cdot 10^{-20} \text{ cm}^2 \cdot \text{molecules}^{-1}$ ,  $I=3.9 \cdot 10^{14} \text{ photons} \cdot \text{cm}^{-2} \cdot \text{s}^{-1} \cdot \text{nm}^{-1}$   
 $k \approx 1.2 \cdot 10^{-5} \text{ s}^{-1} \cdot \text{nm}^{-1}$ .

430 nm:  $q=0$ ,  $\sigma=60 \cdot 10^{-20} \text{ cm}^2 \cdot \text{molecules}^{-1}$ ,  $I=4 \cdot 10^{14} \text{ photons} \cdot \text{cm}^{-2} \cdot \text{s}^{-1} \cdot \text{nm}^{-1}$   
 $k = 0 \text{ s}^{-1} \cdot \text{nm}^{-1}$ .

The figure you draw will show a maximum in  $k$  around  $\lambda=380 \text{ nm}$  (compare with Figure 11-1 in Jacob for photolysis of  $\text{O}_3$ ).

b) Integrate over all wavelengths,  $k = \int q(\lambda)\sigma(\lambda)I(\lambda)d\lambda$ . The unit is then  $\text{s}^{-1}$ . This integration was already made in exercise 9:3, where a wavelength interval was given and all quantities were assumed to be constant within this interval.



Net reaction:



The net reaction is obtained by removing molecules that are products in one step, but reactants in the following step. As an example, we note that O is formed in reaction (1), but consumed again in step (3). Therefore, there is no net production of O. The importance of the net reaction above is that  $2\text{O}_3$  are consumed without consuming the catalyst (X or XO)! There are several other catalytic cycles consuming  $\text{O}_3$  in a similar way.

b) X can be different compounds:

X	XO
OH	HO <sub>2</sub>
NO	NO <sub>2</sub>
Cl	ClO
Br	BrO

10:2) a) Production of HO<sub>X</sub>-radicals starts with photolysis of  $\text{O}_3$  followed by the formation of OH radicals.



These reactions take place in both stratosphere and troposphere. Note that it is absolutely essential that the oxygen atom  $\text{O}({}^1\text{D})$  is formed, and not  $\text{O}({}^3\text{P})$ . The OH radical reacts further to form other radicals in the  $\text{HO}_x$ -family ( $\text{HO}_2$  and H) through catalytic propagation reactions.

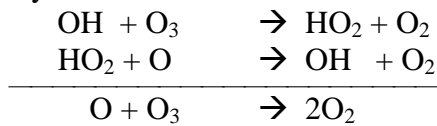
b) Count the number of electrons. An odd number characterizes a radical. The following molecules are radicals in order of appearance: OH, O ( $\text{O}({}^3\text{P})$  is a bi-radical), H and  $\text{HO}_2$ .

c) Propagation steps for  $\text{HO}_x$ -radicals: Reactions (1), (3), (4), (5), (6) and (7).

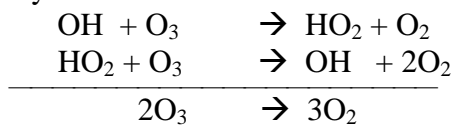
d) Termination steps for  $\text{HO}_x$ -radicals: Reactions (2) and (8).

e) We seek the catalytic reaction cycles for which the net reactions yield an ozone loss without net consumption of any radicals in the  $\text{HO}_x$ -family.

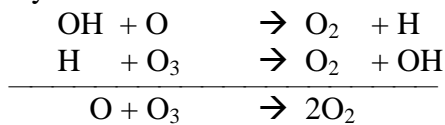
Cycle 1:



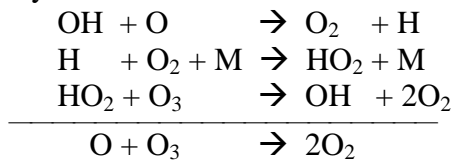
Cycle 2:



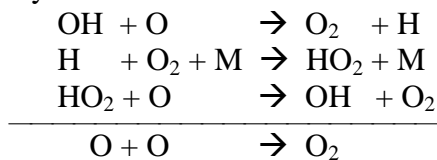
Cycle 3:



Cycle 4:



Cycle 5:



10:3) a) The lifetime of O atoms in the stratosphere ( $M_O = [\text{O}]$ ,  $L_O$  loss rate of O):

$$\tau_o = \frac{M_o}{L_o} = \frac{[\text{O}]}{k_2[\text{O}][\text{O}_2][\text{M}] + k_4[\text{O}_3][\text{O}]} \approx \frac{[\text{O}]}{k_2[\text{O}][\text{O}_2][\text{M}]} = \frac{1}{k_2[\text{O}_2][\text{M}]} = \frac{1}{k_2 C_{\text{O}_2} n_a^2}$$

Here,  $C_{O_2}$  denotes the fraction of  $O_2$  molecules in ordinary air ( $C_{O_2} = 0.21$ ), and  $n_a$  is the number concentration of air molecules (in units of molecules·cm<sup>-3</sup>). This gives  $\tau_O = 1.5 \cdot 10^{-3}$  s at 20 km and  $\tau_O = 2.8$  s at 45 km. We can neglect reaction (4) since it is an insignificant sink of O atoms. Check this assumption when you have calculated  $[O_3]$  in d) below.

A process that governs the stratospheric production of O via photolysis of  $O_2$  and  $O_3$  is the intensity of incoming UV-radiation through reaction (1) and (3). Solar intensity varies on a daily basis (time scale: hours), which is much longer than  $\tau_O$  at both 20 and 45 km altitude. Other factors that control the production and loss of O atoms are meteorological parameters such as pressure and temperature (via  $n_a$ ) and transport of O within the stratosphere (affecting  $k_2$  and  $n_a$ ) and to the troposphere. All these time scales are much longer than  $\tau_O$ . We can therefore assume that the concentration of O atoms in the stratosphere is in steady-state.

b) We have already shown that the O atom in the stratosphere is in steady-state. This means that the O production rate  $P_O$  equals the O loss rate  $L_O$ .

$$P_O = L_O \Leftrightarrow \left. \frac{d[O]}{dt} \right|_{production} = \left. \frac{d[O]}{dt} \right|_{loss} \quad \text{or} \quad \frac{d[O]}{dt} = P_O - L_O = 0$$

The steady-state for O means that the concentration av O is virtually unchanged over the time scales under consideration (seconds, minutes, hours). It does not mean that  $[O]$  is entirely constant over longer time periods, since the processes that govern the production of O vary on a diurnal basis or longer. Other steady-states will then be obtained with other O concentrations. See the arguments in a) above. Further:

$$\left. \frac{d[O]}{dt} \right|_{production} = 2k_1[O_2] + k_3[O_3] \quad \text{and} \quad \left. \frac{d[O]}{dt} \right|_{loss} = k_2[O][O_2][M] + k_4[O_3][O]$$

Since reactions (1) and (4) are much slower than (2) and (3) we can neglect these and write:

$$k_3[O_3] = k_2[O][O_2][M] \Leftrightarrow \frac{[O]}{[O_3]} = \frac{k_3}{k_2[O_2][M]} = \frac{k_3}{k_2 C_{O_2} n_a^2}$$

(From Jacob, Figure 10-5:  $k_3(20 \text{ km}) \approx 5 \cdot 10^{-4} \text{ s}^{-1}$ ;  $k_3(45 \text{ km}) \approx 6 \cdot 10^{-3} \text{ s}^{-1}$ )

Answer:  $[O]/[O_3] = 7 \cdot 10^{-7}$  (20 km),  $[O]/[O_3] = 2 \cdot 10^{-2}$  (45 km)

Since  $[O] \ll [O_3]$  then  $[O_X] = [O_3] + [O] \approx [O_3]$  in the entire stratosphere.

c) We assume steady-state conditions for  $O_X$ . Production of  $O_X$  proceeds through the slow reaction (1), while losses are through the slow reaction (4). The fast reactions (2) and (3) only exchanges O for  $O_3$  and vice versa, and will not affect the  $O_X$  concentration. At steady-state, the  $O_X$  production rate equals its loss rate.

$$2k_1[O_2] = 2k_4[O][O_3] \Leftrightarrow [O] = \frac{k_1[O_2]}{k_4[O_3]}$$

The factor 2 appears since two  $O_X$  are formed or consumed in these (see Jacob equation 10-6, page 169). We have already calculated

$$\frac{[O]}{[O_3]} = \frac{k_3}{k_2[O_2][M]} \Leftrightarrow [O_3] = \frac{k_2[O_2][M]}{k_3}[O] \Leftrightarrow$$

$$[O_3] = \frac{k_2[O_2][M]}{k_3} \cdot \frac{k_1[O_2]}{k_4[O_3]} \Leftrightarrow [O_3]^2 = \frac{k_1k_2[O_2]^2[M]}{k_3k_4} \Leftrightarrow [O_3]^2 = \frac{k_1k_2C_{O_2}^2n_a^3}{k_3k_4}$$

d) (According to Jacob, Figure 10-5:  $k_1(20 \text{ km}) \approx 2 \cdot 10^{-13} \text{ s}^{-1}$ ;  $k_1(45 \text{ km}) \approx 5 \cdot 10^{-10} \text{ s}^{-1}$ )

Answer: (20 km)  $[O_3] \approx 2 \cdot 10^{13} \text{ molecules} \cdot \text{cm}^{-3}$ ,  $[O_3] \approx 10 \text{ ppm}$ .

(45 km)  $[O_3] \approx 3 \cdot 10^{11} \text{ molecules} \cdot \text{cm}^{-3}$ ,  $[O_3] \approx 6 \text{ ppm}$ .

The value at 45 km agrees well with Figure 10-5 in Jacob, while the calculated value at 20 km is too high. The main reason for this is that  $O_x$  is not really in steady-state at this altitude.

10:4) a) The lifetime of Cl-molecules in the stratosphere ( $M_{Cl}=[Cl]$ ,  $L_{Cl}$  loss rate of Cl):

$$\tau_{Cl} = \frac{M_{Cl}}{L_{Cl}} = \frac{[Cl]}{k_1[Cl][O_3] + k_2[Cl][CH_4]} = \frac{1}{k_1[O_3] + k_2[CH_4]}$$

$\Rightarrow \tau_{Cl} = 3.5 \cdot 10^{-2} \text{ s}$ . Since  $k_1[O_3] = 28.5 \text{ s}^{-1}$ , which is much larger than  $k_2[CH_4] = 7.3 \cdot 10^{-3} \text{ s}^{-1}$ , then the most important sink for Cl is the reaction with  $O_3$ .

The lifetime of ClO-molecules in the stratosphere ( $M_{ClO}=[ClO]$ ,  $L_{ClO}$  loss rate of ClO):

$$\tau_{ClO} = \frac{M_{ClO}}{L_{ClO}} = \frac{[ClO]}{[ClO] \cdot (k_3[O] + k_5[NO] + k_6[HO_2] + k_7[NO_2][M])} = \frac{1}{1.14 \cdot 10^{-3} + 3.15 \cdot 10^{-2} + 1.8 \cdot 10^{-4} + 2.86 \cdot 10^{-4}}$$

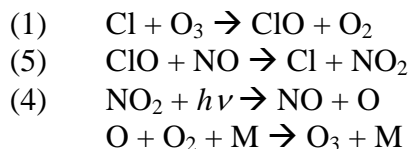
$\Rightarrow \tau_{ClO} = 30 \text{ s}$ . The dominant sink for ClO is reaction (5) with NO.

b) Consider what causes the catalytic  $O_3$  loss (see Exercise 10.1). The net reaction must yield an  $O_3$  loss. Here the reactions are propagated by Cl and ClO.

Since  $k_5[NO] > k_3[O]$ ,  $k_6[HO_2]$  and  $k_7[NO_2][M]$  according to the exercise above, then most ClO-molecules will react with NO. This reaction will not cause catalytic  $O_3$  loss (see exercise c). In order to get a net loss of  $O_3$ , then ClO must react with O instead.

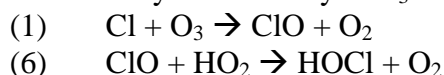
The lifetime of Cl with respect to reaction (1) is  $1/k_1[O_3] = 1/28.5 \text{ s} = 0.035 \text{ s}$ , while the lifetime for ClO with respect to reaction (3) is  $1/k_3[O] = 880 \text{ s}$ . Since reaction (1) is much faster than (3), reaction (3) limits the catalytic  $O_3$  loss. In other words, if reaction (3) had been faster, then the  $O_3$  loss would also have proceeded faster.

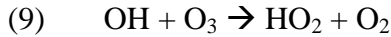
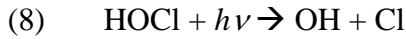
c) If ClO reacts with NO instead of with O, then we get the following net reaction:



This net reaction yields a null cycle, such that all molecules that are consumed are also regenerated in a later step. There is no net production or loss. The concentration of  $O_3$  is therefore not affected when ClO reacts with NO.

d) A reaction cycle for catalytic  $O_3$  loss involving HOCl can be written:





Net reaction:  $2\text{O}_3 \rightarrow 3\text{O}_2$

Reaction (6) with  $\text{ClO} + \text{HO}_2$  is limiting, since the lifetime of  $\text{ClO}$  with respect to this reaction is  $1/k_6[\text{HO}_2] = 5600 \text{ s}$ , while reaction (1) is much faster (see exercise b above). We have already shown that reaction (3) is limiting for the catalytic  $\text{O}_3$  loss with respect to reactions (1) and (3).

The ratio between the rates of  $\text{O}_x$  loss is:

$$\frac{L_{\text{O}_3(1,3)}}{L_{\text{O}_3(1,6,8,9)}} = \frac{2k_3[\text{ClO}][\text{O}]}{2k_6[\text{ClO}][\text{HO}_2]} = \frac{k_3[\text{O}]}{k_6[\text{HO}_2]} = 6.4$$

The factor 2 appears since each cycle consumes two  $\text{O}_x$ -molecules ( $\text{O}_3$  and  $\text{O}$ ). The cycle via  $\text{HOCl}$  is thus much slower than via reaction (1) and (3).

e)  $[\text{ClO}_x] = [\text{ClO}] + [\text{Cl}]$ . The reactions that consume  $\text{ClO}_x$  are (2), (6) and (7). Other reactions only exchanges  $\text{Cl}$  and  $\text{ClO}$  (or does not include any  $\text{ClO}_x$ -molecule whatsoever). Reservoirs for  $\text{ClO}_x$  are  $\text{HCl}$ ,  $\text{HOCl}$  and  $\text{ClNO}_3$ .

$$\tau_{\text{ClO}_x} = \frac{M_{\text{ClO}_x}}{L_{\text{ClO}_x}} = \frac{[\text{ClO}] + [\text{Cl}]}{k_2[\text{Cl}][\text{CH}_4] + k_6[\text{ClO}][\text{HO}_2] + k_7[\text{ClO}][\text{NO}_2][M]}$$

The concentrations  $[\text{ClO}]$  and  $[\text{Cl}]$  are unknown. We know that the  $\text{Cl}$  atom is short-lived (exercise a), and that we therefore could assume a steady-state for  $\text{Cl}$ . In that case we have a balance between production and loss of  $\text{Cl}$  atoms ( $P_{\text{Cl}} = L_{\text{Cl}}$ ).

$$L_{\text{Cl}} = k_1[\text{Cl}][\text{O}_3] + k_2[\text{Cl}][\text{CH}_4]$$

$$P_{\text{Cl}} = [\text{ClO}] \cdot (k_3[\text{O}] + k_5[\text{NO}] + k_8[\text{HOCl}])$$

We note that  $P_{\text{Cl}} \approx L_{\text{ClO}}$

$$L_{\text{ClO}} = [\text{ClO}] \cdot (k_3[\text{O}] + k_5[\text{NO}] + k_6[\text{HO}_2] + k_7[\text{NO}_2][M]) \approx [\text{ClO}] \cdot (k_3[\text{O}] + k_5[\text{NO}])$$

For  $P_{\text{Cl}}$  the term  $k_8[\text{HOCl}]$  can be neglected compared to the others. Thus  $P_{\text{Cl}} \approx L_{\text{ClO}} \Rightarrow L_{\text{Cl}} \approx L_{\text{ClO}}$ . Further:

$$\frac{\tau_{\text{Cl}}}{\tau_{\text{ClO}}} = \frac{[\text{Cl}]}{L_{\text{Cl}}} \cdot \frac{L_{\text{ClO}}}{[\text{ClO}]} \approx \frac{[\text{Cl}]}{[\text{ClO}]} \approx 1.2 \cdot 10^{-3} \text{ mol/mol}$$

We calculated the lifetimes of  $\text{Cl}$  and  $\text{ClO}$  in exercise a. Let  $r = [\text{Cl}]/[\text{ClO}] \ll 1$ :

$$\tau_{\text{ClO}_x} \approx \frac{1}{k_2 r [\text{CH}_4] + k_6 [\text{HO}_2] + k_7 [\text{NO}_2][M]} = 2.1 \cdot 10^3 \text{ s} = 35 \text{ min.}$$

The lifetime of  $\text{ClO}_x$  is 70 times longer than for  $\text{ClO}$ , and as much as 60000 times longer than for  $\text{Cl}$ . An efficient exchange between  $\text{Cl}$  and  $\text{ClO}$  can occur several times before any of these  $\text{ClO}_x$ -molecules end up in a reservoir.

11:1)

$$a) \tau_{\text{OH}} = \frac{[\text{OH}]}{k_1[\text{CO}] \cdot [\text{OH}] + k_2[\text{CH}_4] \cdot [\text{OH}] + k_3[\text{HCHO}] \cdot [\text{OH}]} = \frac{1}{k_1[\text{CO}] + k_2[\text{CH}_4] + k_3[\text{HCHO}]}$$

$\tau_{OH} \approx 0.5$  s. This is a rather typical value for  $\tau_{OH}$  in the troposphere. The reaction with CO dominates the loss rate and largely determines the lifetime of OH. (CO:  $\tau_{OH} \approx 0.65$  s, CH<sub>4</sub>:  $\tau_{OH} \approx 3.0$  s, HCHO:  $\tau_{OH} \approx 7.8$  s).

b) Yes, since this time is short compared to the variability of other factors controlling the production and loss of OH, for instance the temporal variability of UV-radiation and mixing of air masses.

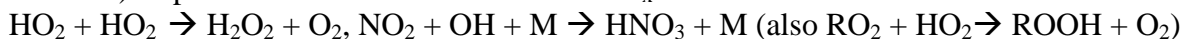
c) At steady-state, there is balance between production and loss rates of OH radicals:

$$P_{OH} = k_4 \cdot [HO_2] \cdot [NO] = k_1 \cdot [CO] \cdot [OH] + k_2 \cdot [CH_4] \cdot [OH] + k_3 \cdot [HCHO] \cdot [OH] = L_{OH}$$

$$[OH] = \frac{k_4 [HO_2] \cdot [NO]}{k_1 [CO] + k_2 [CH_4] + k_3 [HCHO]} = \tau_{OH} \cdot k_4 [HO_2] \cdot [NO]$$

d)  $[OH] = 3.9 \cdot 10^6$  molecules·cm<sup>-3</sup> (0.00014 ppb). It is worth noting that the hydroxyl radical, which is absolutely essential for the entire tropospheric chemistry and the ability of the atmosphere to cleanse itself from hazardous trace gases, is found at very low concentrations.

e) Important termination reactions for HO<sub>x</sub>-radicals:



11:2) a) Each oxidized CH<sub>4</sub> molecule will sooner or later produce a molecule of formaldehyde HCHO, although there are several reaction pathways (Jacob, section 11.3.3). The lifetime of HCHO is sufficiently short ( $\tau_{HCHO} \approx 1/k_1 \approx 1$  day) for us to assume a steady-state for formaldehyde:

$$\frac{d[HCHO]}{dt} = k_2 [CH_4] [OH] - k_1 [HCHO] = 0 \Rightarrow [HCHO] = \frac{k_2}{k_1} [CH_4] [OH]$$

$$b) \Rightarrow [OH] = \frac{k_1 [HCHO]}{k_2 [CH_4]}$$

In the calculations, we normally use concentrations expressed in units of molecules·cm<sup>-3</sup>, and not ppbv (Jacobs equation 1.6). Here there is no need to recalculate the concentrations from units of ppbv since the same scaling factors are found in both numerator and denominator.

	[OH] molecules·cm <sup>-3</sup>
Present	2.0·10 <sup>5</sup>
Pre-industrial	2.3·10 <sup>5</sup>
Glacial	1.1·10 <sup>5</sup>

In exercise 11:1,  $[OH] = 3.9 \cdot 10^6$  molecules·cm<sup>-3</sup>, which is much higher than for the case "present" in this exercise. The main difference is the intensity of solar radiation. The example in exercise 11.1 was for a sunny late morning in southern Germany, and the UV radiation can be assumed to have been rather intense. In exercise 11.2 the location is Greenland, and results in an average [OH] taken over the full year, that is also during night and dark winter when no OH is produced.

c) The decrease in tropospheric [OH] from pre-industrial time to present can be explained by today's elevated concentrations of both CH<sub>4</sub> and CO. Anthropogenic methane originates largely from agriculture and waste treatment, while carbon monoxide mainly comes from combustion of fossil fuels. Both CH<sub>4</sub> and CO are oxidized in the atmosphere by OH, which lowers [OH]. Since the concentrations of O<sub>3</sub> and NO<sub>x</sub> have also increased, the decrease in [OH] is rather modest. As we know, O<sub>3</sub> and NO<sub>x</sub> increase OH production (Jacob, section 11.6).

d) Concentrations of N<sub>2</sub>O, CH<sub>4</sub> and N<sub>2</sub>O were all lower during the last glacial period (ice age) compared to pre-industrial time. The gases N<sub>2</sub>O and CH<sub>4</sub> were lower since the biosphere was less active, and water vapour H<sub>2</sub>O was lower since cold air (ice age) is unable to hold as much water vapour as warm air. As a result, the catalytic O<sub>3</sub> loss in the stratosphere (via NO<sub>x</sub> and HO<sub>x</sub>) should have been less efficient during the glacial period. The tropopause might also have been somewhat lower due to less convection, which would give a thicker stratosphere. A thicker stratospheric O<sub>3</sub> layer would reduce the intensity of UV radiation in the troposphere, and thus lower also the production of OH radicals.

13:1) You have probably already learnt the basic rules for determining oxidation numbers in previous chemistry courses.

Carbon: CO(g) = +2, CO<sub>2</sub>(g) = +4, HCO<sub>3</sub><sup>-</sup> = +4, CO<sub>3</sub><sup>2-</sup> = +4

Nitrogen: NO(g) = +2, NO<sub>2</sub>(g) = +4, N<sub>2</sub>O(g) = +1, NO<sub>3</sub>(g) = +6, N<sub>2</sub>O<sub>5</sub>(g) = +5, HNO<sub>2</sub>(g) = +3, HNO<sub>3</sub>(g) = +5, NO<sub>3</sub><sup>-</sup> = +5

Sulphur: H<sub>2</sub>S(g) = -2, SO<sub>2</sub>(g) = +4, HSO<sub>3</sub><sup>-</sup> = +4, SO<sub>3</sub><sup>2-</sup> = +4, H<sub>2</sub>SO<sub>4</sub>(g) = +6, SO<sub>4</sub><sup>2-</sup> = +6

13:2) a) HNO<sub>3</sub> is formed in the gas phase reaction NO<sub>2</sub> + OH → HNO<sub>3</sub>(g), which is also an important termination reaction for both HO<sub>x</sub><sup>-</sup> and NO<sub>x</sub>-radicals.

b) NO<sub>2</sub>: N(IV), HNO<sub>3</sub>(g): N(V).

$$c) K_2 = \frac{[NO_3^-] \cdot [H^+]}{[HNO_3(aq)]} \Rightarrow \frac{[NO_3^-]}{[HNO_3(aq)]} = \frac{K_2}{[H^+]} \gg 1$$

Nitrate ions NO<sub>3</sub><sup>-</sup> dominate. Since [H<sup>+</sup>] = 10<sup>-pH</sup> (unit M), then [H<sup>+</sup>] varies between 10<sup>-3</sup> M and 10<sup>-6</sup> M. The ratio K<sub>2</sub>/[H<sup>+</sup>] >> 1 for all reasonable values of pH. The conclusion is that the strong acid HNO<sub>3</sub> (nitric acid) dissociates almost completely in aqueous solution and releases H<sup>+</sup> ions.

$$d) K_H = \frac{[HNO_3(aq)]}{[HNO_3(g)]} \quad [total - N(aq)] = [HNO_3(aq)] + [NO_3^-]$$

$$K_2 = \frac{[NO_3^-] \cdot [H^+]}{[HNO_3(aq)]} \Rightarrow [NO_3^-] = K_2 \cdot \frac{[HNO_3(aq)]}{[H^+]}$$

$$K_H^* = \frac{[total - N(aq)]}{[HNO_3(g)]} = \frac{[HNO_3(aq)] + [NO_3^-]}{[HNO_3(g)]} = \frac{[HNO_3(aq)] + K_2 \cdot \frac{[HNO_3(aq)]}{[H^+]}}{[HNO_3(g)]} =$$



$$\frac{[HNO_3(aq)] + K_2 \cdot \frac{[HNO_3(aq)]}{[H^+]}}{K_H} = K_H \cdot \left(1 + \frac{K_2}{[H^+]}\right) \approx K_H \cdot \frac{K_2}{[H^+]}$$

Since we have already shown that  $K_2/[H^+] \gg 1$  for all reasonable values of pH then the effective Henry's law constant  $K_H^*$  is always greater than  $K_H$ .

$$e) K_H^* = \frac{[total - N(aq)]}{[HNO_3(g)]} = \frac{[total - N(aq)]}{p_{HNO_3}} \Rightarrow [total - N(aq)] = K_H^* \cdot p_{HNO_3} \Rightarrow$$

$$[total - N(aq)] = K_H \cdot \left(1 + \frac{K_2}{[H^+]}\right) \cdot p_{HNO_3}$$

The gas phase concentration of nitric acid is given as  $p_{HNO_3} = 0.1 \text{ ppb} = 10^{-10} \text{ atm}$ . When we use  $K_H^*$  we get a  $[total-N(aq)] = 6.45 \text{ M}$ . If we use (erroneously)  $K_H$  we get  $[total-N(aq)] = 2.1 \cdot 10^{-5} \text{ M}$ .

The dissociation of nitric acid is absolutely decisive for its solubility. The same is true to varying extent for all water-soluble gases that dissociate in the aqueous phase (for instance  $SO_2$ ).

13:3) a) S(IV) for all.

b) pH in cloud and rain water is typically between 4-5 (rain water in Skåne in southern Sweden has  $pH \approx 4.3$ , see also Jacob Figure 13-1). For pH in the interval 3-6, >90% of all sulphur is present as bisulfate ions  $HSO_3^-$  (see the figure). Assuming that there are no compounds present that can buffer pH in the aqueous phase, we can argue as follows. The more S(IV) that is shifted from  $SO_2(g) \cdot H_2O$  towards  $HSO_3^-$  and  $SO_3^{2-}$ , the more free hydrogen ions  $H^+$  are formed, which counteracts the further dissolution of S(IV). The reason for this is that one  $H^+$  ion is formed in each step (2) and (3), which will shift both these equilibria towards the left. A balance between how much S(IV) that can be dissolved and how much  $H^+$  that is formed is achieved in a broad pH interval ranging between 3-6.

We can also calculate this more quantitatively. See the figure in this exercise. We can find a low pH ( $\approx 2$ ) where  $[SO_2(g) \cdot H_2O] = [HSO_3^-]$ , and a larger pH ( $\approx 7$ ) where  $[HSO_3^-] = [SO_3^{2-}]$ . We can calculate these pH more accurately:

$$K_2 = \frac{[HSO_3^-] \cdot [H^+]}{[SO_2(g) \cdot H_2O]} \quad \text{and if } [SO_2(g) \cdot H_2O] = [HSO_3^-] \text{ then } [H^+] = K_2$$

$pH = -\log([H^+]) = -\log(K_2) = 1.9$ . In a similar way,  $pH = -\log(K_3) = 7.2$  when  $[HSO_3^-] = [SO_3^{2-}]$ . If we see the reactions (2) and (3) as acid-base-equilibria, then we can interpret the pH value for which the concentrations for the acid and the base are equal as  $pK_a$  values ( $pK_a = -\log(K_a)$  where  $K_a$  is the equilibrium constant for the acid-base-equilibrium in question). Only by looking at the equilibrium constants for (2) and (3) we can see that for a pH between 1.9 and 7.2 the equilibria must be shifted towards  $[HSO_3^-]$ .

c) S(VI). Sulphur has been oxidized.

$$d) K_1 = \frac{[SO_2(g) \cdot H_2O]}{[SO_2(g)]} = \frac{[SO_2(g) \cdot H_2O]}{p_{SO_2}} \Rightarrow [SO_2(g) \cdot H_2O] = K_1 \cdot p_{SO_2}$$

$$K_2 = \frac{[HSO_3^-] \cdot [H^+]}{[SO_2(g) \cdot H_2O]} \Rightarrow [HSO_3^-] = \frac{K_2 \cdot [SO_2(g) \cdot H_2O]}{[H^+]} = \frac{K_2 \cdot K_1 \cdot p_{SO_2}}{[H^+]}$$

$$K_3 = \frac{[SO_3^{2-}] \cdot [H^+]}{[HSO_3^-]} \Rightarrow [SO_3^{2-}] = \frac{K_3 \cdot [HSO_3^-]}{[H^+]} = \frac{K_1 \cdot K_2 \cdot K_3 \cdot p_{SO_2}}{[H^+]^2}$$

$$K_4 = \frac{[H_2O_2(aq)]}{[H_2O_2(g)]} = \frac{[H_2O_2(aq)]}{p_{H_2O_2}} \quad K_6 = \frac{[O_3(aq)]}{[O_3(g)]} = \frac{[O_3(aq)]}{p_{O_3}}$$

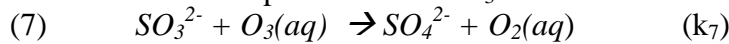
For oxidation of sulphur via hydrogen peroxide  $H_2O_2$ :

$$\frac{d[SO_4^{2-}]}{dt} = k_5 [H_2O_2(aq)] \cdot [HSO_3^-] \cdot [H^+] = k_5 \cdot K_4 \cdot p_{H_2O_2} \cdot [HSO_3^-] \cdot [H^+] \Rightarrow$$

$$\frac{d[SO_4^{2-}]}{dt} = K_1 \cdot K_2 \cdot K_4 \cdot k_5 \cdot p_{SO_2} \cdot p_{H_2O_2}$$

This oxidation rate via hydrogen peroxide  $H_2O_2$  is independent of pH (that is  $[H^+]$ ).

For oxidation of sulphur via ozone  $O_3$ :



$$\frac{d[SO_4^{2-}]}{dt} = k_7 [SO_3^{2-}] \cdot [O_3(aq)] = k_7 \cdot [SO_3^{2-}] \cdot K_6 \cdot p_{O_3} \Rightarrow$$

$$\frac{d[SO_4^{2-}]}{dt} = k_7 \cdot \frac{K_1 \cdot K_2 \cdot K_3 \cdot K_6}{[H^+]^2} \cdot p_{SO_2} \cdot p_{O_3}$$

This oxidation rate via ozone  $O_3$  is however strongly dependent of pH ( $[H^+]$ ).

e) Since the aqueous phase oxidation of sulphur via hydrogen peroxide  $H_2O_2$  is independent of pH, then the oxidation can proceed until all  $SO_2$  or  $H_2O_2$  are consumed. That the cloud drop becomes very acidic is irrelevant in this case. Furthermore, the reaction is very fast and all hydrogen peroxide can be consumed within minutes after the formation of the cloud. The supply of hydrogen peroxide is often the limiting factor. The aqueous phase oxidation of sulphur via ozone will however come to a complete halt as pH decreases, which makes this reaction self-limiting. It is therefore of less consequence for the acidification of soils and waters in comparison with the oxidation via hydrogen peroxide.

f) Hydrogen peroxide  $H_2O_2$  is formed in the gas phase in a termination step for the  $HO_x$ -radical  $HO_2$  according to:

